ICCT25

27th IUPAC International Conference on Chemical Thermodynamics

July 20 to 24th, 2025
Faculty of Sciences
University of Porto

BOOK OF ABSTRACTS

Editor: José C. S. Costa
Faculty of Science, University of Porto, Portugal

U.PORTO

Book of Abstracts of the 27th IUPAC International Conference on Chemical Thermodynamics
ICCT2025
27th IUPAC International Conference on Chemical Thermodynamics - 20th to 24th July 2025
University of Porto, Faculty of Science
Porto
Portugal

Editor
José C. S. Costa
University of Porto, Faculty of Science

ISBN
978-989-35992-9-7

Publisher
Organizing Committee of ICCT2025

PARTNERS AND SPONSORS

COMMITTEES

Advisory Board

Kazuya Saito, University of Tsukuba, Japan
Luís M. N. B. F. Santos, University of Porto, Portugal
João A. P. Coutinho, University of Aveiro, Portugal
Watson Loh, Campinas State University, Brazil
Kenneth Kroenlein, Citrine Informatics, Boulder, USA
J. P. Martin Trusler, Imperial College London, U.K.
Margarida Costa Gomes, Laboratoire de Chimie ENS Lyon, France
Luis Galicia-Luna, Instituto Politécnico Nacional, Mexico
Margarida Bastos, University of Porto, Portugal
Eric May, University of Western Australia, Australia
Dorothy Beckett, NIST, USA
Ricardo Torre, Centro Universitário FEI, Brazil
Caroline Vargas, University of Graz, Austria
Brian Woodfield, Brigham Young University, USA
Josefa Fernández, University of Santiago de Compostela, Spain

Local Organization Committee

Luís M. N. B. F. Santos (Chair), University of Porto
João A. P. Coutinho (Co-Chair), University of Aveiro
Jorge M. Gonçalves (Co-Chair), University of Porto
José C. S. Costa (Secretary), University of Porto
Eduardo F. Marques, University of Porto
Margarida Bastos, University of Porto
Carlos F. R. A. C. Lima, University of Porto
Simão Pinho, Polytechnic Institute of Bragança
Mónia A. R. Martins, Polytechnic Institute of Bragança
Ana I. M. C. Lobo Ferreira, University of Porto
Inês C. M. Vaz, University of Aveiro
Olga Ferreira, Polytechnic Institute of Bragança
Helena Passos, University of Porto
Carlos F. P. Miranda, University of Porto
Rodrigo M. A. Silva, University of Porto
Alexandre C. P. M. Alves, University of Porto
Artur F. M. Farinha, University of Porto
Soraia R. M. R. Silva, University of Porto

CONTENTS

FOREWORD

The ICCT2025 | **27th IUPAC International Conference on Chemical Thermodynamics** was held in Porto, Portugal, from July 20th to 24th, 2025. The event was organized by the Faculty of Sciences of the University of Porto in partnership with the Portuguese Society of Chemistry (SPQ). The technical sessions took place at the Faculty of Sciences, offering a dynamic and inspiring setting for meaningful discussions and knowledge exchange among researchers and industry professionals in the field of Chemical Thermodynamics.

The **IUPAC International Conferences on Chemical Thermodynamics (ICCT)** are a well-established conference series focusing on the fundamentals, modeling, and applications of Chemical Thermodynamics. The conference comprehensively addresses a broad range of topics, including the physicochemical and biological properties of organic and inorganic compounds, as well as their potential applications.
In recent years, the growing relevance of Chemical Thermodynamics has attracted interest from multidisciplinary fields such as chemistry, physics, biology, and materials engineering. As a result, Chemical Thermodynamics has become a central theme in the advancement of science and technology across various domains. Research in this field continues to play a vital role in expanding scientific knowledge and driving innovation.

ICCT2025 provided an exceptional platform for researchers worldwide to present their latest findings and share valuable insights. By bringing together academic scientists from across the globe, the conference aimed to foster dialogue on a wide spectrum of topics and promote collaboration. The ultimate goal was to cultivate a socially engaging and intellectually stimulating environment that inspires new scientific advancements, particularly in the context of sustainable development.

Conference Topics:
S01 - Energy and Sustainability
S02 - Bio and Pharmaceutical Materials
S03 - Phase Equilibria and Fluid Properties
S04 - Organic Materials and Polymers
S05 - Inorganic Materials and Metals
S06 - Ionic Fluids and Deep Eutectic Solvents
S07 - Soft Matter, Colloids, and Complex Fluids
S08 - Surfaces, Interfaces, and Confinement
S09 - Modelling and Simulation
S10 - Instrumentation and Methods

This **Abstracts Book** includes all contributions submitted to the conference, featuring the Rossini Lecture, the IACT Junior Award Lecture, 6 Plenary Lectures, 7 Keynote Lectures, 2 Sponsor Lectures, 94 Oral Communications, and 86 Poster Communications. ICCT2025 was attended by approximately 230 participants representing 28 countries (14 from Europe, 7 from Asia, 3 from North America, 2 from South America, 1 from Africa, and 1 from Oceania).

The conference sessions were held in one main auditorium and three additional rooms at the Faculty of Sciences of the University of Porto:

- **Ferreira da Silva Auditorium** (FC6/FCUP)
- **Room A** and **Room B** (FC2/FCUP)
- **Room C** (FC3/FCUP)

Plenary and Keynote Lectures were held in the Ferreira da Silva Auditorium, while Oral Communications were conducted concurrently in Rooms A, B, and C.

Authors bear sole responsibility for the accuracy, style, and quality of their abstracts, which are reproduced and edited faithfully from the original submissions. The valuable contributions of all authors are sincerely acknowledged.

University of Porto, July 2025

List of Communications

PLENARY LECTURES & AWARDS

Rossini Award/Lecture

IACT Junior Award/Lecture

Plenary Lectures

Keynote Lectures

Sponsor Lectures

ORAL COMMUNICATIONS

ORAL_O1 - Energy and Sustainability

ORAL_O2 - Bio and Pharmaceutical Materials

ORAL_O3 - Phase Equilibria and Fluid Properties

ORAL_O9 - Modelling and Simulation

ORAL_10 - Instrumentation and Methods

POSTER COMMUNICATIONS

POSTER_P1 - Energy and Sustainability

POSTER_P2 - Bio and Pharmaceutical Materials

POSTER_P3 - Phase Equilibria and Fluid Properties

POSTER_P4 - Organic Materials and Polymers

POSTER_P5 - Inorganic Materials and Metals

POSTER_P6 - Ionic Fluids and Deep Eutectic Solvents

POSTER_P7 - Soft Matter, Colloids, and Complex Fluids

POSTER_P8 - Surfaces, Interfaces, and Confinement

POSTER_P9 - Modelling and Simulation

POSTER_10 - Instrumentation and Methods

LECTURES

Rossini Lecture	RL
IACT Junior Award/Lecture	IACT_L
Plenary Lectures	PL1 to PL6
Keynote Lectures	KL1 to KL7
Sponsor Lectures	SP_L1 to SP_L2

Fast scanning calorimetry and its contribution to chemical thermodynamics

Rossini Award/Lecture | RL

Christoph Schick*

University of Rostock, Institute of Physics &Competence Center CALOR, Rostock, Germany

**christoph.schick@uni-rostock.de*

The development of fast scanning calorimetry[1] was initially driven by two main objectives: (i) the investigation of minute sample amounts, such as films in the nanometer range,[2] and (ii) the study of phase transitions at high cooling and heating rates.[3] This lecture will focus on the latter aspect, emphasizing chemical thermodynamics. Due to their low addenda heat capacity, free-standing silicon nitride membranes are commonly used as fast-scanning calorimetric sensors. The sensor comprises a thin-film thermometer and a thin-film heater, both situated in the central part of the membrane. Under non-adiabatic conditions, it is possible to achieve controlled fast cooling rates up to 10^6 K/s and similarly high heating rates.[1]
During fast heating, the decomposition of the sample may be suppressed, making high-temperature phase transitions in thermally labile compounds accessible. Notable examples include the melting of biomolecules such as silk fibroin, nucleobases, peptides, amino acids, and others – for reviews, see [1, 4-6]. A particularly remarkable result is the exceptionally high melting temperature of guanine, measured as (862 ± 4) K.[7] In addition to melting, the evaporation, and sublimation of extremely low-volatile and thermally labile compounds, such as ionic liquids, nucleobases, or pharmaceuticals, have also been studied.[8, 9]
The combination of high heating and cooling rates enables the investigation of the thermal properties, including specific heat capacity, of deeply supercooled liquids of fast-crystallizing compounds,[10] the estimation of their glass-forming ability,[11] and last but not least, detailed studies of the crystallization and crystal nucleation in polymers, metals, and other materials.[1, 12]
The fundamentals of the technique, along with selected results from the aforementioned studies, will be discussed in the lecture.

Acknowledgments
The author acknowledges all students, coworkers and colleagues contributing to the successful development of fast scanning calorimetry and financial support from the German Science Foundation (DFG), the European Union, and the government of the Russian Federation.

References

1. C. Schick and V. Mathot, *Fast Scanning Calorimetry*, Springer, Cham, 2016.
2. S. L. Lai, G. Ramanath, L. H. Allen, P. Infante and Z. Ma, *Appl. Phys. Lett.* 1995, **67**, 1229-1231.
3. S. A. Adamovsky, A. A. Minakov and C. Schick, *Thermochim. Acta* 2003, **403**, 55-63.
4. C. Schick, T. A. Mukhametzyanov and B. N. Solomonov, *Reviews and Advances in Chemistry* 2021, **11**, 1-72.
5. F. Yi and D. A. La Van, *Wiley Interdisciplinary Reviews: Nanomedicine and Nanobiotechnology* 2012, **4**, 31-41.
6. F. Yi and D. A. LaVan, *Appl. Phys. Rev.* 2019, **6**, 031302.
7. A. Abdelaziz, D. H. Zaitsau, N. Kuratieva, S. P. Verevkin and C. Schick, *Phys. Chem. Chem. Phys.* 2019, **21**, 12787-12797.
8. M. Ahrenberg, M. Brinckmann, J. W. P. Schmelzer, M. Beck, C. Schmidt, O. H. Keßler, U. Kragl, S. P. Verevkin and C. Schick, *Phys. Chem. Chem. Phys.* 2014, **16**, 2971-2980.
9. A. Abdelaziz, D. H. Zaitsau, A. Buzyurov, A. A. Minakov, S. P. Verevkin and C. Schick, *Thermochim. Acta* 2019, **676**, 249-262.
10. D. N. Bolmatenkov, M. I. Yagofarov, T. A. Mukhametzyanov, M. A. Ziganshin, C. Schick and B. N. Solomonov, *Thermochim. Acta* 2020, **694**, 178805.
11. S. E. Lapuk, L. S. Zubaidullina, M. A. Ziganshin, T. A. Mukhametzyanov, C. Schick and A. V. Gerasimov, *Int. J. Pharm.* 2019, **562**, 113-123.
12. Y. Gao, B. Zhao, J. J. Vlassak and C. Schick, *Prog. Mater Sci.* 2019, **104**, 53-137.

Magnetic refrigeration for hydrogen liquefaction

IACT Junior Award/Lecture | IACT_L

Liam D. Tenardi[1], Fuyu Jiao[1], Paul L. Stanwix[1], Eric F. May[1,2], Michael Johns[1,2], and Saif Z.S. Al Ghafri[1,2,*]

[1]*Fluid Science and Resources Group, The University of Western Australia, Perth, Australia*
[2]*Future Energy Exports Cooperative Research Centre, Perth, Australia*

[*]*saif.alghafri@uwa.edu.au*

Liquid hydrogen is an attractive means of energy storage for transportation as it has a higher energy density than compressed hydrogen. Magnetic refrigeration provides a potential pathway for liquefaction in small-scale facilities. It replaces conventional vapor compression cycles with magnetocaloric materials (MC) utilizing the magnetocaloric effect (MCE), where the temperature and magnetic entropy of these materials change due to magnetic field variations. Net cooling required for liquefaction is achieved when these MC materials are used in a magnetic refrigeration cycle, such as a Magnetic Brayton Refrigeration Cycle. This technology can potentially provide a higher energy efficiency (above 50%), a lower capital investment (50% less compared to existing liquefiers) and lower operational cost (SEC can be less than 6 kWh/kgLH2)[1]. However, the operating temperature change associated with MC materials is often limited to a few kelvin due to the small adiabatic temperature difference caused by the MCE[2]. Furthermore, a large knowledge gap exists between fundamental materials science (e.g., MC material properties) and realizable engineering applications.

To address this knowledge gap and current challenges, we designed and commissioned a lab scale magnetic refrigeration liquefaction facility, to test the performance of various magnetocaloric materials. It is complemented by a numerical simulation, implemented in COMSOL Multiphysics, to evaluate the experimental design characteristics. The simulation considers the mass, momentum and energy conservations of the refrigeration system and MC materials. It allows for the effect of various system parameters to be characterized in terms of the overall refrigeration performance (applied magnetic field, MC material properties, cycle frequency, etc.). We demonstrate how the magnetic refrigeration cycle works and compare the simulated stages to preliminary temperature distributions and liquefaction tests. The magnetic refrigeration liquefaction facility and accompanying simulation allow for screening of magnetocaloric materials to assist the development of magnetic refrigeration cycles for future liquefaction facilities.

Acknowledgments
The authors would like to acknowledge the technical work of Craig Grimm in developing the apparatus. This work has been supported by the Future Energy Exports CRC (www.fenex.org.au) whose activities are funded by the Australian Government's Cooperative Research Centre Program. This is FEnEx CRC Document 24.RP2.0202.

References

1. R. Ihnfeldt, T. Feng, R. Chen and S. Jin, *Technical and Economic Analysis: Small Scale Cryogenic Magnetic Refrigeration Systems*, U.S. Department of Energy, General Engineering & Research, L.L.C.
2. N. Terada and H. Mamiya, *Nature Communications* 2021, **12**, 1212.

Redefining energy: Thermodynamics at the heart of the hydrogen and carbon capture and utilization revolution

Plenary Lecture | PL1

Lourdes F. Vega[1,*]

[1]*Research and Innovation Center on CO_2 and Hydrogen (RICH Center) and Department of Chemical and Petroleum Engineering, Khalifa University of Science and Technology, PO Box 127788, Abu Dhabi, United Arab Emirates*

**lourdes.vega@ku.ac.ae*

The transition to sustainable energy systems is one of the greatest scientific and societal challenges of the 21st century. Meeting growing global demands for energy, while preserving environmental integrity and economic development, requires a comprehensive approach addressing supply, demand, security, and affordability. The Paris Agreement has promoted national commitments toward net-zero emissions by 2050, and both the International Energy Agency (IEA)[1] and the International Renewable Energy Agency (IRENA)[2] identify hydrogen and carbon capture, utilization, and storage (CCUS) as critical technologies for achieving these targets. However, recent progress assessments reveal that deployment of CCUS and hydrogen technologies remains significantly off-track.

After a general overview on the situation regarding the energy transition, this presentation explores how thermodynamics provides a foundational framework to accelerate innovation in this space, guiding the design and evaluation of efficient, scalable, and sustainable energy systems.

We present recent advances by our research team in the design of materials for CO_2 capture and CO_2 valorization[3,4], hydrogen production, and catalytic systems for bio-oil upgrading[5]. These developments leverage thermodynamic modeling, atomistic simulations, and machine learning techniques to identify and optimize novel materials and reaction pathways. Selected candidates have been experimentally validated, while others identified via AI-enhanced computational screening offer promising directions for future experimental exploration. We also highlight ongoing work on 2D materials for proton-conductive membranes in PEM hydrogen applications[6], emphasizing the interplay between thermodynamic insights and advanced materials discovery.

Acknowledgments

Financial support for this work was provided by Khalifa University, through the RICH Center (RC2-2019-007). Additional support has been provided by the Research and Innovation Center for Graphene and 2D-Materials (RIC2D Center) funded by the United Arab Emirates Presidential Court.

References

1. International Energy Agency (2022), Energy System Overview, IEA, Paris https://www.iea.org/reports/energy-system-overview, License: CC BY 4.0
2. World Energy Transitions Outlook 2022: 1.5°C Pathway. IRENA. March 2022. ISBN: 978-92-9260-429-5 https://www.irena.org/Publications/2022/Mar/World-Energy-Transitions-Outlook-2022
3. L. F Vega, D. Bahamon, I. I. I Alkhatib, *ACS Sustainable Chemistry & Engineering* 2024, **12**, 5357-5382.
4. Y. Li, D. Bahamon, J. Albero, N. López, L. F. Vega, *Journal of CO_2 Utilization* 2024, **80**, 102692.
5. S. AlAreeqi, D. Bahamon, I. I. I. Alkhatib, K. Polychronopoulou, L. F. Vega. *Biofuel Research Journal* 2024, **11**, 2194-2210.
6. J. Tong, Y. Fu, D. Domaretskiy *et al*. *Nature* 2024, **630**, 619-624.

Ion trios – Cause of ion specific interactions in aqueous solutions and path to a better pH definition

Plenary Lecture | PL2

Eric F. May[1,*] and Peter M. May[2]

[1] *The University of Western, Australia*
[2] *Murdoch University, Australia*

**eric.may@uwa.edu.au*

Many important thermodynamic calculations for aqueous systems are profoundly limited because ion specific interactions have not been understood. Here an alternative modelling paradigm with compelling advantages is presented based on fundamental insights regarding ion-ion interactions at higher electrolyte concentrations. We also show how an intense ongoing controversy regarding single ion activity coefficients (SIACs) can be resolved and how SIACs can be quantified in full thermodynamic compliance using an overlooked convention. SIAC values can in fact be determined unequivocally and compatibly from two independent types of measurement at trace concentrations. These developments promise important advances, especially in defining pH and modelling multicomponent aqueous systems.

Thermodynamic insights into the solubility enhancement: hydrotropy, eutectic mixture, and cocrystal formation

Plenary Lecture | PL3

Mirjana Minceva*

Biothermodynamics, TUM School of Life Sciences, Technical University of Munich, Germany

**mirjana.minceva@tum.de*

Improving the aqueous solubility of active pharmaceutical ingredients (APIs) remains one of the most pressing challenges in the development of effective pharmaceutical formulations. This lecture discusses solubility enhancement strategies from a thermodynamic perspective, focusing on eutectic mixture formation, cocrystallization, and the use of hydrotropes. By analyzing the solid–liquid equilibrium (SLE) and molecular interactions in API–excipient–water systems, we shed light on the principles governing solubility modulation. Drawing on both experimental and theoretical insights, we demonstrate how solubility is influenced by melting properties and liquid-phase nonideality. Through case studies involving APIs and excipients such as nicotinamide, caffeine, and urea, we show how activity coefficient models can predict phase behavior, guide excipient selection, and support formulation development. From conceptual frameworks to predictive models and validation by SLE measurements, this talk connects fundamental thermodynamics with practical API formulation science. The goal is to inspire a paradigm shift—from trial-and-error experimentation to mechanism-driven design—in addressing the solubility bottleneck in modern pharmaceutics.

Thermodynamic quantities in the phase diagram database

Plenary Lecture | PL4

T. Abe[1,*]

[1]*Research Centre for Structural Materials, National Institute for Materials Science 1-2-1 Sengen, Tsukuba, Ibaraki, 305-0047, Japan*

[*]*abe.taichi@nims.go.jp*

The CALPHAD (CALculation of PHAse Diagrams)[1] has started in the 1960s. Since then, the various alloy systems have been critically assessed based on the CALPHAD methodology. In this procedure called CALPHAD-type thermodynamic assessment, the Gibbs energy of the phases is assessed and made available to the scientific community through databases written in the Thermodynamic DataBase format (the TDB file). Although encrypted, the TDB files for multi-component systems are available for software packages such as Thermo-Calc[2] and PANDAT.[3] To construct a large thermodynamic database, there are many issues, which will be addressed in this talk from the view of the CALPHAD-type assessments. Some topics will be as follows:

Phase diagram database and its expansion

The thermodynamic database format (TDB) is not easy to read/write for first-touch users. In other words, it is one of the major difficulties in expanding the applications of the phase diagram database. To approach this problem, we have been constructing an open database: CPDDB (Computational Phase Diagram Database[4]), where the phase diagram data are provided in SVG and JSON formats[4], and the Gibbs energy functions in TDB and XML format (XMLTDB project).[5] The TDB and XML files can be converted to each other on the software package, e.g., OpenCALPHAD.[6]

Acceleration of the data accumulation

Experimental data (or estimations from *ab initio* calculations) are particularly important for the assessment of phase diagrams. As it requires long-time annealing to reach the equilibrium, even for binary systems, it takes a lot of effort and time. To speed up, we are trying high-throughput techniques where inhomogeneous conditions are utilized effectively. Another way of acceleration can be the utilization of machine learning. A web application, AiPHAD[7], can suggest alloys with the highest uncertainty score in the compositional space.

Application of the database

In addition to the above two topics, some applications of the thermodynamic databases will be presented: e.g. the metastable sublimation of SiC, Scheil/equilibrium solidifications and ideal DSC curves for the MoSiBTiC system, etc.

Further improvements related to the assessments and database

In the CALPHAD, some of the physical consistencies are lost and simplified in the Gibbs energy constructions. For example, thermodynamic quantities below 298.15K are not well described. Moreover, that is the same for metastable states such as liquid at low temperatures, solid at high temperatures, and metastable crystals.

Acknowledgments

The author appreciates Kiyomi HIROSE, Yuki ANDO, Prof. Masao MORISHITA (the database developers in our group), and Dr. Ryo Tamura (the developer of the AIPHAD). This work was partly supported by the JST-CREST (JPMJC22C3), and by MEXT Program: Data Creation and Utilization-Type Material Research and Development Project (Digital Transformation Initiative Center for Magnetic Materials) Grant Number JPMXP1122715503, and Data Creation and Utilization Type Material Research and Development Project Grant NumberJPMXP1122684766.

References

1. H.L. Lukas, S.G. Fries, B. Sundman, *Computational Thermodynamics*, Cambridge Univ. Press, Cambridge, 2007.
2. Thermo-Calc AB, https://thermocalc.com/, (Accessed March 2025).
3. Computherm (PANDAT), https://computherm.com/, (Accessed March 2025).
4. CPDDB and Digi-PD on MatNAVI, https://doi.org/10.48505/nims.3060, (Accessed March 2025).
5. XMLTDB project, https://github.com/sundmanbo/XMLTDB, (Accessed March 2025).
6. OpenCALPHAD (open and free software), http://www.opencalphad.com/, (Accessed March 2025).
7. AiPHAD project, https://aiphad.org/, (Accessed March 2025).

Chemical thermodynamics study of energy materials

Plenary Lecture | PL5

Quan Shi[1,*]

[1]*Thermochemistry Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Liaoning Province Key Laboratory of Thermochemistry for Energy and Materials, Dalian Technology Innovation Center for Energy Materials Thermodynamics, Liaoning Province, Dalian 116023, PR China*

**shiquan@dicp.ac.cn*

Energy materials serve as the carriers for energy conversion, storage, and utilization. In these energy-related processes, chemical thermodynamics plays an irreplaceable role in providing guiding principles for the efficient conversion and clean utilization of energy materials. Consequently, the study of the thermodynamic properties of energy materials is of great significance for the design and synthesis of advanced energy materials. In this lecture, I will discuss the recent research progress of our group in the chemical thermodynamic study of energy materials. First, I will present our work on constructing adiabatic calorimeters for thermodynamic property measurement. We designed and developed a refrigerator-cooled adiabatic calorimeter for measuring the heat capacity of condensed matters within the temperature range of 4 to 100 K. The optimized repeatability and accuracy were determined to be within 0.8% and 1.5%, respectively. Additionally, we developed an adiabatic calorimeter for thermal safety assessment and used it to study the thermal decomposition reaction of di-tert-butyl peroxide. Second, I will elaborate on the thermodynamic property studies of various energy materials, including phase change materials (PCMs), magnetic materials, and CO_2 adsorption materials. These studies demonstrate that heat capacity calorimetry is a powerful tool for investigating the thermodynamic properties of energy materials. Finally, I will introduce the concept of "Spatiotemporal Phase Change Materials" we proposed recently, in which the thermodynamic properties of PCMs can be regulated to achieve controllable utilization of latent heat. Based on this concept, we designed and synthesized a series of erythritol-based composite phase change materials, which show promising potential in the field of long-term thermal energy storage and controllable utilization. In summary, this lecture outlines the research work of our group in calorimetry techniques, thermodynamic property analysis and regulation of energy materials, highlighting the critical role of chemical thermodynamics in the research and practical application of energy materials.

Keywords: Energy materials, calorimetry, heat capacity, thermodynamic property, phase change materials.

References

1. J. Luo, N. Yin, J. Lu, Z. Tan, Q. Shi, *Rev. Sci. Instrum.* 2024, **95**, 035114.
2. H. Yan, N. Yin, J. Luo, B. Wu, Z. Tan, Q. Shi, *Thermochim. Acta* 2023, **726**, 179555.
3. Y. Kou, S. Wang, J. Luo, K. Sun, J. Zhang, Z. Tan, Q. Shi, *J. Chem. Thermodyn.* 2019, **128**, 259.
4. J. Luo, H. Zheng, X. Wang, N. Yin, Y. Meng, Z. Tan, Q. Shi, *J. Chem. Thermodyn.* 2022, **170**, 106785.
5. H. Yan, H. Yang, J. Luo, N. Yin, Z. Tan, Q. Shi, *Chinese Chem. Lett.* 2021, **32**, 3825.
6. J. Luo, J. Zhang, N. Yin, T. Wang, Z. Tan, W. Han, Q. Shi, *Chem. Eng. J.* 2022, **442**, 136210.
7. Y. Li, Y. Kou, K. Sun, J. Chen, C. Deng, C. Fang, Q. Shi, *J. Energy Chem.* 2023, **80**, 228.
8. J. Chen, Y. Kou, K. Sun, H. Liu, X. Zhang, C. Fang, Q. Shi, *Mater. Today Sustain.* 2023, **22**, 100398.
9. J. Chen, Y. Kou, S. Zhang, X. Zhang, H. Liu, H. Yan, Q. Shi, *Angew. Chem. Int. Ed.* 2024, **63**, e202400759.

Equilibrium and non-equilibrium thermodynamics using 1-D and 3-D density functional theory

Plenary Lecture | PL6

Frederico Wanderley Tavares[1,*]

[1]*Federal University of Rio de Janeiro, Rio de Janeiro, Brazil*

[*]*tavares@eq.ufrj.br*

The 1-D and 3-D classical Density Functional Theory (cDFT), consistent with the PC-SAFT and Peng-Robinson equations of state, are used to investigate the adsorption isotherms and local densities of pure hydrocarbons, H_2, and CO_2, and their mixtures in crystalline-structure materials (like MOF-5) and amorphous materials (like nanoporous carbons). The cDFT calculations reveal that the adsorption process is influenced by the fluid-fluid spatial correlations between the fluid molecules and the external potential produced by the solid structure. These findings are supported by a comparison with experimental data and Grand Canonical Monte Carlo (GCMC) simulations of the adsorbed amount and density profiles of the adsorbed fluid inside the solid. We also explore the impact of the non-crystalline structure of amorphous carbon nanopores on fluid structure and adsorption isotherms, as well as fluid-fluid and fluid-solid interactions. The c-DFT approach provides local fluid structure and then permits the description of the dynamic behavior, far from equilibrium, of non-uniform fluids at confined or non-confined conditions. The Dynamic classical Density Functional Theory (DDFT) is used to describe how hard-sphere nanoparticles behave when confined to an external oscillating potential (optical tweezers) at different dynamics regimes. We also analyze the dynamics of phase transitions related to spinodal decomposition (phase separation process driven by thermodynamic instability) and microphase formation of colloid systems such as lamellar, sigma, and hexagonal phases.

References

1. E. Soares, A. G. Barreto Jr., F. W. Tavares, *Fluid Phase Equilibria* 2023, **574**, 113887.
2. L. J. dos Santos, E. Soares, A. G. Barreto Jr., F. W. Tavares, *Adsorption* 2024, **30**, 583-594.
3. V. de Morais Sermoud, A. de Freitas Gonçalves, A. G. Barreto Jr., Luís F. M. Franco, F. W. Tavares, M. Castier, *Fluid Phase Equilibria* 2024, **586**, 114177.

Maximizing the value of your data

Keynote Lecture | KL1

Kenneth Kroenlein*

Citrine Informatics, Boulder, USA

**kkroenlein@citrine.io*

Individual researchers invest a great deal of time and resources in the generation of scientific and engineering data. Performing high quality experiments requires careful planning and execution. Identifying which experiments will warrant that scale of investment has been a perennial challenge to academia. Engagement with practitioners from industry and government has historically been a primary channel for revealing anecdotal evidence for domains where engineers could benefit in the near term from more-grounded design data. Classic design-of-experiments can give guidance for how to efficiently choose diverse experimental conditions but often propose investing a lot of time in regions lacking interesting dynamics because of the underpinning frequentist formulation. Additionally, once an experimental study is complete, those data are likely to be pulled into large databases or regressions, where quantitative statements of reliability can be stripped away.

The increase in computing power and advances in numerical techniques have enabled substantial shifts in how technical data propagates. By understanding and leveraging these techniques, researchers can maximize the impact that their data-generation investment yields. The traditional pipelines for data transmission will be discussed, and practical examples of how improvements in automated document parsing, such as large language models coupled with retrieval-augmented generation, are removing many of the labor-intensive aspects of structuring and conditioning data for downstream use. Particular emphasis will be given to the impact of qualitative statements of reliability, which have traditionally operated as a shibboleth for those performing critical evaluation of literature data. Further discussion will be devoted to uncertainty in the models derived from such aggregations, including epistemic variation and its connection to the importance of regularization within complex models as applied to small data contexts. With this understanding, it is then possible to apply sequential design techniques to identify in a quantitative sense how much impact a given experiment can have, and to strategically decide which experiments are most prudent based on their associated costs and uncertainties.

Turning a curse into an opportunity: How thermodynamics can help selecting the right organic crystal phase for a specific application

Keynote Lecture | KL2

Manuel E. Minas da Piedade*

Centro de Química Estrutural, Institute of Molecular Sciences, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal

**memp@fc.ul.pt*

The ability to plan and control the assembly of organic molecules in crystals to produce materials tailored for an application is a topic of significant current interest. This interest has been fostered by the challenges in terms of fundamental research and the opportunities offered for innovation and patenting in industries that strongly rely on the production of functional organic solids with highly reproducible properties, such as optoelectronics, photonics, energetic materials, agrochemicals, and, particularly, pharmaceuticals. At the center stage, within this scope, have been strategies focused on the selective preparation of polymorphs and co-crystals. Polymorphism, the phenomenon where a molecule can crystallize into more than one crystal structure, can be a curse or a blessing. Because a specific crystal structure often exerts a significant effect on the solid-state properties of a compound, each polymorph corresponds, in fact, to a different material. Controlling polymorphism, therefore, becomes essential to ensure the manufacture of products with highly reproducible properties. It also provides a means, at least to a certain extent, to tune the properties of a product in view of an application, without changing the molecule involved. Co-crystallization, the preparation of crystalline solids composed of two or more different neutral or ionic molecules, has also been widely used as a tool to adjust the physicochemical properties and improve the efficacy of functional materials. The key role played by thermodynamics in the assessment of the suitability of a given polymorph or co-crystal for an application will be illustrated using examples of key active pharmaceutical ingredients studied in our laboratory, such as simvastatin, erlotinib, or monomethyl fumarate (Figure 1).

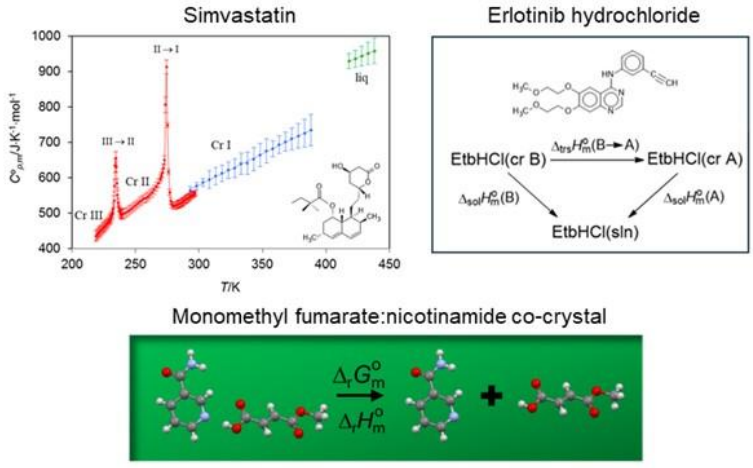


Figure 1

Acknowledgments
Centro de Química Estrutural is a Research Unit funded by Fundação para a Ciência e Tecnologia (FCT) through projects UIDB/00100/2020 and UIDP/00100/2020. Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020.

Assessing concealed thermodynamic properties of deep eutectic solvents and their constituents

Keynote Lecture | KL3

Adriaan van den Bruinhorst[1,2,*], Guillaume Depraetère[2], Chiara Corsini[2], Martin Rosenthal[3], Nithavong Cam[2], Margarida Costa Gomes[2]

[1]*Present: Institute de Chimie de Clermont-Ferrand, Université Clermont Auvergne, 63178 Aubière, France*
[2]*Laboratoire de Chimie de l'ENS de Lyon, CNRS and Université de Lyon, 46 Allée d'Italie, 69364, Lyon, France*
[3]*Department of Chemistry, KU Leuven, Celestijnenlaan 200F, Box 2404, 3001 Leuven, Belgium.*

[*]*adriaan.van_den_bruinhorst@uca.fr*

Mixing solid compounds to prepare liquid solvents; deep eutectic solvents (DESs) introduced this paradigm shift by taking advantage of eutectic phase behaviour. The larger the melting point depression, the broader the temperature and composition range at which the mixture can be used as a solvent. Most organic compounds and/or salts show eutectic melting point depressions upon mixing because they are miscible in the liquid phase but (largely) immiscible in the solid phase. Hence, the number of potential DESs is unimaginable, and a eutectic solvent is to be discovered for each set of physical and chemical properties.

The melting point depression depends on *i*) the pure constituent melting properties and *ii*) the thermodynamics of mixing in the liquid phase (assuming solid immiscibility). Most reported DES constituents melt reversibly; however, some common ammonium-based DES constituents decompose thermally before or upon melting. We overcame this limitation for choline chloride by heating it at 1000–5000 K s^{-1} with fast scanning calorimetry.[1] We confirmed recrystallisation of the melt with synchrotron XRD and measured its melting point and enthalpy of fusion. In addition to the choline chloride results, I will present the unpublished melting properties of other typical ammonium-based DES constituents that are currently still concealed. Contrary to ChCl, studied compounds recrystallised upon cooling at temperatures sufficiently below their melting point, and we could integrate a well-defined crystallisation peak.

After unveiling the melting properties as reference points of the eutectic phase diagram, we assessed the balance between enthalpy and entropy in the total thermodynamics of mixing.[2] To evaluate the concealed excess entropy of mixing, we determined the Gibbs excess energy of mixing from phase equilibrium data and the excess enthalpy of mixing from isothermal calorimetry. The studied DESs show significant excess entropy, and the mixing thermodynamics can even be entropy-dominated. The balance between enthalpy and entropy thus controls the depth of the eutectic. Hence, the large melting point depressions of DESs do not only depend on the strength of the interaction between the DES constituents (e.g. strength of the hydrogen bond) but are significantly affected by the number of (possibly weaker) interactions and available molecular conformations.

I will finish with my vision on the following questions: How do these unveiled thermodynamic properties affect DES discovery? What are the next thermodynamic DES properties to unveil?

References

1. A. van den Bruinhorst, J. Avila, M. Rosenthal, A. Pellegrino, M. Burghammer and M. F. Costa Gomes, *Nature Communications* 2023, **14**, 6684.
2. A. van den Bruinhorst, C. Corsini, G. Depraetère, N. Cam, A. Pádua and M. C. Gomes, *Faraday Discuss.* 2024, **253**, 273-288.

Path from experiment to standard: Development of reference data for sublimation properties

Keynote Lecture | KL4

Vojtěch Štejfa[1,*]

[1] *Department of Physical Chemistry, University of Chemistry and Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic*

[*] *stejfav@vscht.cz*

This talk will highlight the long-term contributions of the Applied Thermodynamics Group at UCT Prague to the development of highly reliable reference values for sublimation pressures and enthalpies. Key aspects of establishing trustworthy thermodynamic correlations of not only sublimation pressures will be explored, including:

- State-of-the-art experimental equipment for vapor pressure measurements at UCT Prague.
- The critical role of integrating crystallographic analysis with the thermodynamic experiments.
- Strategies for assessing and reconciling experimental and literature data.
- The benefit of supplementing vapor pressure data with sublimation enthalpies and heat capacities.
- Common approximations introduced to vapor pressure data treatment and correlations.
- The use of multi-property regression enhancing the reliability of recommended reference values.

The concepts will be illustrated through recent case studies,[1-5] emphasizing both established methodologies and challenges encountered in the process.

The discussion will be placed in the broader context of COST Action 22107 BEST-CSP, which aims to evaluate and compare the accuracy of computational and experimental methods in determining equilibrium temperatures and enthalpy differences between condensed phases. Since direct observation of phase transformations is often hindered by kinetic barriers, sublimation pressure measurements provide an important alternative for assessing equilibrium conditions between the crystal forms.

Additionally, the talk will introduce the ASSURE X23 initiative, which seeks to refine the X23 reference dataset[6] by integrating experimental thermodynamics, computational modeling, and crystallographic analysis. The initiative follows six steps: Analyze, Supplement, Substitute, Unite, Rectify, and Endorse (ASSURE). At present, the first, second, and fourth steps are underway—analysing the origin, reliability and uncertainty of the existing reference data, supplementing the dataset with new high-precision thermodynamic measurements, and uniting the treatment of the thermodynamic data to develop reliable reference sublimation enthalpies. These efforts will ultimately improve the accuracy and usability of the X23 dataset for benchmarking computational methods.

By bridging the precision of experimental thermodynamics with crystallographic analysis and computational insights, it is possible to set new benchmarks with improved reliability of thermodynamic reference data.

Acknowledgments

Support from the COST Action 22107 BEST-CSP: Bringing Experiment and Simulation Together in Crystal Structure Prediction is acknowledged.

References

1. V. Štejfa, S. Chun, V. Pokorný, M. Fulem and K. Růžička, *J. Mol. Liq.* 2020, **319**, 114019.
2. V. Štejfa, V. Pokorný, J. Rohlíček, M. Fulem and K. Růžička, *J. Chem. Thermodyn.* 2021, **160**, 106488.
3. C. Červinka, V. Štejfa, V. Pokorný, P. Touš and K. Růžička, *Cryst. Growth Des.* 2023, **23**, 9011-9024.
4. V. Štejfa, M. Fulem and K. Růžička, *J. Therm. Anal. Calorim.* 2024, **149**, 4709-4720.
5. V. Pouzar, V. Štejfa, M. Fulem and K. Růžička, *J. Phys. Chem. Ref. Data* 2025, **54**, 013101.
6. G. A. Dolgonos, J. Hoja and A. D. Boese, *Phys. Chem. Chem. Phys.* 2019, **21**, 24333-24344.

Mastering fluid properties: The hidden science behind everyday technologies

Keynote Lecture | KL5

Markus Richter[1,*]

[1]*Leibniz University Hannover, Institute of Thermodynamics, An der Universität 1, 30823 Garbsen, Germany*

**m.richter@ift.uni-hannover.de*

At first glance, research on thermophysical properties may not seem to be at the forefront of scientific innovation. However, it plays a critical role in both scientific advancement and industrial applications. Understanding how fluid substances behave under varying conditions of pressure, temperature, and composition is not just a trend – it is a constant necessity that underpins progress across diverse fields. From energy systems to chemical engineering, the demand for accurate data on properties such as density, speed of sound, phase behavior, viscosity, and thermal conductivity is ever-present. This makes thermophysical property research a true evergreen in academia and industry alike.

Today, this research is particularly crucial in supporting the global energy transition. Innovations in renewable energy, cryogenic hydrogen storage, and the development of more efficient refrigeration systems rely heavily on accurately understanding the thermophysical behavior of the fluids involved. These fluids often form asymmetric systems, such as oil-refrigerant mixtures or cryogenic hydrogen with its isomer composition (para- and ortho-hydrogen). Addressing the challenges posed by such mixtures requires approaches beyond the current state of the art, demonstrating that thermophysical property research continues to push scientific boundaries while remaining indispensable to real-world solutions.

Acknowledgements
This work was in part funded by the Deutsche Forschungsgemeinschaft (DFG) within the Research Unit FOR 5595 Archimedes (Oil-refrigerant multiphase flows in gaps with moving boundaries - Novel microscopic and macroscopic approaches for experiment, modeling, and simulation) - project number 510921053.

Simulation of thermodynamic properties in complex liquids. The role and opportunities of machine learning techniques

Keynote Lecture | KL6

Hadrián Montes-Campos[1,2,*], Martín Otero-Lema[1,2], Trinidad Méndez-Morales[1,2] , Luis M. Varela[1,2]

[1]*Grupo de Nanomateriais, Fotónica e Materia Branda, Departamento de Física de Partículas, Facultade de Física, University of Santiago de Compostela, Campus Vida s/n, Santiago de Compostela, 15782, Galicia, Spain.*
[2]*Instituto de Materiais (iMATUS), University of Santiago de Compostela, Campus Vida s/n, Santiago de Compostela, 15782, Galicia, Spain.*

[*]*hadrian.montes@usc.es*

Machine learning force fields have emerged as a powerful alternative to traditional force fields. These force fields allow molecular dynamic simulations with *ab initio*-like accuracy in a fraction of the time. Moreover, they include by construction features like the polarizability of the electronic densities or the reactivity. Thus, they allow the study of reaction kinetics or proton transfer reactions, among others.
In this contribution, we will review how properties of liquids like water and ionic liquids can be predicted using these force fields,[1,2] whether they improve with respect to traditional force fields, and which new effects and properties can be measured.

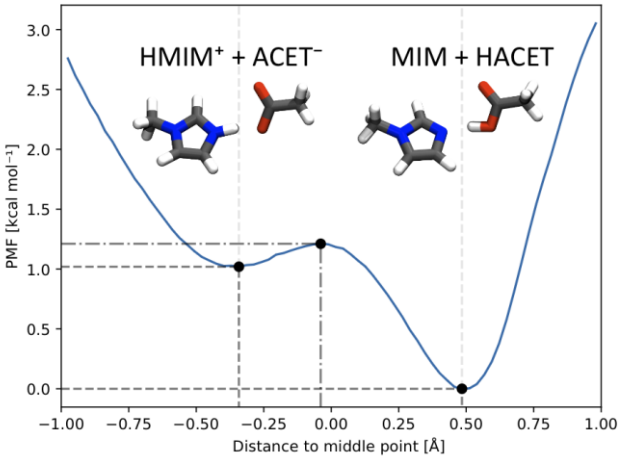


Figure 1: Potential of the mean force for the $HMIM^+ + ACET^- \Leftrightarrow MIM + HACET$. Reproduced from Ref. 3.

Acknowledgements
The financial support of the Spanish Ministry of Science and Innovation (PID2021-126148NA-I00 funded by MCIN/AEI/10.13039/501100011033/FEDER, UE) is gratefully acknowledged. Moreover, this work was funded by the Xunta de Galicia (GRC ED431C 2024/06). M. O. L. thanks the Xunta de Galicia for his "Axudas de apoio á etapa predoutoral" grant (ED481A 2022/236). This work was done within the framework of project HI MOV – "Corredor Tecnolóxico Transfronteirizo de Mobilidade con Hidróxeno Renovable", with reference 0160 HI MOV 1 E, co-financed by the European Regional Development Fund (ERDF), in the scope of Interreg VI A Spain – Portugal Cooperation Program (POCTEP) 2021-2027. This publication and the contract of T. M. M. are part of the grant RYC2022-036679-I, funded by MCIN/AEI/10.13039/501100011033 and FSE+. This work is part of the project CNS2023-144785, funded by MCIN/AEI/10.13039/501100011033 and the European Union "NextGenerationEU"/PRTR.

References

1. H. Montes-Campos, J. Carrete, S. Bichelmaier, L. M. Varela and G. K. Madsen, *J. Chem. Inf. Model.* 2022, **62**, 88-101.
2. J. Carrete, H. Montes-Campos, R. Wanzenböck, E. Heid and G. K. M. Madsen, *J. Chem. Phys.* 2023, **158**, 204104.
3. H. Montes-Campos, M. Otero-Lema and T. Méndez-Morales, *Scientific Reports* 2025, *in press*

The value and limitations of phase boundary data in high-pressure phase behavior studies

Keynote Lecture | KL7

Cara E. Schwarz[1,*]

[1]*Department of Chemical Engineering, Stellenbosch University, Stellenbosch, South Africa*

[*]*cschwarz@sun.ac.za*

High-pressure phase behavior data are needed in the design of high-pressure processes, such as supercritical fluid fractionation. This data provides information on the phase boundaries and the mutual solubilities of the compounds in the systems, therefore inferring solvent requirements and operating temperatures and pressures. Thermodynamic models are making significant strides in describing phase behavior at non-ideal conditions. However, at high pressures significant molecular interactions are present and the systems being considered are often highly asymmetric thus necessitating experimental data to correlate thermodynamic models.

High-pressure phase behavior measurements can usually be divided into two types: Phase equilibrium measurements via an analytic method and phase boundary measurements via a synthetic method. During phase equilibrium measurements the compositions of the co-existing phases are determined therefore providing information on the phase equilibrium between the two phases as well as the locus of the phase boundary. While these types of measurements provide significant quantities of information, they are often tricky to perform, are costly and time-consuming, and usually require highly trained operators.

An alternative to phase equilibrium measurements are phase boundary measurements. Here the user determines, at a known composition, the relationship between the phase transition temperature and pressure. By varying the composition, the phase boundary locus can then be characterized. For binary systems the phase boundary data can be converted to phase equilibrium data, therefore the data are essentially equal. For ternary and multicomponent systems these measurements do not provide information on the composition of the co-existing phases, but they are cheaper, easier and faster to conduct than phase equilibrium measurements. The question thus arises as to the value of phase boundary measurements.

For ternary and multicomponent systems phase boundary data provides information on the locus of the phase boundary. This data can provide information on the solubility of the solvent (usually lower molecular mass compound, e.g. carbon dioxide) in the solutes (usually higher molecular mass compounds e.g. waxes, polymers etc.) and visa versa. From this information the locus of the region of immiscibility can be determined. Further, the phase boundary data can be used to determine if molecular interactions such as association and/or solvation is occurring. These interactions lead to phenomena such as co-solvency, enhanced solubility, reduced solubility, and liquid-liquid holes and islands. Combined, the phase boundary data can therefore provide vital information in the design of high-pressure processes such as quantifying suitable operating regions and solvent requirements.

Unfortunately, phase boundary data does not provide information on the composition of the co-existing phases and although it may suggest separation phenomena such as pseudo-azeotropes, phase equilibrium data are required therefore. However, due to the relatively low cost and ease of obtaining phase boundary data, it can be used to characterize the phase boundaries in detail and well direct but limited phase equilibrium data can be used to determine the compositions of the co-existing phases at the required conditions. Further, for well measured systems, thermodynamic models correlated to phase boundary data can provide a good estimation of the composition of the co-existing phases.

Applications of kinetic analysis using kinetics Neo Software

Sponsor Lecture | SP_L1

Ligia de Souza[1] , Mohammed Bouzbib[2*]

[1]NETZSCH Analyzing & Testing, Life Sciences Division
[2]NETZSCH Analyzing & Testing, Software Neo

**Mohammed.Bouzbib@netzsch.com*

In today's industrial environment, the ability to predict and optimize processes is crucial due to growing demands for efficiency, sustainability, and cost-effectiveness. Accurate predictions help reduce waste, conserve energy, and ensure consistent product quality, while optimizing fine-tunes processes for optimal results. In contexts like polymer binder burnout, curing behavior prediction, and protein denaturation processes. These capabilities lead to shorter cycle times and products that meet precise specifications. Ultimately, Kinetics Neo Software empowers industries to enhance performance and achieve significant cost savings.

NETZSCH Kinetics Neo Software is an advanced tool for analyzing temperature-dependent chemical processes, enabling the creation of kinetic models under various conditions. These models are invaluable for predicting chemical behavior and optimizing processes through simulation to achieve desired outcomes.

This work reviews the applications of kinetic analysis using Kinetics Neo Software, focusing on three critical areas: optimizing burnout process in powder metallurgy via Thermogravimetric Analysis (TGA) , predicting curing behavior from shear viscosity data using rheological analysis, and predicting protein denaturation during the pasteurization process through Differential Scanning Calorimetry (DSC). By using model-based and model-free approaches, based on ICTAC Kinetics Committee recommendations for analysis of multi-step kinetics[1,2], we can determine the kinetics parameters such as Activation Energy (Ea) and the Pre-exponential Factor (A), enabling prediction and process optimization through simulation (Figure 1).

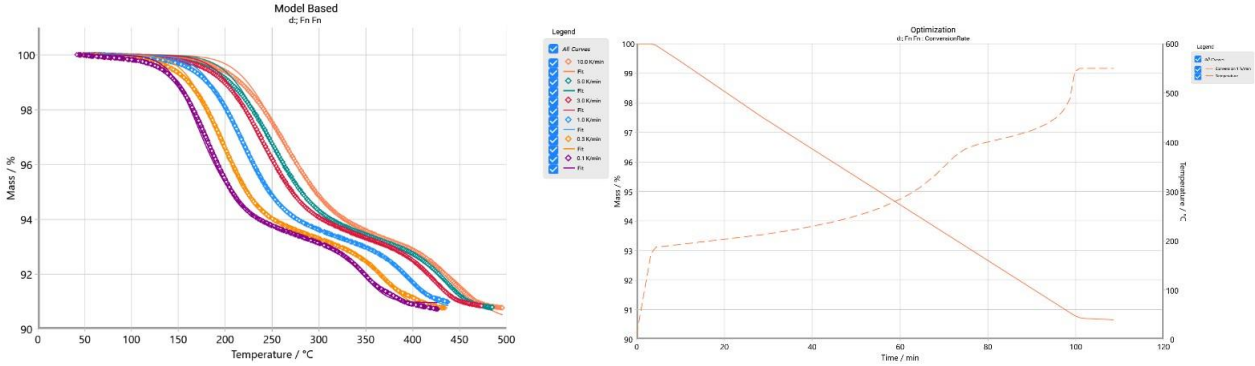


Figure 1: Figure 1 Left: shows six thermogravimetric measurements carried out at different heating rates in a nitrogen atmosphere. Right: the optimum temperature profile for the polymer burnout under laboratory conditions. For the best material quality, a constant mass-loss rate of 1 %/min should be maintained over the entire process

References

1. E. Moukhina, *Journal of Thermal Analysis and Calorimetry* 2012, **109**, 1203-14.
2. S. Vyazovkin, A. K. Burnham, L. Favergeon, N. Koga, E. Moukhina, L.A. Pérez-Maqueda & N. Sbirrazzuoli, *Thermochimica Acta* 2020, **689**, 178597.

An advanced heat flux DSC operated in the power compensation mode

Sponsor Lecture | SP_L2

Laurent Zoppi, Jürgen E. K. Schawe

Mettler-Toledo, Analytical, Nänikon, Switzerland

The instrument presented by Boersma in 1955[1] can be considered the starting point for the development of disk type heat flux differential scanning calorimeters (DSC). In this type of DSC, a single furnace contains thermocouples or heat flow sensors with positions for refence and sample. This type of DSC has been further developed by commercial suppliers and is widely used. One of the advantages of this type of DSC is the high sensitivity and robustness.

The alternative power compensated DSC technique was first developed first by O'Neil in 1964[2]. In this approach, the power required for compensate for heat is measured. The measurement system consists two small furnaces installed in a cooled metal block. This concept is used for conventional DSC and fast DSC using chip calorimeters (Flash DSC).

An advantage is the relatively short signal time constant, τ, which is given not only by the heat transfer conditions in furnace and sample, but also by the parameter of the controller of the difference temperature. The new DSC type presented is based on a conventional heat flux DSC, which has been extended with additional heating elements and temperature sensors for power compensation. This new DSC type was developed to combine the robustness of the heat flux DSC with the signal time constant of a power compensated DSC.

The new developed instrument has electrical power calibration for outstanding accuracy, small time constant for high resolution, improved sensitivity and excellent baseline stability.

The performance of this device is demonstrated using heat capacity measurements and fast transformations as examples.

References

1. S. L. Boersma, *Journal of the American Ceramic Society* 1955, **38**, 281-284.
2. M. J. O'Neill, *Analytical Chemistry* 1964, **36**, 1238-1245.

ORAL COMMUNICATIONS (O)

Does the oxygen functionality really improve the thermodynamics of reversible hydrogen storage with LOHC?

Highlighted ORAL_HO1.1 - Energy and Sustainability

Sergey P. Verevkin[1,3,*], Riko Siewert[1,2], Karsten Müller[1,2]

[1]*University of Rostock, Institute of Technical Thermodynamics, Germany*
[2]*University of Rostock, Competence center CALOR at the Department Life, Light & Matter*
[3]*Samara State Technical University, Russia*

[*]*sergey.verevkin@uni-rostock.de*

Liquid Organic Hydrogen Carriers (LOHCs) are aromatic molecules that are being considered for the safe storage and release of hydrogen. The thermodynamic properties of a range of aromatic ethers were investigated using various experimental and theoretical methods to assess their suitability as LOHC materials. The absolute vapor pressures were measured for benzyl phenyl ether, dibenzyl ether and 2-methoxynaphthalene using the transpiration method. The standard molar enthalpies and entropies of vaporization/sublimation were derived from the temperature dependence of the vapor pressures. The combustion energies of benzyl phenyl ether and dibenzyl ether were measured using high-precision combustion calorimetry, and their standard molar enthalpies of formation were derived from these data. High-level quantum chemical calculations were used to calculate the standard molar enthalpies of formation in the gas phase for benzyl phenyl ether, dibenzyl ether and 2-methoxynaphthalene. The latter values agreed very well with the experimental results obtained in this work. The thermodynamic properties of the hydrogenation/dehydrogenation reactions in liquid phase in LOHC systems based on methoxy-benzene, diphenyl ether, benzyl phenyl ether, dibenzyl ether and 2-methoxynaphthalene were derived and compared with the data for similarly structured hydrogen carriers based on benzene, diphenylmethane, 1,2-diphenylethane, 1,3-diphenylpropane and naphthalene. The influence of the oxygen functionality on the thermodynamic properties of the hydrogenation/dehydrogenation reactions was evaluated.

Acknowledgments
The authors wish to thank Prof. Peter Wasserscheid from the Friedrich-Alexander-Universität Erlangen-Nürnberg for valuable discussions. This project has been funded by the Free State of Bavaria through the project "Oxo-LOHC-Autotherme und ultratiefe Wasserstoff-Freisetzung aus LOHC-Systeme - Oxo-LOHC", (grant number: 84-6665a2/201/11). This work was supported by the Ministry of Science and Higher Education of the Russian Federation (Project No. FSSE-2023-0003) under the state assignment of Samara State Technical University.

Thermodynamics of C-net zero: Investigations of 'free' energy from 2nd law bypass processes for climate sustainability and mobility

ORAL_O1.2 - Energy and Sustainability

Roland Koster[1], Natalia Martsinovich[2], Michael Simpson[2], Leslie Woodcock[3,*]

[1]Kammerath & Weiss Gmbh, Germany; [2]University of Sheffield, UK; [3]University of Algarve, Portugal

*lvwoodcock@ualg.pt

The United Nations International Panel on Climate Change (IPCC) policy target of C-net zero CO_2 emissions, from fossil fuel combustion processes, is based upon an assumption that the greenhouse gas hypothesis (GGH), and a related climate change hypothesis (CCH), have been established as scientific truth. The evidence from computer modeling alone, however, is questionable. Assumptions that determine the mean temperature gradient ('lapse rate') violate the 2nd Law of thermodynamics.[1] Fluctuations from solar radiation, insolation effects, photosynthesis bioprocesses, geothermal heat, and events, *inter alia*, have a much greater effect on the atmospheric global warming index (GWI) = 0.85 K since 1970, presently 0.0175 K/per year than does the increase in concentration [CO_2] from 280 to 400 ppm in the atmosphere since 1850.[2] There is a consensus amongst many chemical engineers. However, there still remains a more compelling case for C-net zero, or not depleting the Earths supply of fossil fuels in the next 100 years, by continuing to burn it up for heating and transport, including electricity for cars via natural gas, and power used in production of solar panels. The Earth's chemical, food processing, and pharmaceutical industries have inherited coal, oil, and gas reserves of raw materials that could supply feedstocks for a thousand years. It could be burned up for electricity and mobility by end of century.

Figure 1: Thermodynamic efficiency of muscle as an engine conundrum: We report preliminary investigations into artificial systems that could replicate the efficiency that nature has evolved for muscle as an engine. Muscle power cannot be explained by equilibrium classical thermodynamics. Energy from ADP hydrolysis is converted to work before it is dissipated in accord with 2nd Law. The contraction process converts 70% of enthalpy from carbohydrate digestion into work with zero DT between source and sink. Nature has by-passed the 2nd law of classical thermodynamics and its constraints in the evolution of animals and humans as bio-engines.

A muscle functions like a fuel cell. Food is constantly transported into the cell and oxidized to form CO_2 and H_2O, which are constantly removed. The combustion processes in the cell are mediated by chiral enzymes and chiral structures on organelles. Therefore, the electrons don't flow directly from the reducing agent to the oxidizing agent but rather via a detour, as in a fuel cell. In the muscle, part of the detour goes into the formation of ATP, mechanical work, and hydrolysis of ATP, while in the fuel cell, part of the detour goes into electrical work. New computer experiments will verify the general invalidity of Carnot-Gibbs second law and how it is by-passed to obtain environmental energy more efficiently from feedstocks, carbohydrates, sugar cane, or fossil fuels. We suggest solutions on the same premise ATP, ADP, and AMP are chiral chemicals that react via chiral enzymes that may be non-ergodic in heat transfer between the degrees-of-freedom in transverse dimensions. Molecular and mesoscale computer experiments on minimalist models of fibrous carbon nanotubes[3], for prototype quasi-bio-engines to compete on efficiency with gasoline or diesel, engines, or electric motors, more economically.

References

1. L. V. Woodcock, *Entropy* 2022, **24**, 459.
2. M. Simpson, *Journal of Sustainable Development* 2024, **17**, 137.
3. J. Foroughi, *et al.* (11 authors), *Science* 2011, **334**, 494-497.

Aqueous redox flow batteries using iron complex materials as redox couple

ORAL_O1.3 - Energy and Sustainability

Mingyu Shin, Sungmin Park, and Yongchai Kwon*

Department of Chemical and Biomolecular Engineering, Seoul National University of Science and Technology, 232 Gongneung-ro, Nowon-gu, Seoul, 01811, Republic of Korea

**kwony@seoultech.ac.kr*

Aqueous Redox flow batteries (ARFBs) are promising technology for large-scale energy storage systems. For improving the performance and stability of the ARFBs, the determination of proper active materials is most crucial.[1,2] The active materials are dissolved into supporting electrolytes, and such developed two electrolytes like anolyte and catholyte, are stored in a tank, determining cell voltage and maximum solubility. In turn, the capacity and power density of ARFBs are decided. Vanadium has been played as the role so far.[3] However, due to its low reserves and rapid cost fluctuation, many attempts have been made to replace it with other materials. As the alternative, iron (Fe) based complexes coordinated with different ligands are considered due to the benefits of wide redox potential window, high solubility to supporting electrolyte, low crossover rate, and relatively cheap price.[1,4] In this presentation, as shown in Figure 1[5], the electrochemical properties and kinetic parameters of Fe-based complexes such as iron-2,2-bis(hydroxymethyl)-2,2',2'-nitrilotriethanol (Fe(BIS-TRIS)) are evaluated quantitatively to determine their optimal condition. In turn, cycle tests of ARFBs using them are implemented to measure their performance and stability. As a result, it is proved that ARFB using Fe complexes as redox active materials is viable enough to compete with vanadium RFB and lithium batteries in some prospects.

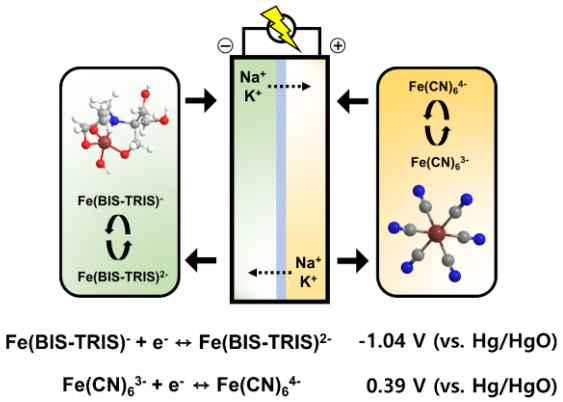


Figure 1: A schematic of an aqueous redox flow battery using Fe-based complexes as a redox couple.

Acknowledgments
This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF), funded by the Ministry of Education (2021R1A6A1A03039981).

References

1. M. Shin, C. Noh and Y. Kwon, *Chem. Eng. J.* 2023, **453**, 139738.
2. M. Shin, S. Oh, H. Jeong, C. Noh, Y. Chung, J. W. Han and Y. Kwon, *Int. J. Energy Res.* 2022, **46**, 8175-8185.
3. D. Emmel, S. Kunz, N. Blume, Y. Kwon, T. Turek, C. Minke and D. Schröder, *Nat. Commun.* 2023, **14**, 6672.
4. M. Shin, C. Noh, Y. Chung and Y. Kwon, *Chem. Eng. J.* 2020, **398**, 125631.
5. M. Shin, S. Park, K. Hyun and Y. Kwon, *Chem. Eng. J.* 2023, **471**, 144682.

A qualitative methodology for antisolvent selection for partial acylglycerols removal from biodiesel + glycerol systems using the COSMO-SAC model

ORAL_O1.4 - Energy and Sustainability

Arthur Gabriel do Nascimento[1], Guilherme José Máximo[2], Roberta Ceriani[3,*]

[1,3]*School of Chemical Engineering, University of Campinas, Avenida Albert Einstein, 500, Campinas, Brazil*
[2]*School of Food Engineering, University of Campinas, Rua Monteiro Lobato, 80, Campinas, Brazil*

**ceriani@unicamp.br*

With the Brazilian plan to increase the biodiesel/diesel level to 20% by 2030, new concerns about these blends' stability have emerged. Some studies[1,2] demonstrated that partial acylglycerols, which are produced in the transesterification reaction, can form solid residues that damage automotive parts. Our research is related to the partition of monoacyl- and diacylglicerols (MAG and DAG) between biodiesel-rich and glycerol-rich phases at the end of the transesterification, while adding an antisolvent that would promote the migration of the partial acylglycerols to the glycerol-rich phase. The lack of liquid-liquid equilibrium experimental data for the biodiesel + glycerol + PAG mixture favors the development of a qualitative methodology for antisolvent selection. This work used the COSMO-SAC method for calculating the activity coefficient at infinite dilution (γ_i^{∞}) of selected compounds at 298.15 K to characterize the different candidate antisolvents. Using the JCOSMO compound database,[3] it was possible to map and classify the behavior of a variety of substances and predict the effects of chemical class and chain size (Figure 1). It was found that the methodology could differentiate the behavior of MAG and DAG, as the latter has a more pronounced apolar character. Also it was shown that long-chain n-alkanes, cycloalkanes and diols are, in general, antisolvents for the system of interest, while alcohols and short-chain esters have the opposite effect.

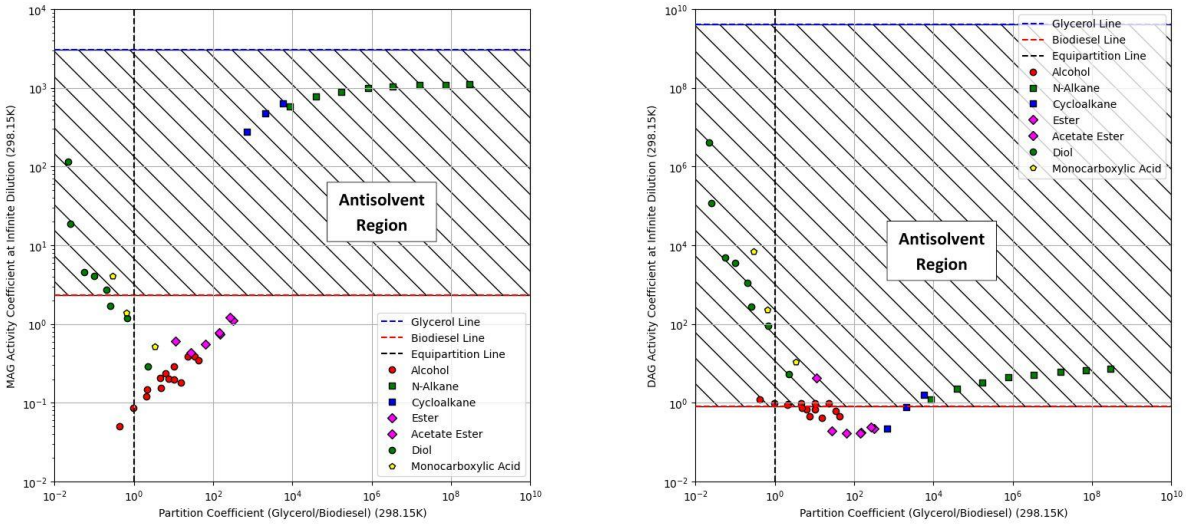


Figure 1: Distribution of candidate antisolvents by the proposed methodology.

Acknowledgements
The authors thank Coordenação de Aperfeiçoamento de Pessoal de Nível Superior, Brasil (CAPES), Financial Code 001 and the Fundação de Amparo à Pesquisa do Estado de São Paulo, Brasil (FAPESP), Centro Paulista de Estudos da Transição Energética (CPTEn), Financial Codes 2021/11380-5, and Conselho Nacional de Desenvolvimento Científico e Tecnológico, Brasil (CNPq), 304518/2022-0 (individual grant), and Fundação de Desenvolvimento da Unicamp (FAEPEX).

References

1. L. Seniorita, E. Minami and H. Kawamoto, *J. Am. Oil Chem. Soc.* 2021, **98**, 727-735.
2. I. Paryanto, T. Prakoso, E. A. Suyono and M. Gozan, *Fuel* 2019, **258**, 116104.
3. F. Ferrarini, G. B. Flôres, A. R. Muniz and R. P. de Soares, *AIChE J.* 2018, **64**, 3443-3455.

Extraction of microalgal chlorophyll for eco-friendly wool dyeing: From Chemistry to the process thermodynamics

ORAL_O1.5 - Energy and Sustainability

Alexandre M. S. Jorge[1], Pedro R. M. Pedroso[1], and Jorge F. B. Pereira[1,*]

[1]*CERES, FCTUC, Department of Chemical Engineering, University of Coimbra, Rua Sílvio Lima, Pólo II - Pinhal de Marrocos, 3030-790 Coimbra, Portugal*

**jfbpereira@eq.uc.pt*

Microalgae are a sustainable source of valuable compounds, including chlorophyll, which can be used across various industries such as food, cosmetics, and textiles. These microorganisms are particularly attractive for chlorophyll production due to their high pigment content (around 7 wt%) and their ability to grow rapidly in non-arable areas without requiring freshwater, fertilizers, or pesticides.[1] These characteristics make microalgae a promising, renewable source for producing chlorophyll and other co-products, including those used in textile dyeing. However, large-scale application faces challenges due to the need for cost-effective and environmentally friendly extraction methods, as current processes often rely on solvents, increasing both costs and environmental risks.[2] This study investigates the use of chlorophyll extracted from *Chlorella vulgaris* NIVA CHL-108 for wool dyeing.[3] Aqueous two-phase systems (ATPS), consisting of ethanol and sodium hydroxide, were employed for chlorophyll extraction, and the chlorophyll-rich phase was then used for dyeing both mordanted and unmordanted wool. The results demonstrated 87% chlorophyll uptake after two dyeing cycles on unmordanted wool, while mordanted wool achieved a 98% recovery of copper ions. This research proposes two integrated, circular ATPS-based platforms for chlorophyll extraction, concentration, and dyeing, highlighting key challenges to industrial-scale adoption and suggesting strategies to overcome these obstacles. Ultimately, this study shows that ATPS-based platforms offer a simple, cost-effective, and sustainable solution for both chlorophyll extraction and its application in textile dyeing.

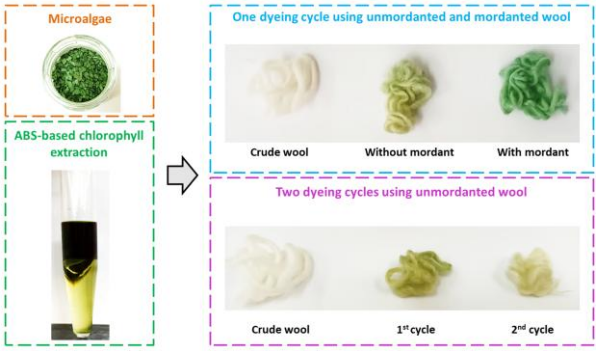


Figure 1. Process for Extracting, Concentrating, and Applying Microalgal Chlorophyll in Wool Dyeing.

Acknowledgments

CERES is supported by the Fundação para a Ciência e a Tecnologia (FCT) through the projects UIDB/ EQU/00102/2020 and UIDP/EQU/00102/2020. The authors thank Algaementum for providing the microalgae used in this study. J.F.B. Pereira and A. M. S. Jorge acknowledge the FCT for funding project DRI/India/0044/2020 (https://doi.org/10.54499/DRI/India/0044/2020) and Fundação Calouste Gulbenkian for funding the project "DyeLoop".

References

1. A. M. Ferreira, A. C. Leite, J. A. P. Coutinho and M. G. Freire, *Sustainable Chemistry* 2021, **2**, 764-777.
2. M. E. Rosa, A. M. Ferreira, C. M. S. S. Neves, M. R. Almeida, R. Barros, A. C. Cristovão, A. C. A. Sousa, P. M. Reis, L. P. N. Rebelo, J. M. S. S. Esperança, J. A. P. Coutinho and M. G. Freire, *Green Chemistry* 2023, **25**, 1852-1864.
3. A. M. S. Jorge, P. R. M. Pedroso and J. F. B. Pereira, *J Clean Prod* 2024, **451**, 142009.

Aqueous solubility enhancement with AI designed hydrotropes

ORAL_O1.6 - Energy and Sustainability

Margarida D. Pinhão[1,*], João A. P. Coutinho[1], Dinis O. Abranches[1]

[1]*CICECO- Aveiro Institute of Materials, University of Aveiro*

[*]*margaridapinhao@ua.pt*

Nonpolar compounds are not well dissolved in water, so organic solvents must be used to process them. Unfortunately, these solvents are usually toxic, highly flammable, non-biodegradable, have higher costs, and are overall non-sustainable.

Due to their amphiphilic properties, hydrotropes can increase the solubility of hydrophobic solutes in water. Thus, aqueous hydrotropes can replace the usage of organic solvents in diverse applications, from pharmaceuticals to agrochemicals, leading to safer and greener processes. The mechanism of hydrotropy involves the non-polar portions of hydrotropes interacting with the solute molecules, surrounding them and preventing their aggregation and consequent precipitation. Due to the complexity of hydrotropic mixtures, it is yet to be found an accurate model to predict how solubility will vary with the molecular structure of the hydrotrope or its concentration in water. Moreover, there are no extensive and consistent datasets of solubility in hydrotropic systems, further complicating the task of understanding its mechanism and developing predictive models. Machine learning (ML) techniques help predict the properties of different compounds, bypassing the need for extensive experimental trial-and-error campaigns, saving time and resources. This is particularly true of Gaussian processes (GPs), a type of non-parametric stochastic ML model that has been recently shown to excel in the prediction of physicochemical properties of organic compounds using small and scarce datasets.[1]

Given the need for accurate predictive models in hydrotropy, together with the recent successes of GP-based ML models, the objective of this work is to develop a GP model capable of predicting the aqueous solubility of syringic acid in hydrotropic systems. Syringic acid was chosen due to being a model molecule with a broad database. Its phenolic nature and relevance in pharmacological, chemical and food industries combined with its low solubility in water at room temperature, contribute to its dissolution with organic solvents. In terms of hydrotropes, the starting point was alkanediols, which possess linear or branched non-polar hydrocarbon chains and two polar hydroxy groups, so their action as hydrotropes to aggregate with the solute is expected.

Starting with experimental data previously reported in the literature, it was demonstrated that GPs are able to accurately predict the solubility of syringic acid in aqueous solutions of alkanediols. Using this approach, ML helped quantify the optimal concentration range of the alkanediols for maximum solubility effect, showing its efficiency. Based on minimal experimental data, this ML technique allows an outstanding performance on evaluating the ideal molecular weight of the hydrotrope and its effect in increasing the solubility of the solute. A minimum hydrotrope mass may not be enough to surround the solute molecules but at higher masses it will be more favorable for them to self-aggregate which also depends on its hydrophobic balance, so its concentration and composition are crucial for the desired hydrotropic action. Furthermore, we analyzed a larger dataset of hydrotropes without experimental data, using sigma profiles as molecular descriptors.[2] Sigma profiles for alkanediols were obtained with COSMO-RS, based on the charge-surface ratio calculated using DFT. Sigma profiles are representations of molecules as surfaces with charged segments, they represent electron density asymmetries between atoms with different electronegativities and the influence of the atoms in the molecular polarity. Using this dataset to train a GP model, it analyzed the interaction between the regions with different polarities of the hydrotrope and the solute and their implications on the solubility of the syringic acid. Aiming for maximum solubility and minimum uncertainty, the model predicted which alkanediols are the best suited to increase the solubility in water.

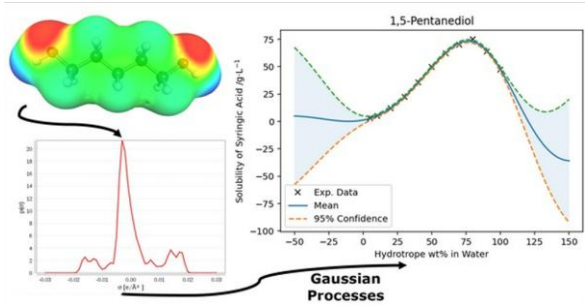


Figure 1: Schematic illustration of a Gaussian process predicting the aqueous solubility of Syringic acid in the presence of a hydrotrope

References

1. D. O. Abranches, B. P. Soares, A. M. Ferreira, S. Shimizu, S. P. Pinho, J. A. P. Coutinho, *Phys. Chem. Chem. Phys.* 2022, **24**, 7624-7634.
2. D.O. Abranches, E.J. Maginn, Y.J. Colón, Proc. Natl. Acad. Sci. U.S.A. 2024, **121**, e2404676121.

Incorporating positional entropy into statistical thermodynamics: Phase changes, colligative properties, and concentration batteries

ORAL_O1.7 - Inorganic Materials and Metals

Brian F. Woodfield[1,*], Lee D. Hansen[1], H. Dennis Tolley[2]

[1] *Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah U.S.A*
[2] *Department of Statistics, Brigham Young University, Provo, Utah U.S.A.*

**brian_woodfield@byu.edu*

Classical thermodynamics is incomplete because the entropy of particle distribution was not included. Incorporating positional entropy into thermodynamics requires modifying the second law to state that systems maximize the joint distribution of energy *and* particles. This talk develops statistical models for this joint distribution using solid-liquid and liquid-vapor phase changes as examples. Systems where the only process is an increase in positional microstates show that increased probability, not a decrease in energy or an increase in the distribution of energy, is the driver for these processes. In this talk, osmosis in a straight, vertical tube is used to show that a concentration gradient of particles can be used to do work against an opposing force. Concentration batteries are used to illustrate that changing the constraints on a system changes the statistical equilibrium state of a system, thus justifying the need to use a joint distribution in the second law. Concentration batteries also provide further evidence that concentration gradients of particles are concurrent with a potential energy that is not subject to the law of conservation of energy, and thus, must be described as a probability field.

Insulin - the detailed story: Biothermodynamic analysis of insulin

Highlighted ORAL_HO2.1 - Bio and Pharmaceutical Materials

Marko E. Popović[1,*], Vojin Tadić[2], Marija Mihailović[1]

[1]*University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Njegoševa 12, 11000 Belgrade, Serbia*
[2]*Department for Experimental Testing of Precious Metals, Mining and Metallurgy Institute, Zeleni Bulevar 35, 19210 Bor, Serbia*

**marko.popovic@ihtm.bg.ac.rs*

Insulin was discovered 100 years ago and has been well studied from the perspectives of life and biomedical sciences.[1] Insulin is simultaneously a biomolecule and medicine (pharmaceutical compound).[1,2] As such, it is used in medicine.[1,2] Its chemical formula has been known for a long time.[1] However, its thermodynamic properties have not been determined. This research reports chemical and biothermodynamic properties of biosynthesis of insulin. It reports for the first time the molecular and empirical formulas, biosynthesis reactions, and thermodynamic properties of molecules and their biosynthesis for human preproinsulin, proinsulin, insulin chain A, insulin chain B, insulin, signal peptide and intermediate peptide (C-peptide).[3] Based on these, metabolic reactions were formulated for conversion of preproinsulin to insulin and their thermodynamic feasibility was analyzed.

The process of translation produces preproinsulin, which is then converted into insulin. The metabolic pathway that converts preproinsulin into insulin is made of signal peptide removal, intermediate peptide removal, disulfide bond formation and peroxide decomposition reactions. Gibbs energies of these reactions are shown in Figure 1. Gibbs energy changes of the signal peptide removal and intermediate peptide removal reactions are slightly positive, which means that they are not thermodynamically favorable. However, Gibbs energies of the disulfide bond formation and peroxide decomposition reactions are highly negative. This is why Gibbs energy of the entire metabolic pathway is negative, which makes it feasible.

The disulfide bond formation and peroxide decomposition reactions remove the products of the signal peptide removal and intermediate peptide removal reactions. The removal of reaction products, according to the Le Chatelier's principle pulls the equilibrium of the signal peptide removal and intermediate peptide removal reactions towards products. This makes these reactions feasible, even though they have a slightly positive Gibbs energy.

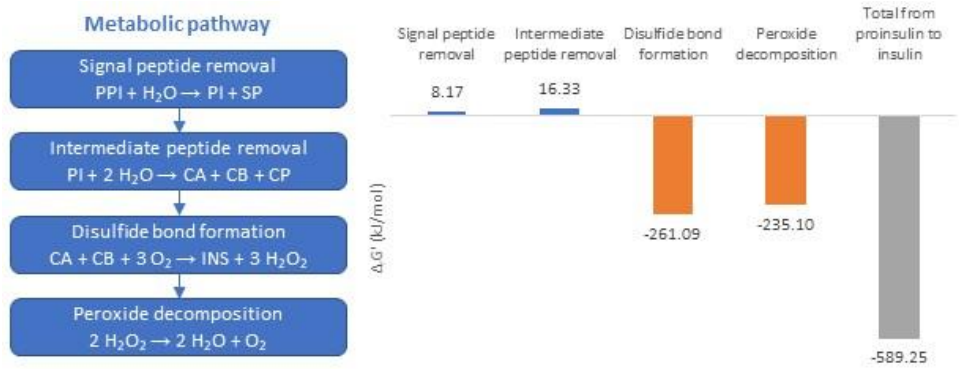


Figure 1: Gibbs energies of reactions in the metabolic pathway that converts preproinsulin into insulin Symbols: PPI preproinsulin, PI proinsulin, SP signal peptide, CA insulin chain A, CB insulin chain B, INS insulin, $\Delta_r G'$ standard reaction Gibbs energy at 37°C.

Acknowledgments
This work was supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Grant No. 451-03-136/2025-03/200026).

References

1. V. Sugumar et al. *Pharmaceutics* 2022, **14**, 1406.
2. D. Beran et al., *The lancet. Diabetes & endocrinology* 2022, **10**, 17-18.
3. M. Popovic, V. Tadić and M. Mihailović, *J. Biomol. Struct. Dyn.* 2024, **42**, 10388-10400.

Chemical stability of amorphous pharmaceuticals: Water clusters and acid/base relationships

ORAL_O2.2 - Bio and Pharmaceutical Materials

Shaoxin Feng,[1] Tapiwa Chiura,[1] Christian Schöneich,[2] Alain Hedoux,[3] Evgenyi Shalaev[1,*]

[1]AbbVie, Irvine, CA 92612, USA. [2]University of Kansas, Lawrence, KS, 66047. [3]Univ. Lille, CNRS, INRAE, Centrale Lille, UMR 8207 - UMET - Unité Matériaux et Transformations, F-59000, France.

[*]evgenyi.shalaev@abbvie.com

Molecular mobility is commonly invoked to explain various aspects of stability of amorphous pharmaceuticals, including, e.g., destabilizing role of water and temperature dependence of degradation rates. It has become increasingly clear, however, that comprehensive description of the underlying fundamental principles requires consideration of structural aspects (e.g., hydrogen bonding and water clustering patterns) and media properties (e.g., proton transfer and matrix polarity). To address the structural and media aspects of stability of pharmaceutical glasses, our investigations include solid[1-3] and liquid[4] amorphous systems, reacting species from small molecules[2] to peptides[1,4] and proteins,[1,3] and chemical reactions such as amide and glycosidic bonds hydrolysis[2] and deamidation of asparagine (Asn).[1,4]

Objective of the present study is to link rate of Asn deamidation of a peptide in amorphous matrixes with water content/activity (a_w), structure, and apparent acidity. Methods: Deamidation of Asn-peptide in freeze-dried amorphous polyvinyl pyrrolidone (PVP) and disaccharide (sucrose and trehalose) amorphous matrixes at several temperatures and water activities is quantified by high performance liquid chromatography. Raman spectroscopy was used to monitor OH-stretching and HOH bending. Hammett acidity function (H_{2-}) was determined by measuring protonation of probe molecules with UV/vis diffuse reflectance spectroscopy. Results and Conclusions: (i) In the PVP lyophiles, two a_w regions are observed for both deamidation and OH stretching, with the threshold at a_w of approx. 0.1 to 0.2 (Figure 1, left and center). This result supports the hypothesis that acceleration of deamidation at a_w>0.1 is linked to water clustering. (ii) Deamidation of the peptide in the PVP matrix is faster than in disaccharides formulations, while H_{2-}, of PVP is higher (e.g., higher basicity) (Figure 1, right), which is consistent with the base catalysis of deamidation.

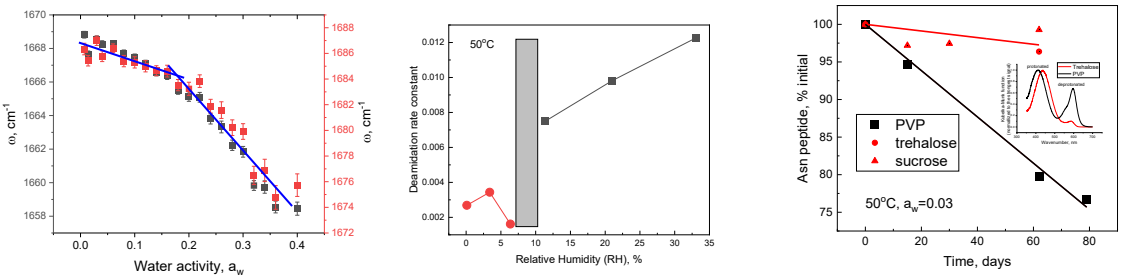


Figure 1: RH dependence of the Raman spectral bands positions (left) and Asn deamidation rate constant (center) in PVP lyophiles; Asn deamidation kinetics in freeze-dried peptide+ PVP and peptide+trehalose formulations lyophilized from solutions with pH 7.5 (right). Inset: UV/vis diffuse reflectance spectra of chlorophenol red in freeze-dried trehalose and PVP.

Acknowledgements and Disclosures

TC, SF and ES are AbbVie employees and may own AbbVie stock. AbbVie sponsored and partially funded the study, and contributed to the design, participated in data collection, analysis, and interpretation, and wrote, reviewed, and approved the final publication. TC acknowledges support from AbbVie R&D postdoctoral fellowship.

References

1. S. Ohtake et al, *J Pharm Sci* 2018, **107**, 42.
2. D Heger et al, Beyond pH: Acid/Base Relationships in Frozen and Freeze-Dried Pharmaceuticals, in *Principles and Practices of Lyophilization in Product Development and Manufacturing*, AAPS Advances in the Pharmaceutical Sciences Series (AAPS, volume **59**), F Jameel (Ed), 2023, pp. 39-61.
3. S Feng et al, *Mol Pharm*, 2025, **22**, 1462.
4. T Chiura et al, *Int J Pharm* 2025, **674**, 125420.

Relative thermodynamic stability of famciclovir polymorphs

ORAL_O2.3 - Bio and Pharmaceutical Materials

Luciano C. R. Rais[1], João A. Baptista[2], M. Fátima M. Piedade[3,4], M. Ermelinda S. Eusébio[2], Éder T. G. Cavaleiro[1], Ricardo A. E. Castro[2,5*]

[1]*Instituto de Química de São Carlos, Universidade de São Paulo, 13566-590 São Carlos, Brazil*
[2]*Centro de Química de Coimbra, Institute of Molecular Sciences, Departamento de Química, Faculdade de Ciências, Universidade de Coimbra, 3004-535 Coimbra, Portugal*
[3]*Centro de Química Estrutural, Institute of Molecular Sciences, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa, Portugal*
[4]*Centro de Química Estrutural, Institute of Molecular Sciences, Departamento de Engenharia Química, Faculdade de Ciências, Universidade de Lisboa, 1749-016 Lisboa, Portugal*
[5]*Faculdade de Farmácia, Universidade de Coimbra, 3000-548 Coimbra, Portugal*

**rcastro@ff.uc.pt*

Famciclovir (FCV), Figure 1, is a prodrug used in the treatment of hepatitis B virus, varicella-zoster virus, and herpes simplex virus types 1 and 2.[1] A previous study revealed the existence of four polymorphs[2] and a hydrate form.[2,3] The crystal structures have only been solved for form I[2] and the hydrate.[3]
In this work, a detailed investigation of forms I and II of famciclovir was carried out. The commercially available FCV was determined, in this investigation, to be crystalline form I. Crystallization experiments from different solvents were carried out and reproducible conditions to obtain polymorph II disclosed. Moreover, single crystals of form II could be grown and its crystal structure solved for the first time. The infrared spectra of both polymorphs were compared and interpreted with the assistance of the simulated spectrum of the conformer in one of the crystal structures. This was obtained using Gaussian software (version 6.0.16), after optimization, using the def2-TZVP basis set and the B3LYP density functional.
The thermal behavior of both polymorphs was investigated by differential scanning calorimetry (DSC) and the solubilities of each form in ethanol obtained both by the gravimetric method and the polythermal method. The relative thermodynamic stability of both polymorphs was assessed, an enantiotropic system, both from the DSC measurements and the solubility data. Challenges of both methodologies are presented and discussed.

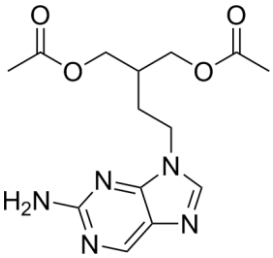


Figure 1: Famciclovir – [2-(acetyloxymethyl)-4-(2-aminopurin-9-yl)butyl] acetate

Acknowledgements
Funding for this study was obtained from Fundação de Amparo à Pesquisa do Estado de São Paulo, 2019/22217-8, by Eder Cavalheiro, and from Coordenação de Aperfeiçoamento de Pessoal de Nível Superior, 001, by Luciano C.R. Rais. Coimbra Chemistry Center/Institute of Molecular Sciences (CQC/IMS) is supported by FCT, Foundation for Science and Technology (UIDB/00313/2020, UIDP/00313/2020. Thanks are due to UCQFarma for the use of the PXRD facility. J.A.B. acknowledges FCT for financial support (PhD grant UI/BD/150859/2021).

References

1. S. Mubareka, V. Leung, F. Y. Aoki, D. C. Vinh, *Expert. Opin. Drug Saf.* 2010, **9**, 643.
2. L. Vella-Zarb, U. Baish, *Crystals* 2021, **11**, 129.
3. M. R. Harnden, R. L. Jarvest, A. M. Z. Slawin, D. J. Williams, *Nucleos. Nucleot.* 1990, **9**, 499.

Solubility enhancement of active pharmaceutical ingredients through hydrotropy: Experimental investigation and thermodynamic modeling

ORAL_O2.4 - Bio and Pharmaceutical Materials

Sahar Nasrallah[1,*], Alexander Wendler[1], Sebastian Hallweger[2] and Mirjana Minceva[1]

[1] *Laboratoire de Chimie, CNRS & ENS de Lyon, France*
[2] *Laboratório de Espectroscopia Molecular, Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo, Brazil*

[*]*sahar.nasrallah@tum.de*

Enhancing the solubility of hydrophobic active pharmaceutical ingredients (APIs) is crucial for effective drug formulation. Hydrotropy offers a promising strategy, but selecting an appropriate hydrotrope and its optimal concentration requires a comprehensive understanding of the solid-liquid equilibrium (SLE) phase behavior in the API-hydrotrope-water system. However, experimental determination of the complete SLE phase diagram at different temperatures is challenging and labor-intensive. This study presents a thermodynamic-based approach to predict API solubility in the API-hydrotrope-water solution, considering API-hydrotrope, API-water, and hydrotrope-water interactions. Using lidocaine, procaine and benzocaine as model APIs and nicotinamide, caffeine, and urea as hydrotropes, the SLE phase diagram of a ternary API-hydrotrope-water system was predicted using the component melting properties and activity coefficients calculated with the Non-Random Two-Liquid (NRTL) model. The binary interaction parameters of the NRTL model were derived from experimental SLE data for API-hydrotrope, API-water, and hydrotropes-water binary systems. The predicted SLE diagrams of the ternary API-hydrotrope-water system revealed that the studied system are eutectic systems with maximum API solubility at the eutectic point. Furthermore, thermodynamic analysis has shown that an efficient hydrotrope strongly interacts with both the API and water, with nicotinamide providing the highest solubility enhancement. This study demonstrates the potential of thermodynamic modeling as a powerful tool for guiding hydrotropes selection and determining their concentrations to achieve targeted API solubility in water.

Structural and thermodynamic insights into photoresponsive liposomes

ORAL_O2.5 - Bio and Pharmaceutical Materials

Dmitriy Moreira[1], Elsa C. Loureiro[1], Isabel S. Oliveira[1], Nuno Basílio[2], Eduardo F. Marques[1,*]

[1] *CIQUP, IMS, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto 4169-007, Porto, Portugal*
[2] *LAQV-REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516, Caparica, Portugal*

**efmarque@fc.up.pt*

Liposomes are self-assembled enclosed bilayers formed by phospholipids, which hold an internal solvent pocket (Fig. 1). These colloidal structures hold great relevance as membrane models for biophysical studies, as nanoreactors and nanotemplates, and especially as nanocarriers in drug delivery, where they improve the efficiency and efficacy of the entrapped therapeutic agents.[1] Stimuli-responsive liposomes, particularly those responsive to light, offer precise spatiotemporal control over drug release.[2] This work focuses on developing light-responsive liposomes composed of a zwitterionic phospholipid (DPPC) and novel 2-hydroxychalcone-based amphiphiles (Fig. 1). The latter act as stimuli-sensitive elements as they possess a photochromic unit that is part of the multistate chemical network of flavylium compounds (Fig. 1), previously explored in smart drug delivery systems.[2] This study investigates the impact of the different light-sensitive 2-hydroxychalcones, varying in charge and alkyl chain length, on the properties of the liposomes, resorting to microDSC, electrophoretic light scattering, light microscopy, UV-vis and fluorescence spectroscopies. Results show that the chalcone compounds enhance the colloidal stability of the liposomes, decrease their gel-to-liquid crystal phase transition temperature, and enhance their loading properties towards an hydrophilic probe. Moreover, light irradiation affects the fluidization temperature and the surface charge of the liposomes, with effects varying depending on the chalcone molecular structure.

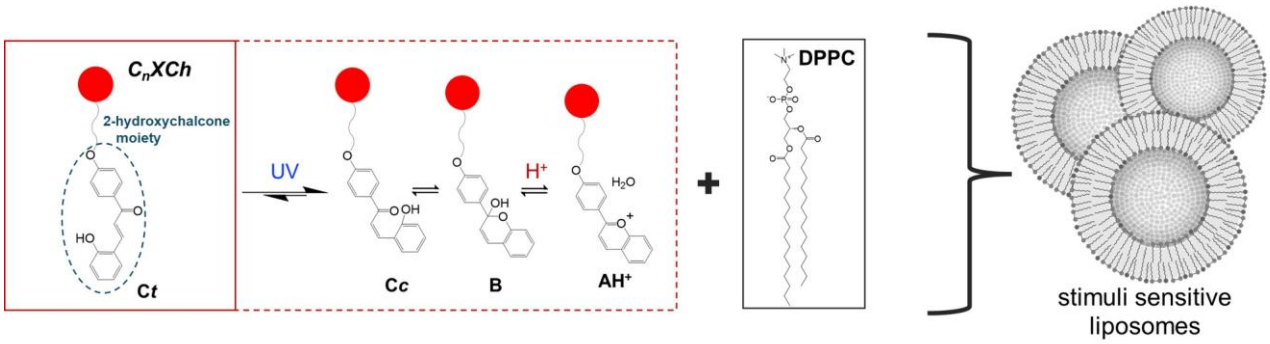


Figure 1: Molecular structures of the compounds involved in the formation of the photosensitive liposomes and the respective reactions undergone by the 2-hydroxychalcone derivatives upon irradiation with or without acidification of the medium.

Acknowledgements
We thank FCT, FEDER/COMPETE and P2020|COMPETE for financial support through projects POCI-01-0145-FEDER-032351 (PhotoSAN), 2022.05543.PTDC (Smart4Vir), UID/QUI/0081/2020, IMS (LA/P/0056/2020), and UID/QUI/50006/2019. Dmitriy Moreira also acknowledges financial support from FCT through the PhD grant 2021.06067.BD.

References

1. E. Rideau, R. Dimova, P. Schwille, F. R. Wurm, K. Landfester, *Chem. Soc. Rev.* 2018, **47**, 8572-8610.
2. D. Moreira, O. Regev, N. Basílio, E. F. Marques, *J. Colloid Interface Sci.* 2023, **650**, 2024-2034.

Thermodynamics of water-driven separation of ionic liquid mixtures

Highlighted ORAL_HO3.1 - Phase Equilibria and Fluid Properties

Margarida Costa Gomes[1,*], Beatriz R. de Moraes[2], Hanne Oorts[1], Rômulo Ando[2], Agílio Padua[1]

[1] *Laboratoire de Chimie, CNRS & ENS de Lyon, France*
[2] *Laboratório de Espectroscopia Molecular, Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo, Brazil*

**margarida.costa-gomes@ens-lyon.fr*

Mixing ionic liquids (ILs) offers a powerful strategy to fine-tune their properties without the need for complex synthesis. However, a drawback of using IL mixtures is their nonvolatility which makes separation and recycling challenging. To address this limitation, we recently introduced a mild and efficient method using water at ambient conditions to recover the original ILs.
We show how to successfully separate equimolar IL mixtures containing hydrophobic (bis(trifluoromethylsulfonyl)imide, $[NTf_2]^-$) and hydrophilic (acetate, $[OAc]^-$) anions with common cations such as 1-butyl-3-methylimidazolium ($[C_4C_1Im]^+$) or 1-methoxyethyl-3-methylimidazolium ($[(C_3O)C_1Im]^+$), achieving over 99% purity as determined by ^{1}H-NMR.[1] The addition of water also proves effective to separate mixtures with distinct cations, such as 1-decyl-3-methylimidazolium acetate ($[C_{10}C_1Im][OAc]$) and 1-(2-(2-methoxyethoxy)ethyl)-3-methylimidazolium ($[(C_5O_2)C_1Im][NTf_2]$).
The miscibility threshold for each mixture can also be determined by Isothermal Titration Calorimetry (ITC) and is marked by a discontinuity in heat (Q) upon water addition, revealing that stronger cation-anion interactions lead to larger miscibility windows. As expected, mixtures with distinct cations and anions can undergo anion metathesis during phase separation, highlighting the importance of balancing cation hydrophobicity and cation-anion affinity[2] to control the efficiency of the separation.

Acknowledgments
B.R.M. acknowledges funding from Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP), grants: 2020/09250-3 and 2023/06957-7.

References

1 B.R. de Moraes *et al. Angew. Chem. Int. Ed.* 2025, **64**, e202503863.
2 B.R. de Moraes *et al. J. Phys. Chem. B* 2024, **128**, 4759-4769.

Assessing the polarity of polymer/polymer aqueous two-phase systems via the Owens-Wendt method

ORAL_O3.2 - Phase Equilibria and Fluid Properties

Alexandre M. S. Jorge[1*], João A. P. Coutinho[2], and Jorge F. B. Pereira[1]

[1]*CERES, FCTUC, Department of Chemical Engineering, University of Coimbra, Rua Sílvio Lima, Pólo II - Pinhal de Marrocos, 3030-790 Coimbra, Portugal*
[2]*CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal*

**alexandrej@eq.uc.pt*

Aqueous Two-Phase Systems (ATPS) have been widely explored as innovative liquid-liquid extraction techniques for various (bio)molecules across multiple disciplines. However, the underlying intermolecular interactions governing their formation and partitioning remain insufficiently understood, posing challenges for developing predictive models for large-scale applications. Recent studies have shown that contact angle (CA) measurements combined with the Owens-Wendt model provide a powerful approach to determining the surface tension components of aqueous mixtures, offering deeper insights into their structural and intermolecular dynamics. This study employs CA measurements and the Owens-Wendt method to assess the polar and dispersive surface tension components of different ATPS. Specifically, polarity variations in polymer/polymer systems composed of polyethylene glycol 600 g/mol (PEG600) and polypropylene glycol 400 g/mol (PPG400) were examined in both monophasic and biphasic mixtures. Initially, the surface energy components of various substrates were determined using de-ionized water and dimethyl sulfoxide as reference liquids. Subsequently, CA measurements were conducted for monophasic mixtures and ATPS phases at different tie-line lengths (TLL), allowing the correlation of polar and dispersive contributions to surface energy with phase composition. The findings confirm that the Owens-Wendt method effectively captures polarity changes in ATPS, providing novel insights into their formation and partitioning behaviors. This approach enhances our understanding of ATPS thermodynamics and contributes to the development of more accurate predictive models for their optimization in various applications.

Acknowledgments
CERES is supported by the Fundação para a Ciência e a Tecnologia (FCT) through the projects UIDB/ EQU/00102/2020 and UIDP/EQU/00102/2020. This work was partly developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MEC (PIDDAC). J.F.B. Pereira and A. M. S. Jorge acknowledge FCT for funding the project DRI/India/0044/2020) and Fundação Calouste Gulbenkian for funding the project "DyeLoop".

References

1. A. M. S. Jorge, G. M. C. Silva, J. A. P. Coutinho and J. F. B. Pereira, *Physical Chemistry Chemical Physics* 2024, **26**, 7308-7317.
2. A. M. S. Jorge, J. A. P. Coutinho and J. F. B. Pereira, *Sep Purif Technol* 2023, **320**, 124183.
3. Z. Zhang, *Colloids Surf A Physicochem Eng Asp* 2023, **676**, 132223.

Hydrodynamics of aqueous two-phase systems separation

ORAL_O3.3 - Phase Equilibria and Fluid Properties

Alexandre M. S. Jorge[1], João A. P. Coutinho[2], and Jorge F. B. Pereira[1,*]

[1]*CERES, FCTUC, Department of Chemical Engineering, University of Coimbra, Rua Sílvio Lima, Pólo II - Pinhal de Marrocos, 3030-790 Coimbra, Portugal*
[2]*CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal*

**jfbpereira@eq.uc.pt*

Aqueous Two-Phase Systems (ATPS) have been extensively studied as a promising extraction platform for various (bio)molecules.[1] However, their industrial application remains limited due to challenges such as insufficient understanding of partitioning and separation mechanisms, a lack of predictive models, incompatibility with conventional extraction equipment, and a scarcity of large-scale studies.[2] To address these limitations, this study investigates the phase separation hydrodynamics of different ATPS. Among a general overview on the ATPS hydrodynamics, a deeper analysis will be focused on cholinium chloride-based ATPS. Mixing time (Tm) and phase settling time (Ts) were analyzed at 25 °C and 50 °C to assess their impact on system performance. The findings revealed that Ts is independent of Tm, with polymer/salt systems exhibiting prolonged settling times (Ts > 6 h), whereas salt/salt systems displayed significantly faster phase separation (Ts < 150 s). The enhanced separation efficiency in salt/salt ATPS is primarily attributed to the strong salting-out effect of the inorganic salts. Among the physicochemical properties examined, phase density emerged as the most critical factor influencing ATPS formation. Furthermore, a well-defined biphasic operation region was established for [Ch]Cl/salt-based systems, offering practical guidelines for integrating these systems into industrial-scale extraction processes using conventional mixer-settler units.

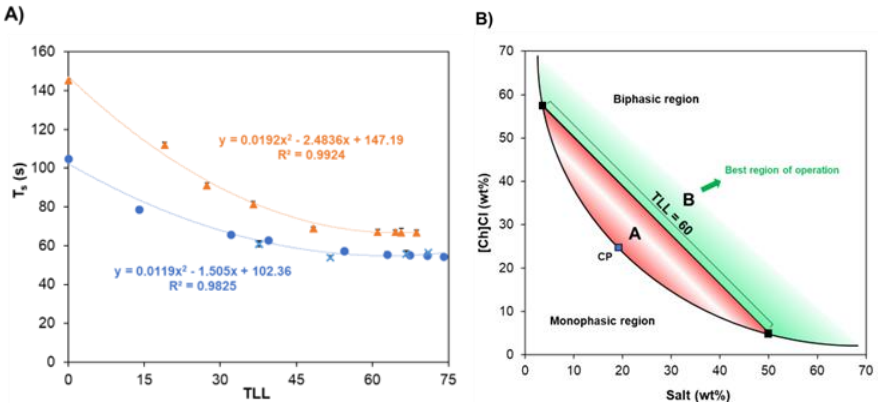


Figure 1: Ts values as a function of TLL at 25 °C (A) (● – mixture points of [Ch]Cl/K_3PO_4; (▲– mixture points of [Ch]Cl/K_2HPO_4; × – mixture points from Shahrihari *et al.*[2]; and generic best region of operation for [Ch]Cl-based ABS. Adapted from Jorge *et al.*[1].

Acknowledgments
CERES is supported by the Fundação para a Ciência e a Tecnologia (FCT) through projects UIDB/ EQU/00102/2020 and UIDP/EQU/00102/2020. The work was partly developed in CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MEC (PIDDAC). J.F.B. Pereira and A. M. S. Jorge acknowledge FCT for funding the project DRI/India/0044/2020 (DOI: 10.54499/DRI/India/0044/2020) and Fundação Calouste Gulbenkian for funding the project "DyeLoop".

References

1. A. M. S. Jorge, J. A. P. Coutinho and J. F. B. Pereira, *Sep Purif Technol* 2023, **320**, 124183.
2. S. Shahriari, L. C. Tomé, J. M. M. Araújo, L. P. N. Rebelo, J. A. P. Coutinho, I. M. Marrucho and M. G. Freire, *RSC Adv.* 2013, **3**, 1835-1843.

Thermophysical properties and environmental relevance of three dichlorobenzaldehyde isomers

ORAL_O3.4 - Phase Equilibria and Fluid Properties

Bruno D. A. Pinheiro*, Ana R. R. P. Almeida, Manuel J. S. Monte

Research Center in Chemistry of University of Porto (CIQUP), Institute of Molecular Sciences (IMS), Department of Chemistry and Biochemistry (DQB), Faculty of Sciences of University of Porto (FCUP), Rua do Campo Alegre, P-4169-007 Porto, Portugal

up201100352@edu.fc.up.pt

Understanding the volatility and solubility of organic compounds is essential for evaluating their environmental fate and managing the pollution risks associated with their use.[1] By combining sublimation and solubility data — derived from vapor pressure and aqueous solubility measurements — other key environmental mobility parameters such as the Gibbs energy of solvation (hydration) and Henry's law constants can be determined. In this work, the vapor pressures of both condensed phases (crystalline and liquid) of 2,3-, 2,4-, and 2,6- dichlorobenzaldehydes were measured using a static method based on capacitance diaphragm manometers.[2] From these measurements, the standard molar enthalpies, entropies, and Gibbs energies of sublimation and vaporization were derived. Phase diagrams (*p*,*T*) were constructed in the vicinity of the triple points for each compound. The aqueous solubility (Sw) of the three isomers at 298.15 K was determined using the shake-flask method[3], followed by UV-Vis spectroscopy. Thermal analysis of the five compounds was conducted using differential scanning calorimetry, from which fusion properties and crystalline heat capacities were determined. Combining the experimental results, the Gibbs energy of solvation and Henry's law constants were calculated, providing valuable insights into the environmental mobility and behaviour of these halogenated benzaldehydes across various contexts.

.

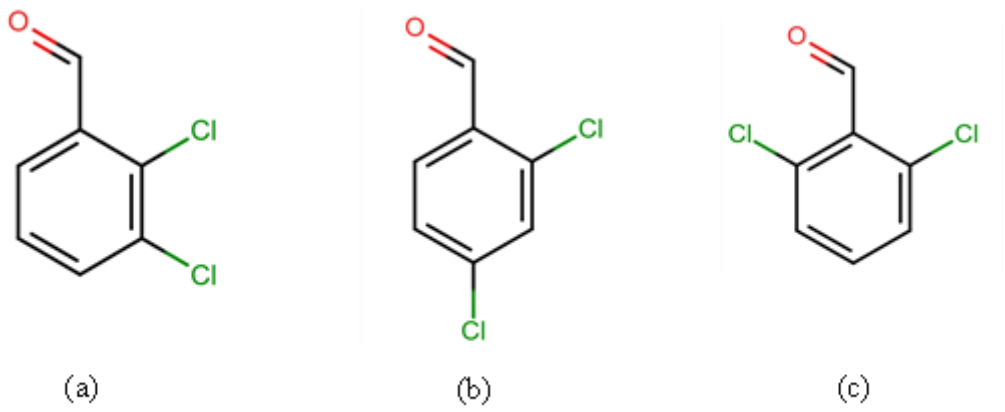


Figure 1: Structural Formula of (a) 2,3-dichlorobenzaldehyde, (b) 2,4-dichlorobenzaldehyde, and (c) 2,6-dichlorobenzaldehyde.

Acknowledgements
This work was supported by the Fundacão para a Ciência e Tecnologia (FCT) (funded by national funds through the FCT/MCTES (PIDDAC)) to CIQUP, Faculty of Sciences, University of Porto (Project UIDB/00081/2020) and IMS - Institute of Molecular Sciences (LA/P/0056/2020). ARRPA is financed by national funds through the FCT-I.P., in the framework of the execution of the program contract provided in paragraphs 4, 5, and 6 of art. 23 of Law no. 57/2016 of 29 August, as amended by Law no. 57/2017 of 19 July. BDAP thanks FCT for the award of a PhD research grant (UI/BD/152715/2022).

References

1. M.J.S Monte, A.R.R.P Almeida, *Chemosphere* 2017, **189**, 590.
2. M.J.S. Monte, L.M.N.B.F. Santos, M. Fulem, J.M.S. Fonseca and C.A.D. Sousa, *J. Chem. Eng. Data* 2006, **5**, 757.
3. A. Veseli, S. Žakelj and A. Kristl, Drug Dev. *Ind. Pharm* 2019, **45**, 1717.

Thermophysical properties of high CO_2 mixtures: Experiments and theory

ORAL_O3.5 - Phase Equilibria and Fluid Properties

Erich T. Tiuman[1], Jean P. Longo[1], Felipe K. Marozo[1], David S. Kabacznik[1], Eduardo N. Santos[1], Marco J. Silva[2], Rigoberto E. M. Morales[1], Moisés A. Marcelino Neto[1*]

[1]*Multiphase Flow Research Center (NUEM), Federal University of Technology – Paraná (UTFPR). Rua Deputado Heitor Alencar Furtado 5000, Bloco N, CEP 81280-340, Curitiba, Brazil.*
[2]*Institute of Measurement Technology, Johannes Kepler University Linz. Altenberger Str. 69, 4040 Linz, Áustria.*

[*]*mneto@utfpr.edu.br*

In oil fields, Multiphase Flow Meters (MPFMs) play a crucial role in reservoir management and production[1] optimization by providing real-time measurements of oil, gas, and water flow rates. Their use eliminates the need for dedicated test separators, reducing hardware requirements in both onshore and offshore applications[2]. The recent discovery of CO_2-rich pre-salt reservoirs has heightened the need to assess MPFM performance under elevated CO_2 conditions[3]. This study experimentally and theoretically investigates the impact of dissolved CO_2 in a CO_2-dodecane mixture on its thermophysical and electrical properties. Experiments were conducted over a pressure range of 1 to 170 bar and temperatures from 5 to 80°C, analyzing CO_2 solubility (0–100%) and its effects on viscosity, density, and electrical permittivity. A thermodynamic model based on the Cubic Plus Association (CPA) equation of state was applied for comparison with experimental results. Figure 1 and Figure 2 present all experimental data alongside model predictions and the deviation between them, respectively, demonstrating their agreement. The EoS was tuned using all experimental data acquired from the bench by adjusting the binary interaction parameter (k_{ij}), resulting in an average deviation of 2.86% between the model and experimental data.

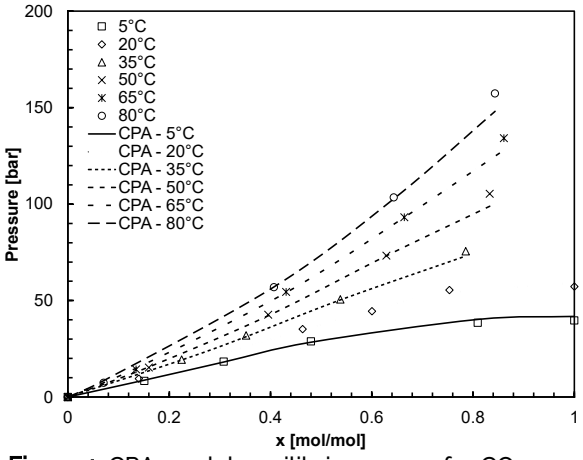


Figure 1: CPA model equilibrium curve for CO_2 + n-dodecane plotted with experimental points.

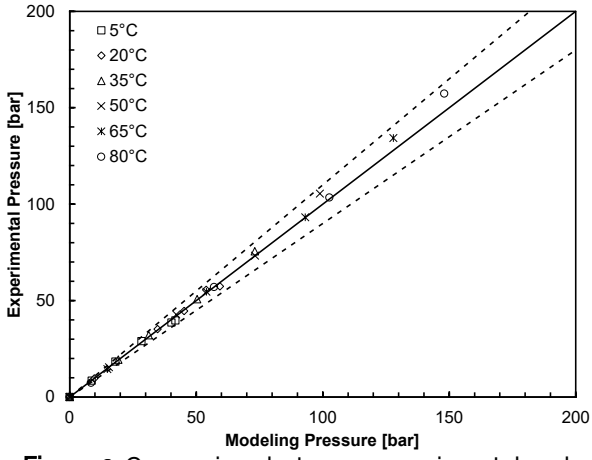


Figure 2. Comparison between experimental and CPA model pressure at different temperatures, with an average deviation of 2.86%.

Acknowledgments
The authors acknowledge the SHELL BRASIL PETRÓLEO LTDA. for the financial support under the Grant No. CW499828

References

1 M. Meribout, A. Azzi, N. Ghendour, N. Kharoua, L. Khezzar and E. AlHosani, *Measurement* 2020, **165**, 108111.
2 G. Falcone, G. F. Hewitt, C. Alimonti and B. Harrison, *Journal of Petroleum Technology* 2002, **54**, 77-84.
3 V. A. de Freitas, J. C. dos S. Vital, B. R. Rodrigues and R. Rodrigues, *J South Am Earth Sci* 2022, **115**, 103760.

Assessing solid-liquid equilibrium by isothermal titration calorimetry

ORAL_O3.6 - Phase Equilibria and Fluid Properties

Guillaume Depraetère*, Nithavong Cam, Agílio Pádua, Margarida Costa Gomes

Chemistry Laboratory, CNRS & ENS Lyon

**guillaume.depraetere@ens-lyon.fr*

Determining the solubility of metal salts in ionic liquids is challenging using visual methods or Differential Scanning Calorimetry (DSC). The slow crystallization kinetics of the metal salts impede accurate Solid-Liquid Equilibrium (SLE) measurements, resulting in significant discrepancies in the limited available literature.
We propose Isothermal Titration Calorimetry (ITC) as an alternative technique to measure the solubility of metal salts in ionic liquids at different temperatures. The results obtained using this approach are shown in Figure 1 for lithium bis(trifluoromethylsulfonyl)imide ($LiNTf_2$) in the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_2C_1Im][NTf_2]$). Each solubility point was obtained by titrating away the excess of metal salt with the solvent to cross the composition of the liquidus line at the working temperature. The results agree with previously obtained literature data[1,2,3] thus validating this new experimental approach. We show how the ITC experiments not only provide accurate solubility data at the studied temperatures but also reveal key thermodynamic properties of dissolution, including the enthalpy of dissolution; the mixing enthalpy and the partial molar excess enthalpy of both components at saturation.

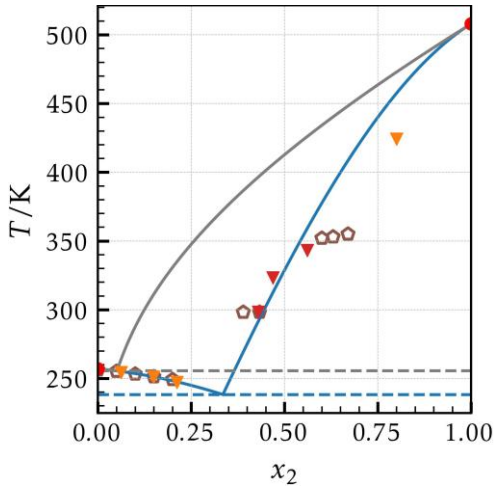


Figure 1: *T-x* phase diagram of (1) $[C_2C_1Im][NTf_2]$ +$LiNTf_2$ (2)

▼ DSC measurement [this work], ⬠ literature data[1,2,3], ▼ ITC measurement [this work]. Grey line corresponds to ideal *T-x* phase diagram, blue line to extrapolation from experimental data, used to guide the eyes.

Acknowledgments
The authors thank A. Van den Bruinhorst for useful discussions.

References

1 J. Asenbauer, N. Ben Hassen, B. D. McCloskey and J. M. Prausnitz, *Electrochim. Acta* 2017, **247**, 1038-1043
2 Q. Zhou, K. Fitzgerald, P. D. Boyle and W. A. Henderson, *Chem. Mater.* 2010, **22**, 1203-1208.
3 A. B. Pereiro, J. M. M. Araújo, F. S. Oliveira, J. M. S. S. Esperança, J. N. Canongia Lopes, I. M. Marrucho and L. P. N. Rebelo, *J. Chem. Thermodyn.* 2012, **55**, 29-36.

PC-SAFT and residual entropy scaling for thermodynamic and transport properties of hydrogen-containing mixtures

ORAL_O3.7 - Phase Equilibria and Fluid Properties

Fufang Yang[1,*], Agílio A. H. Pádua[1]

[1] *Laboratoire de Chimie, ENS Lyon and CNRS, 46 allée d'Italie, 69364 Lyon, France*

**fufang.yang@ens-lyon.fr*

Accurately representing the thermodynamic and transport properties of hydrogen-containing mixtures is becoming increasingly important because these species and their mixtures serve as essential, cleaner energy carriers in the pursuit of more sustainable energy solutions. For instance, blends of hydrogen and light hydrocarbons are useful in the gradual transition to decarbonize fuels. However, their modeling is challenging because of the quantum effects of hydrogen and the strongly asymmetric phase behavior of the mixtures.
In this work, the thermodynamic properties of mixtures of hydrogen with hydrocarbons are modeled using the PC-SAFT model[1,2], with the variable-range parametrization approach for soft repulsion[3], which improves accuracy for caloric properties and critical properties. Various hydrogen parameter sets are compared for the thermodynamic properties of pure hydrogen and its mixtures. Then, the model is combined with the residual entropy scaling (RES) approach.[4,5] The experimental data is critically reviewed for binary mixtures containing hydrogen, including vapor-liquid equilibria, density, caloric properties, viscosity, and thermal conductivity. The PC-SAFT and RES models are evaluated using the curated database. The advantages of the PC-SAFT model compared to the cubic equations of state are discussed.

References

1. J. Gross and G. Sadowski, *Ind Eng Chem Res* 2001, **40**, 1244-1260.
2. J. Gross and G. Sadowski, *Ind Eng Chem Res*, 2002, **41**, 5510-5515.
3. G. Yang and A. A. H. Padua, *Ind Eng Chem Res*, 2025, in press.
4. Y. Rosenfeld, *Phys Rev A* 1977, **15**, 2545-2549.
5. X. Yang, X. Xiao, E. F. May and I. H. Bell, *J Chem Eng Data*, 2021, **66**, 1385-1398.

AI-driven fluid modeling: predicting input parameters of pure-component equations of state with ensemble learning

Highlighted ORAL_HO3.8 - Phase Equilibria and Fluid Properties

Roda Bounaceur, Romain Privat, Francisco Paes, Jean-Noël Jaubert*

Université de Lorraine, CNRS, LRGP, F-54000 Nancy, France

**jean-noel.jaubert@univ-lorraine.fr*

For a pure fluid, an equation of state (EoS) is a mathematical expression that relates pressure, temperature and molar volume. It provides a means to perform fluid phase equilibrium calculations, thereby enabling the estimation of vapor pressures, boiling points and property changes during vaporization. When coupled with a mathematical expression for the ideal gas heat capacity, an EoS can also estimate changes in enthalpy, entropy and exergy. EoS are thus a key component of any industrial process simulator. Among the numerous EoS available in open literature, cubic EoS play a pivotal role because they can be straightforwardly parameterized and are very accurate when applied to non-associating fluids[1]. For example, the most well-known cubic EoSs are those of Peng-Robinson and Redlich-Kwong-Soave. The input parameters for these EoSs are the critical temperature (T_c), the critical pressure (P_c) and the acentric factor (ω). When these properties are not available experimentally, they must be estimated with a high degree of accuracy.
For this reason, an ensemble learning technique that combines several machine learning algorithms has been developed to estimate T_c, P_c and ω for any compound comprising C, H, O, N, S, P, F, Cl, Br and I atoms. The open-source library MORDRED, developed in Python, was used to generate over 1,800 molecular descriptors to characterize the compounds studied. The learning database consists of experimental values for more than 1,700 molecules belonging to numerous chemical families. The accuracy of the proposed model has been tested on a wide range of experimental data and compared with that of various learning models recently reported in the literature. Such a comparison demonstrates the improved accuracy achieved by using the proposed model, which is why a tool was developed and distributed for estimating T_c, P_c and ω from the SMILES (Simplified Molecular Input Line Entry System) notation of a molecule. It is available free of charge at: https://bioscope.streamlit.app/

Keywords: critical properties; ensemble learning; artificial neural network; QSPR; molecular descriptors.

References

1. A. Piña-Martinez, R. Privat and J.N. Jaubert, *AIChE J.* 2022, **68**, e17518.

Evaluation of the surface properties for fluids through the isomorphism with lattice models

ORAL_O3.9 - Phase Equilibria and Fluid Properties

Anastasiia Maslechko[1,*], Vladimir L. Kulinskii[1]

[1]*Department of Physics and Astronomy, Odesa I. I. Mechnikov National University, Ukraine*

[*]*maslechko.an@gmail.com*

This communication is mainly devoted to the attempt to determine the temperature dependence of the surface tension coefficient at the "liquid-vapor" interface in an analytically simple way using isomorphism with lattice models. Kulinskii noticed[1,2] the topological isomorphism of the phase diagrams for lattice model and real substances, and based on empirical relations, such as the law of the rectilinear diameter and the linearity of Zeno-line, constructed geometric affine transformation for the coexisting diagrams in the coordinates (ρ,T). These projective transformations used for evaluation of the thermodynamic properties of the fluid from the respective ones of the Ising model.

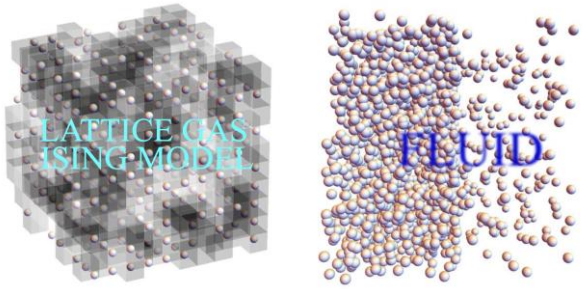


Figure 1: Graphical interpretation of the isomorphism.

The main result is that isomorphism with simple cubic lattices can be applicable to surface properties. For that, in the 2D case, exact Onsager's solution 3 is used, and the theory is compared with data from computer simulations.[4,5] In the 3D case, a comparison of NIST data[6] was performed with developed modified Woodbury's equation[7], which was introduced to cover the right critical behavior. With this, a discussion is raised about the effective thickness of the interface and a physical meaning for the latter is analyzed. In this regard, it is possible additionally to formulate a criterion for the lowest estimation of the temperature at the triple point, which had not previously been done in the application of the projective transformations to the "bulk" properties.
In general, it is shown that similar thermodynamic behavior is observed for dimensionless variables for a fairly wide class of substances. This can be seen as an improvement on the principle of corresponding states.

Acknowledgments
AM gratefully acknowledges VK for the global isomorphism projective transformations invention and interesting topics, and staff members from the former Department of Theoretical Physics for fruitful discussions.

References

1. V. L. Kulinskii, *J. Phys. Chem. B* 2010, **114**, 2852-2855.
2. V. L. Kulinskii, *J. Chem. Phys.* 2010, **133**, 034121.
3. B. Kaufman, L. Onsager, *Phys. Rev.* 1949, **76**, 1244-1252.
4. L.-J. Chen, M. Robert, K. P. Shukla, *J. Chem. Phys.* 1990, **93**, 8254.
5. M. Santra, B, Bagchi, *J. Chem. Phys.* 2009, **131**, 084705.
6. NIST Chemistry WebBook. NIST Standard Reference Database Number 69. https://webbook.nist.gov/chemistry/fluid/. Accessed 20 Feb 2025.
7. A. Maslechko, K. Glavatskiy, V. L. Kulinskii, *J. Mol. Liq.* 2007, **235**, 119-125.

Polyglycols as mass separating agents for fuel and terpene processing

ORAL_O3.10 - Phase Equilibria and Fluid Properties

Aline Zambom[1,2], Mónia A. R. Martins[1], João A. P. Coutinho[2], Simão P. Pinho[1], Olga Ferreira[1,*]

[1]CIMO, LA SusTEC, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal.
[2]CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

*oferreira@ipb.pt

Terpenes and terpenoids are abundant in nature and widely used in pharmaceuticals, cosmetics, and food industries, driving the need for efficient and sustainable separation methods to obtain them in high purity. However, conventional techniques like distillation and solvent extraction often suffer from limitations such as high energy consumption, thermal degradation of terpenes, and using volatile organic solvents of environmental concern. Polyglycols offer a promising alternative as mass separation agents for terpenes and terpenoids due to their low volatility, biodegradability, and low cost.[1]

This study investigates using polyethylene glycol (PEG 400) and polypropylene glycol (PPG 400) as mass separation agents for terpene fractionation and fuel processing. To do so, the infinite dilution activity coefficients of several terpenes and common organic compounds in the polyglycols were obtained by inverse gas chromatography and described by the COnductor like Screening MOdel for Realistic Solvents (COSMO-RS).[2] Overall, COSMO-RS was able to predict the changes in the interactions between solutes and polyglycols as apolarity increased from PEG to PPG.

The separation performance was assessed by estimating the separation factors selectivity, S_{ij}^{∞}, capacity, k_j^{∞}, and solvent performance index, Q_{ij}^{∞} (**Figure 1**). PPG 400 showed better results for separating monoterpene mixtures though Q_{ij}^{∞} were still lower or close to one. On the other hand, PEG 400 resulted in the best overall performance (Q_{ij}^{∞} > 10 and k_j^{∞} > 1) for most of fuel-processing mixtures (alkanes/aromatics separation, desulfurization and denitrification of fuels).

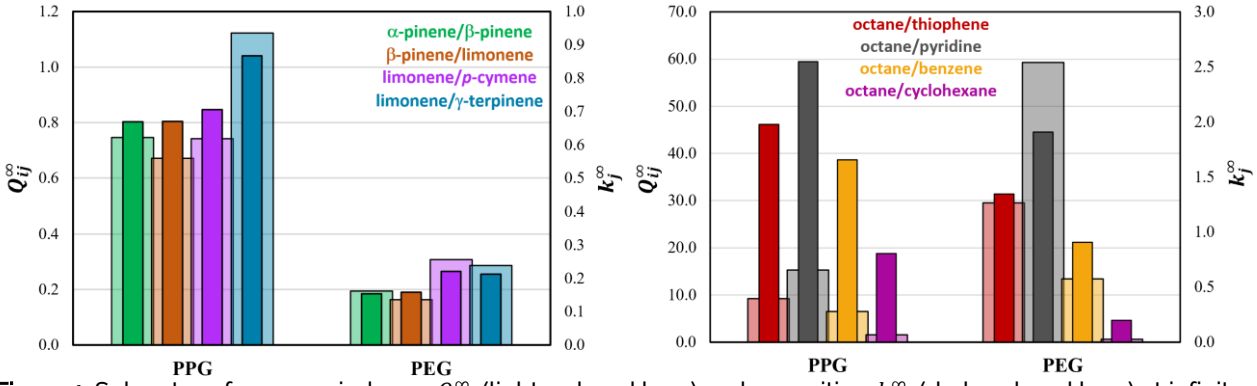


Figure 1: Solvent performance indexes, Q_{ij}^{∞}, (light-colored bars) and capacities, k_{ij}^{∞}, (dark-colored bars) at infinite dilution.

Acknowledgments

This work was supported by national funds through FCT/MCTES (PIDDAC): CIMO, UIDB/00690/2020 (DOI: 10.54499/UIDB/00690/2020) and UIDP/00690/2020 (DOI: 10.54499/UIDP/00690/2020); and SusTEC, LA/P/0007/2020 (DOI: 10.54499/LA/P/0007/2020). National funding by FCT, Foundation for Science and Technology, through the individual research grant ((UI/BD/154740/2023) of A. Zambom.

References

1. M. M. Hoffmann, *COCIS journal* 2022, **57**, 101537.
2. F. Eckert and A. Klamt, *AIChE Journal* 2002, **48**, 369-385.

Nonlocal internal variable and superfluid state in liquid helium

ORAL_O3.11 - Phase Equilibria and Fluid Properties

Vito Antonio Cimmelli*

Department of Fundamental and Applied Sciences
University of Basilicata, Via dell'Ateneo Lucano, 10,
85100, Potenza, Italy

**vito.cimmelli@unibas.it*

We present a model of superfluidity based on the internal variable theory. The internal variables of state allow to model nonequilibrium processes involving complex thermodynamical systems in which classical observable quantities, such as pressure and temperature, are insufficient to describe nonequilibrium phenomena. The nature of these additional nonequilibrium parameters depends on the phenomenon to be modeled, and their evolution is ruled either by ordinary differential equations (local behavior) or by partial differential equations (weakly nonlocal behavior). Here we consider a two-component fluid endowed with a scalar internal variable whose gradient is the counterflow velocity, namely, the difference between the velocities of normal and superfluid components, respectively. The restrictions imposed by the second law of thermodynamics are derived by applying a generalized Coleman-Noll procedure. The basic idea of this methodology is to consider as additional equations to be substituted into the entropy inequality the spatial differential consequences (gradients) of the balance laws, up to the order of the gradients entering the state space. A set of constitutive equations of the Landau-type, with entropy, entropy flux, and stress tensor depending on the counterflow velocity, is obtained. The propagation of thermomechanical perturbations is investigated as well. It is shown that first and second sound waves may propagate along the system with speeds depending on the physical parameters of the two fluids. First sound waves may propagate in the same direction or in the opposite direction of the counterflow velocity, depending on the concentration of normal and superfluid components.

High-pressures phase behavior of CO_2 with *n*-alkane isomers

ORAL_O3.12 - Phase Equilibria and Fluid Properties

Sergiu Sima[1], Catinca Secuianu[1,*], Dan V. Nichita[2]

[1]Department of Inorganic Chemistry, Physical Chemistry and Electrochemistry, Faculty of Chemical Engineering and Biotechnologies, National University of Science and Technology POLITEHNICA Bucharest, 1-7 Gh. Polizu Street, S1, 011061 Bucharest, Romania
[2]CNRS UMR 5150, Laboratoire des Fluides Complexes et leurs Réservoirs, Université de Pau et des Pays de l'Adour, B.P. 1155, 64013, Pau Cedex, France

**catinca.secuianu@upb.ro*

The phase equilibria of carbon dioxide (CO_2) and *n*-alkane isomers play a crucial role in various industrial applications, including enhanced oil recovery, supercritical fluid extraction, and gas processing.[1-2] Understanding the phase behavior of these systems is essential for optimizing separation processes, designing efficient thermodynamic models, and improving the performance of CO_2-based technologies.[3] Due to CO_2's tunable solubility and its ability to act as a solvent under supercritical conditions, its interaction with different isomers of alkanes significantly influences phase behavior, impacting critical parameters such as solubility, density, and phase transitions. Studying these equilibria provides insights into molecular interactions, aiding in the development of more accurate equations of state and facilitating the advancement of environmentally friendly and energy-efficient processes. This work presents new high-pressure phase equilibrium experimental data for various binary systems of CO_2 with n-alkane isomers (e.g., CO_2 + 2,2-dimethylbutane). The experimental data provide insights into phase interactions, including solubilities and critical properties under elevated pressures. Cubic equations of state (EoS) are employed in a predictive approach to model the systems. This methodology enhances the reliability of thermodynamic models for applications in gas processing and supercritical fluid technologies.

Acknowledgments
This work was supported by a grant of Ministry of Research, Innovation, and Digitization, CNCS - UEFISCDI, project number PN-III-P4-PCE-2021-0717, within PNCDI III".

References

1. S. Peper, J.M.S. Fonseca, R. Dohrn, *Fluid Phase Equilibria* 2019, **484**, 126-224.
2. R. Dohrn, S. Peper, C. Secuianu, J.M.S. Fonseca, *Fluid Phase Equilibria* 2024, **579**, 113978.
3. J.-C. de Hemptinne, G.M. Kontogeorgis, R. Dohrn, I.G. Economou, A. ten Kate, S. Kuitunen, L. Fele Žilnik, M.G. De Angelis, V. Vesovic, *Industrial & Engineering Chemistry Research* 2022, **61**, 14664-14680.

Investigation of perfluorohexane as a potential physical solvent for flue gas cleaning: Experimental vapor-liquid equilibrium data and modelling

ORAL_O3.13 - Phase Equilibria and Fluid Properties

Marc M. Tshibangu[1,*], Christophe Coquelet[2], Caleb Narasigadu[3], and Deresh Ramjugernath[4]

[1]*Department of Chemical Engineering, Mangosuthu University of Technology, Jacobs, Durban, 4026, South Africa*
[2]*Université de Toulouse, IMT Mines Albi, CNRS UMR 5302, Centre Rapsodee Campus Jarlard, 81013 Albi CT Cedex 9, France*
[3]*School of Chemicals and Minerals Engineering, Faculty of Engineering, Potchefstroom Campus, North-West University, Potchefstroom 2351, South Africa*
[4]*Department of Chemical Engineering, Faculty of Engineering, Stellenbosch University, Stellenbosch, 7600, South Africa*

[*]*tshibangu.marc@mut.ac.za*

Perfluorocarbons possess atypical properties due to their strong carbon-fluorine bonds, providing exceptional chemical and thermal stability. Their high gas absorption capacity, among other properties, makes them promising candidates for use as physical solvents in industrial applications[1]. In this study, perfluorohexane was investigated as a potential physical solvent for flue gas cleaning in advanced power generation facilities, particularly integrated gasification combined cycle systems.

A key factor in designing gas absorption systems is accurate vapour-liquid equilibrium (VLE) data[2]. However, VLE data for perfluorohexane with common flue gases are scarce. To address this scarcity, phase equilibrium data measurements were conducted for binary systems of perfluorohexane with CO, H_2S, and C_2H_6 using a static-analytical apparatus equipped with a capillary sampler for phase sampling and gas chromatography for composition analysis. Measurement uncertainties were determined to be within 0.04 K for temperature, 0.008 MPa for pressure, and 0.100 for mole fractions for all systems. The measured data were successfully correlated using the direct method, primarily employing the Peng-Robinson equation of state[3] with the Mathias-Copeman alpha function[4] and Wong-Sandler mixing rules[5] incorporating the non-random two-liquid activity coefficient model[6]. The results showed that perfluorohexane exhibited strong high selectivity for CO_2 over CO. In contrast, C_2H_6 and H_2S displayed significant co-absorption with CO_2 at low pressures.

Acknowledgements
This research was funded by the South African Research Chairs Initiative under the Department of Science and Technology and National Research Foundation of South Africa.

References

1. Y. H. Heintz, L. Sehabiague, B. I. Morsi, K. L. Jones and H. W. Pennline, *Energy & Fuels*. 2008, **22**, 3824-3837.
2. D. W. Green and R. H. Perry, Perry's Chemical Engineer's handbook, 8th edition, McGraw-Hill Education, New York, 2008.
3. D. Y. Peng and D. B. Robinson, *Ind. Eng. Chem. Fundam*. 1976, **15**, 59-64.
4. P.M. Mathias and T. W, Copeman, *Fluid Phase Equilib*. 1983, **13**, 91-108.
5. D. S. H. Wong and S. I. Sandler, *AIChE J*. 1992, **38**, 671-680.
6. H. Renon and J. M. Prausnitz, *AIChE. J*. 1968, **14**, 135-144.

Universality of scaled pure fluid equations of state

ORAL_O3.14 - Phase Equilibria and Fluid Properties

Leslie V. Woodcock*

University of Algarve, Department of Physics

**lvwoodcock@ualg.pt*

We report progress towards a thermodynamic-reduced scientific, accurate, equation-of-state for NIST atomic and molecular pure fluids (https://webbook.nist.gov/chemistry/fluid/) with zero adjustable parameters, containing only physical constants. The state functions, density r(p,T), and Gibbs energy G(p,T), exhibit a symmetry, characterised by the rigidity, $w = (dp/dr)_T$, between gaseous and liquid states along any isotherm from critical (T_c) to the Boyle temperature (T_B), on either side of a supercritical mesophase bounded by percolation lines. Cluster expansions in powers of density relate to a supercritical liquid-phase rigidity symmetry (RS) line ($w = r_{rs}(T) = RT$) to gas phase virial coefficients. We show that it is continuous in all derivatives, linear within stable fluid phases, and relates analytically to the Boyle-work line (BW) ($w = (p/r)_T = RT$), and to percolation lines of gas (PB) and liquid (PA) phases by: $r_{BW}(T) = 2r_{PA}(T) = 3r_{PB}(T) = 3r_{RS}(T)/2$ for all $T < T_B$. A remarkable consequence of this symmetry is the same virial coefficients, that describe gas pressure, give liquid state pressures with similar precision in a Dr-powers expansion about the r_{RS}-line.

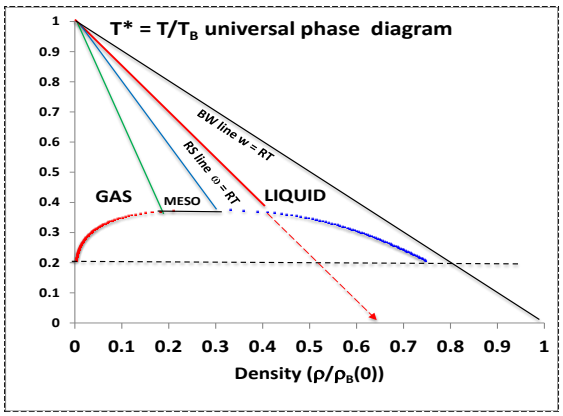


Figure 1: Delineation of fluid states using a reduced Boyle-work line phase diagram. The Boyle-work (BW) line[1] (RT = p/r) decreases linearly with density from T_B, hits a 1st-order liquid-to-crystal transition slightly above the triple point, and interpolates to a BW ground-state density constant $r_B(0)$ at $T \rightarrow 0$. The rigidity-symmetry (RS) line[2] ($RT = (dp/dr)_{\mathbb{N}}$) is simply related to the Boyle line, as also are the percolation lines that bound the supercritical mesophase between gas and liquid. The percolation lines for bonded clusters in gas (PB-green), and gas voids in liquid (PA-blue), also relate to the BW and RS lines. For all isotherms the densities of PB, PA, RS and BW lines, shown, are in the ratio 1:1.5:2:3 respectively.

These simple relationships arise from experimental r(p,T) data showing that the higher virial coefficients (b_n, $n \geq 4$) cancel due to clustering equilibria, or become negligible at all temperatures ($0 < T < T_B$) within the gas phase. The Boyle-work line is related exactly at lower densities as $T \rightarrow T_B$, and accurately for liquid densities, by $r_{BW}(T) = -(b_2/b_3)_T$. The BW and RS lines define new ground-state physical constants. Empirically, we find $r_{RS}(0) = (2/3)r_{BW}(0)$ for argon, CO_2 and H_2O. Given the gas-liquid rigidity symmetry, the entire thermodynamic state functions below T_B are obtainable from $b_2(T)$. The intermolecular pair potential, $f_{ij}(r_{ij})$ determines $b_2(T)$ analytically for all T. Hence, this result is a salient objective of liquid-state theory; $p(\mathbb{N},T)$ equation-of-state is obtainable from a pairwise Hamiltonian $f_{ij}(r_{ij})$ for all fluid states below r_{BW}, without any adjustable parameters.

We demonstrate the accuracy of the reduced equations-of-state along specific isotherms using the examples of Ar, CO_2 and H_2O. Given the basic science, all atomic and molecular fluids in the NIST thermophysical property data bank could be represented to within their experimentally measured uncertainty, using only physical-constant equations-of-state without any *ad hoc* terms.

References

1. J. G. Powles, *J. Phys. (C) Solid State Phys*. 1983, **16,** 503-514.
2. L. V. Woodcock, *Int. J. Thermophysics* 2016, **37**, 24-40.
3. L. V. Woodcock, *J. Modern Physics* 2024, **15**, 613-633.

Phase behavior of both woody and grassy lignins with aqueous renewable solvents: Ternary phase diagrams and thermodynamic modeling

Highlighted ORAL_HO3.15 - Phase Equilibria and Fluid Properties

Mark C. Thies[1,*], Oreoluwa Agede[1], Junhuan Ding[1], Walter G. Chapman[2], Lorenzo Zamagni[2]

[1]*Clemson University, USA*
[2]*Rice University, USA*

[*]*mcths@clemson.edu*

We have discovered that when lignin, the only abundant biopolymer with aromaticity, is mixed with aqueous renewable solvent mixtures (e.g., ethanol–H_2O and acetic acid–water solutions) at mildly elevated temperatures, specific mixture compositions exist where the solid lignin melts to form liquid–liquid equilibrium (LLE), comprised of a polymer (lignin)-rich and a solvent-rich phase. Furthermore, two regions of LLE are frequently formed within the same pseudo-ternary phase diagram at a given T and P, with one being close to the apex for the organic solvent and the other being nearer to the apex for H_2O. Such LLE has been observed and measured for a surprising number of aqueous solvents, including acetic acid, methanol, ethanol, isopropanol, and acetone; however, our focus has been on the renewable aqueous solvents ethanol and acetic acid.

Initial work focused on measuring the ternary phase behavior, including regions of both LLE and solid–liquid equilibrium (SLE), of kraft softwood lignin with ethanol–water and acetic acid–solutions, but more recently we have investigated the systems hybrid poplar (hardwood) lignin–ethanol–water and corn stover–ethanol–water, with the HP and CS lignins being recovered by alkaline pretreatment instead of from kraft black liquors. Although the kraft processing of wood still dominates the worldwide production of cellulose products, a small but rapidly growing alternative is the generation of compostable, molded-fiber cellulose products (including plates, bowls, and containers) from agricultural residues, including switchgrass, miscanthus, and corn stover. Thus, there is increasing interest in lignins derived from these agricultural residues because they have no unpleasant smell, a significant advantage for some of the newer proposed applications (e.g., for plastics).

Comparison of the similarities and differences that exist among the lignin–renewable solvent–water ternary phase diagrams for the three types of lignin, namely softwood, hardwood, and grass-based, will be presented for the first time. Additionally, the first thermodynamic modelling of these systems with PC-SAFT, and the challenges involved, will also be presented.

Towards thermal performance: Di-*n*-alkyl adipates for efficient low-temperature thermal energy storage

ORAL_O3.16 - Phase Equilibria and Fluid Properties

Maria C.M. Sequeira[1*], Timur Nikitin[2], Fernando J.P. Caetano[3,4], Hermínio P. Diogo[1], João M.N.A. Fareleira[1], Rui Fausto[2,5]

[1] *Centro de Química Estrutural, Institute of Molecular Sciences, Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal*
[2] *CQC-IMS, Departamento de Química, Universidade de Coimbra, Rua Larga, 3004-535 Coimbra, Portugal*
[3] *Departamento de Ciências e Tecnologia, Universidade Aberta, Rua da Escola Politécnica, 147, 1269-001 Lisboa, Portugal*
[4] *Centro de Química Estrutural, Institute of Molecular Sciences, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal*
[5] *ERA-Chair Spectroscopy@IKU, Faculty of Sciences and Letters, Dept. of Physics, Istanbul Kultur Univ., Ataköy Campus, Bakirköy 34156, Istanbul, Turkey*

**maria.sequeira@tecnico.ulisboa.pt*

The development of efficient and sustainable thermal energy storage (TES) systems is crucial for improving energy efficiency in various applications, especially at low temperatures, such as cryogenic cooling, cold storage, logistics and transportation. Phase change materials (PCM) play a key role in TES, as they allow the storage and release of significant amounts of latent heat during phase transitions. In this context, our research group has been working on new materials, particularly binary systems, with potential application as PCM for efficient low-temperature TES[1]. As a result, di-*n*-alkyl adipates have recently emerged as promising candidates due to their favorable thermal properties, chemical stability, and phase change behavior[2].
Our previous work[2] focused on the binary system of diethyl and dibutyl adipates, highlighted the potential of adipates as low-temperature PCM, motivating further research into their solid-liquid phase change behavior and structure-property relationships. Building upon this initial study, we have expanded our research into a broader range of di-*n*-alkyl adipates.
One of the key aspects of our current research is the identification of eutectic compositions within adipate-based binary systems. Eutectic mixtures are particularly attractive as PCM enabling tunable phase transition temperatures to match specific TES requirements. Through the careful combination of results obtained from Differential Scanning Calorimetry (DSC), Hot-Stage Microscopy (HSM), and Raman Spectroscopy, a detailed phase diagram was methodically crafted to highlight the intricate eutectic behavior of these systems, identifying compositions that optimize thermal performance. In this study, the interplay between alkyl chain length and thermal behavior, particularly the influence of odd–even effects in binary systems is also approached. By selecting mixtures that combine odd-odd, even-odd or even-even alkyl substituent arrangements, we have explored possible impacts on solid-liquid phase change behavior. Our results do not reveal a clear and distinct effect, as they all evidenced eutectic phase diagrams. Our findings contribute to the growing field of organic PCM, demonstrating that di-*n*-alkyl adipates are viable candidates for low-temperature TES applications. By elucidating their phase change behavior, we provide a foundation for the innovative development of next-generation thermal storage materials, paving the way for more advanced and efficient solutions.

Acknowledgments
This work was supported by Fundação para a Ciência e a Tecnologia (FCT), Portugal, Projects UIDB/00100/2020, UIDP/00100/2020, UIDB/00313/2025, UIDP/00313/2025, IMS—LA/P/0056/2020UIDB/00100/2020. M.C.M. Sequeira acknowledges the PhD grant funded by FCT ref. UI/BD/152239/2021. The ERA-Chair Spectroscopy@IKU - (Project number: 101184899) is funded by the European Research Agency under the HORIZON-WIDERA-2023-TALENTS-01-01 Program.

References

1. J. Du, B. Nie, Y. Zhang, Z. Du, li Wang, Y. Ding, *Journal of Energy Storage* 2020, **28**, 101238.
2. M. C. M. Sequeira, B. A. Nogueira, F. J. P. Caetano, H. P. Diogo, J. M. N. A. Fareleira, R. Fausto, *International Journal of Thermophysics* 2023, **44**, 165.

Measurement and modelling of liquid-liquid equilibrium for the water + propan-2-ol + cyclopentanol ternary system

ORAL_O3.17 - Phase Equilibria and Fluid Properties

Caleb Narasigadu*, Natasha Venter, Zandi Mthaketh, John O. Bamikole

School of Chemical and Minerals Engineering, Faculty of Engineering, Potchefstroom Campus, North-West University, Potchefstroom 2351, South Africa

Caleb.Narasigadu@nwu.ac.za

Bio-fuels are considered renewable sources of energy that are environmentally friendly and can also serve as substitutes and complement to fossil fuels, thereby increasing the octane rating and engine efficiency[1]. Bio-alcohols such as ethanol, propanol and others are often produced via fully fossil-free routes. A significant limitation in the production of bio-alcohol is the presence of water as a coproduct[2].

In this study, liquid-liquid extraction of propan-2-ol from its aqueous mixture using cyclopentanol as a solvent was explored at different temperatures (298.15, 308.15, 318.15 and 328.15) K. The experiment was carried out in a double-walled glass liquid-liquid equilibrium (LLE) cell employing the direct analytical method and the phase samples were analyzed with a Shimadzu gas chromatograph (GC). The obtained LLE data were modelled using the NRTL[3] and UNIQUAC[4] activity models to account for the nonideality in the systems. To ensure that the estimated parameters of the activity models replicate phase behaviour similar to the experimental data, predict the accurate number of phases without spurious phase prediction, and satisfy the Gibbs stability criterion, the homotopy continuation was introduced in the problem formulations as constraints along with other thermodynamic considerations[5] and solved with the developed hybrid of pelican and gorilla troop optimisation algorithm (PGOA)[6].

The experimental result shows that the distribution of propan-2-ol in cyclopentanol is higher than in water, and cyclopentanol has a high selectivity for propan-2-ol, which shows that cyclopentanol is a good solvent for extracting propan-2-ol in an aqueous solution. It was also observed that as the temperature increases, the selectivity of cyclopentanol increases. The estimated parameters for both NRTL[3] and UNIQUAC[4] models correctly predicted the phase behaviour of the systems. It was found that all the tie-lines were below the surface of the Gibbs free energy of the mixing, which indicates that the estimated parameters predicted stable phases. It was found that both NRTL and UNIQUAC parameters are consistent with experimental phase behaviour, that the system is a type I LLE system, and that partial miscibility exists in the water + cyclopentanol subsystem.

In conclusion, the new LLE data shows that cyclopentanol is a good solvent for the extraction of propan-2-ol in an aqueous solution. The estimated NRTL[3] and UNIQUAC[4] parameters accurately predicted phase behaviour that is stable and consistent with experimental phase behaviour and can be used for designing and optimizing an efficient extraction process of propan-2-ol from water with cyclopentanol as the solvent.

Acknowledgements

The authors would like to thank the National Research Foundation of South Africa and the North-West University for funding this project.

References

1. B. Elvers and A. Schütze, *Handbook of Fuels: Energy Sources for Transportation*, Wiley-VCH, 2nd edn., 2021.
2. A. Mejía, M. Cartes, G. Chaparro and E. A. Müller, *J Mol Liq* 2024, **397**, 124087.
3. H. Renon and J. M. Prausnitz, *American Institute of Chemical Engineers Journal* 1968, **14**, 135-144.
4. D. S. Abrams and J. M. Prausnitz, *American Institute of Chemical Engineers Journal* 1975, **21**, 116-128.
5. J. O. Bamikole, C. Narasigadu and N. Seedat, *Fluid Phase Equilib* 2025, **595**, 114421.
6. J. O. Bamikole and C. Narasigadu, *Chemical Engineering Research and Design* 2023, **194**, 163–178.

Volumetric properties and bubble point pressures of synthetic oil under gas injected

ORAL_O3.18 - Phase Equilibria and Fluid Properties

Sérgio M. Vilas-Boas[1], Fernanda P. Pelaquim[1,*], Ivanei F. Pinheiro[1], Vanessa C. B. Guersoni[1], Mariana C. da Costa[2], Paulo T. V. e Rosa[3]

[1]*Center for Energy and Petroleum Studies (CEPETRO), University of Campinas, 13083-896, Brazil*
[2]*School of Chemical Engineering (FEQ), University of Campinas, 13083-896, Brazil*
[3]*Institute of Chemistry (IQ), University of Campinas, 13083-896, Brazil*

[*]*pelaquim@unicamp.br*

The knowledge of PVT properties is essential for predicting and evaluating oil and gas production performance in reservoirs, as these properties influence critical aspects of both flow assurance and reservoir engineering.[1] In particular, density and viscosity govern fluid transport through pipelines and the porous media, while bubble pressure point (BPP) plays a central role in several engineering calculations, such as material balance, inflow performance modeling, reservoir simulation, and the design of Enhanced Oil Recovery (EOR) strategies.[1,2] This work investigates the BPP and volumetric behavior of model synthetic oil + injected gas mixtures. The synthetic oil is modeled by a heptane + toluene mixture (0.69:0.31 mole ratio), while the injected gas is represented by CH_4 or a mixture of CO_2 + CH_4 (0.81:0.19 mole ratio). BPP measurements were conducted in a stainless-steel PVT cell using the well-established Constant Composition Expansion (CCE) method over the (304.7–363.2) K temperature range. Two approaches, the Visual and the Stepwise method, were employed for the BPP determination. Additionally, liquid-phase density data were measured using a high-pressure vibrating U-tube densimeter across the (293.2–363.2) K temperature and (5–90) MPa pressure ranges. To complement the experimental analysis, the Tamman-Tait equation[3] was used to fit the density data and derived additional volumetric properties, namely the isothermal compressibility (κ_T) and the isobaric thermal expansivity (α_p). Furthermore, the Soave-Redlich-Kowng[4] (SRK) and Peng-Robinson[5] (PR) equations of state (EoSs) were applied to describe the BPP and the liquid-phase density. Mixtures with varying injected gas to model synthetic oil ratios were analyzed in both volumetric and phase equilibrium studies. Regarding the experiments, BPP values ranging from 0.8 to 22.2 MPa were obtained for the studied systems. Excellent agreement was achieved between the BPP values determined by the Visual and Stepwise methods (average absolute deviation — AAD = 0.03 MPa). The experimental density data and derived properties indicate regular fluid volumetric behavior. The Tamman-Tait equation accurately represented the density data, achieving an average relative deviation (ARD) of 0.06 %. For the EoS modeling, the SRK (ARD = 5.8%) and PR (ARD = 6.0%) provided similar performances in describing BPP data, while PR (ARD = 2.0%) significantly outperforms SRK (ARD = 11.2%) in predicting the liquid-phase densities. Improved accuracy was obtained by applying the Peneloux volume-translation correction[6] to both EoSs for modeling liquid density data.

Acknowledgements
We gratefully acknowledge the support of EPIC – Energy Production Innovation Center, hosted by the Universidade Estadual de Campinas (UNICAMP) and sponsored by Equinor Brazil and FAPESP – São Paulo Research Foundation (2017/15736-3 and EMUs Process and/or scholarship process). We acknowledge support from ANP (Brazil's National Oil, Natural Gas and Biofuels Agency) via the R&D levy, and the Center for Energy and Petroleum Studies (CEPETRO).

References

1. M. A. Ahmadi, S. Zendehboudi, L. A. James, A. Elkamel, M. Dusseault, I. Chatzis and A. Lohi, *J Pet Sci Eng* 2014, **123**, 207-216.
2. A. N. El-hoshoudy, A. B. Farag, O. I. M. Ali, M. H. EL-Batanoney, S. E. M. Desouky and M. Ramzi, *Fuel* 2013, **112**, 277-282.
3. J. H. Dymond and R. Malhotra, *Int J Thermophys* 1988, **9**, 941-951.
4. G. Soave, *C. En. Sci* 1972, **27**, 1197-1203.
5. D.-Y. Peng and D. B. Robinson, *Ind. Eng. Chem.*, 1976, **15**, 59-64.
6. A. Péneloux, E. Rauzy and R. Fréze, *Flui Phase Equilib* 1982, **8**, 7-23.

Molecular dynamics meets gravimetry: Paving the way to accurate dew-point densities

ORAL_O3.19 - Phase Equilibria and Fluid Properties

M. Sekulla[1], L. Bernardini[1], M. Kohns[2], M. Richter[1,3*]

[1] *Applied Thermodynamics, Chemnitz University of Technology, 09107 Chemnitz, Germany*
[2] *Laboratory of Engineering Thermodynamics, RPTU Kaiserslautern, 67663 Kaiserslautern, Germany*
[3] *Leibniz University Hannover, Institute of Thermodynamics, An der Universität 1, 30823 Garbsen, Germany*

**m.richter@mb.tu-chemnitz.de*

Reliable and accurate thermophysical property data are essential for efficient and safe operation in energy conversion, chemical processes, and environmental management. In particular, the knowledge of dew-point densities is crucial as it governs critical industrial operations, including equipment design, operational safety, and process optimization.[1] Among various thermophysical properties, the dew-point density is especially relevant because it marks the transition from the homogeneous vapor phase to the onset of condensation. Moreover, properties near the phase boundary are highly relevant for developing equations of state.

Currently, the most accurate method for measuring dew-point densities is gravimetric densimetry based on magnetic-suspension balances.[2,3] Although significant progress has been made in gravimetric density measurement techniques, systematic deviations persist near saturation, primarily due to adsorption phenomena at solid surfaces within the measurement devices. These phenomena involve two main aspects: (1) uncertainties arising from the influence of the adsorbate on the apparent mass and volume of the sinkers, and (2) compositional shifts in fluid mixtures caused by selective adsorption of individual components.[4]

In recent years, we have developed an integrated approach combining Molecular Dynamics Simulations (MDS) with gravimetric density and adsorption measurements obtained using the novel Four-Sinker Densimeter[5,6] (FSD) to correct for these effects.[7,8] MDS provides predictive, atomic-scale insights into adsorbate structures on surfaces representative of those within measurement devices, allowing for detailed investigations of adsorbate densities and, for mixtures, their composition. In this work, we studied the adsorption of the pure components carbon dioxide, ethane, and propane and the binary mixture of carbon dioxide and propane with various compositions. The obtained data enabled us to develop an empirical model that relates the adsorbate density to the proximity of the bulk phase to saturation.[8] Moreover, recent simulations on selective adsorption allow for well-founded assumptions regarding the adsorbate composition behavior when approaching the dew line. These findings will improve measurements obtained with the FSD and reduce uncertainties in other thermophysical property measurements, such as speed of sound or viscosity.

In summary, we demonstrate that our simulation approach yields excellent agreement between simulated and measured data, highlighting how our combined method effectively addresses adsorption-related uncertainties in thermophysical property measurements.

References

1. G. M. Kontogeorgis, R. Dohrn, I. G. Economou, J.-C. De Hemptinne, A. Ten Kate, S. Kuitunen, M. Mooijer, L. F. Zilnik, V. Vesovic, *Ind. Eng. Chem. Res.* 2020, **60**, 4987-5013.
2. W. Wagner, R. Kleinrahm, *Metrologia* 2004, **41**, 24-39.
3. X. Yang, R. Kleinrahm, M. O. McLinden, M. Richter, *Int. J. Thermophys.* 2023, **44**, 169.
4. M. Richter, R. Kleinrahm, *J. Chem. Thermodyn.* 2014, **74**,58-66.
5. K. Moritz, R. Kleinrahm, M. O. McLinden, M. Richter, *Meas. Sci. Technol.* 2017, **28**, 127004.
6. L. Bernardini, R. Kleinrahm, K. Moritz, et al., *Int. J. Thermophys.* 2024, **45**, 49.
7. M. Sekulla, M. Kohns, and M. Richter, *Ind. Eng. Chem. Res.* 2023, **62**, 19884-19892.
8. M. Sekulla, L. Bernardini, S. Werth, M. Kohns, M. Richter, *Ind. Eng. Chem. Res.* 2024, **63**, 16907-16914.

Accurate predictions of phase equilibria and thermophysical properties: A CALPHAD-based approach for metals and slag

ORAL_O3.20 - Phase Equilibria and Fluid Properties

Rui Zhang[1,*], Huahai Mao[1], Lina Kjellqvist[1], Reza Naraghi[1], Qing Chen[1,2]

[1] *Thermo-Calc Software AB, Sweden*
[2] *Materials Science and Engineering, KTH Royal Institute of Technology, Sweden*

**rui@thermocalc.se*

The prediction of phase equilibria and thermophysical properties is crucial for understanding high-temperature metallurgical processes, where complex interactions occur between metals and slag. Accurate modeling of these processes is essential for optimizing industrial practices such as steelmaking and refining, where phase transformations and inclusion formation significantly influence the quality of the final product.

To support this, databases like TCOX database[1] developed using the CALPHAD (Calculation of Phase Diagram) approach offer a comprehensive thermodynamic framework. TCOX database models the interactions between liquid steel and slag, incorporating all major steel alloying elements and key slag components. It uses an ionic liquid model to describe the liquid phase across a wide compositional range, from metallic (steel) to oxide (slag). Additionally, TCOX includes essential metallic and non-metallic solid phases, enabling precise predictions of inclusion formation, solidification behavior of steel and slag, and steel–slag–refractory interactions.

To control and optimize industrial processes and to understand and simulate geological phenomena, accurate data on slag properties is required, which typically involve both thermochemical and thermophysical aspects. The thermochemical properties include integral molar properties such as Gibbs energies and enthalpies, as well as partial molar properties, such as the activities of slag components. Thermophysical properties, on the other hand, encompass viscosity, surface tension, conductivity, resistivity and so on. However, both thermochemical and thermophysical properties are structure-dependent and thus mutually related. This interrelationship makes it essential to combine these properties when investigating slag behavior.[2] Models for molar volume, surface tension, viscosity, conductivity and resistivity have been developed and implemented in Thermo-Calc software.[3] By leveraging total Gibbs energy minimization, these models link slag structure with thermodynamic descriptions, enabling accurate and physically meaningful predictions across a wide compositional and temperature range.

Combining experimental data with computational thermodynamics allows for more precise control over phase equilibria and material properties. The present work will show and discuss selected examples where this approach enhances understanding and prediction of complex oxide systems.

References

1. TCOX – TCS Metal Oxide Solutions Database, v14.0 by *Thermo-Calc Software AB*, 2024.
2. R. Zhang, S. Hallström, H. Mao, L. Kjellqvist, Q. Chen, *ISIJ International* 2021, **61**, 1379-1388.
3. J.O. Andersson, T. Helander, L. Höglund, P.F. Shi, and B. Sundman, Thermo-Calc and DICTRA, Computational tools for materials science, *Calphad* 2002, **26**, 273-312.

The crucial factors of liquid-liquid equilibria: The proper choice of reference systems

Highlighted ORAL_HO3.21 - Phase Equilibria and Fluid Properties

Wolffram Schröer[1], Sabine Wagenfeld[2], and Bernd Rathke[2,*]

[1]*Institut für Anorganische und Physikalische Chemie, Universität Bremen, Germany*
[2]*Technische Thermodynamik, Universität Bremen, 28359 Bremen, Germany*

[*]*rathke@uni-bremen.de*

The background knowledge of the phase behavior is a prerequisite for a basic understanding of thermophysical properties. A number of systematic studies focusing on liquid-liquid equilibria were published during the last decades. As some studies have been focused on specific tasks, e.g., extraction, the avoidance of a demixing (fuel technology) or the optimization of specific formulations (pharmaceutics or cosmetics), scientific driven systematic studies are rare. Experimental results are often described in terms of empirical or semi-empirical or group contribution models, sometimes more sophisticated simulations corroborate the results.
A critical assessment of the experimental and theoretical data is rather tricky, as different components with their different thermophysical properties and their versatile molecular interactions might result in inextricable contributions to (a) uncertainties of the experimental data and (b) the quantitative determination / calculation of molecular interactions.
Therefore, we have performed systematic investigations on the liquid-liquid phase behavior of mixtures of normal alkanes with the molecular solvents ethanol or acetonitrile. Both types of mixtures show partial miscibility with upper critical solution temperatures, which are shifted systematically when the chain lengths of one component and, therefore, the molecular interactions are varied gradually. The main objective was to identify systematic trends of the phase behavior. Ethanol as a polar molecule connected with a dipole moment comparable to water is able to form hydrogen bonds. Acetonitrile exhibits a high dipole moment and shows partial miscibility with a couple of common molecular liquids, typically connected with the appearance of upper critical points. Acetonitrile allows for the study of molecular interactions influenced by a dipole moment without the appearance of hydrogen bonds. The present work contributes to the open discussion, if acetonitrile – alkane mixtures might be suitable as reference systems for the verification of experimental procedures for the determination of liquid-liquid phase equilibria.
The systems studied so far show limited miscibility with upper critical solution temperatures (UCSTs), they show variations from a asymmetric shape to an almost symmetrical one. The UCST decreases with decreasing length of the alkyl-chains of the alkane. Both classes of systems show the same universal critical behavior. The variations of the parameters are mainly determined by the size of the alkyl-chains. A simple determination of the free enthalpies on basis of a Flory-Huggins like approach allows for a description and partially a prediction of UCSTs of the different systems.

As the temperature range covered by these studies lead to an appreciable change of vapor pressure during the LLE determination the use of mixtures of ethyl ammonium nitrate and the normal alcohols - octanol or heptanol – are discussed as they can be regarded as real isobaric LLE.

Geological and thermodynamic influences on gas hydrate stability: Insights from the black sea and sea of marmara

ORAL_O3.22 - Phase Equilibria and Fluid Properties

O. Fandino[1,*], A, Heidari[1], C. Agnissan[1], C. Gumpier[2], M. Tariq[3], J. Esperança[3], A. Desmedt,[2,4] L. Ruffine[1,5]

[1] *Geo-Ocean, Univ Brest, CNRS, Ifremer, UMR6538, F-29280 Plouzane, France*
[2]*Institut des sciences moléculaires, UMR 5255 CNRS, Univ. Bordeaux, Talence, France*
[3]*LAQV, REQUIMTE, Dep de Química, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal*
[4] *Laboratoire Léon Brillouin, UMR12 CEA-CNRS, Saclay, France*
[5] *IFPEN, 1-4 Av. du Bois Préau, 92852 Rueil-Malmaison, France*

[*]*olivia.fandino.torres@ifremer.fr*

Gas hydrates are crystalline solids composed of water and gas molecules that form under low-temperature and high-pressure conditions. Found in continental margin sediments and permafrost regions, they constitute one of Earth's largest methane reservoirs. The hydrate-bound gas composition varies depending on its origin: microbial gas hydrates contain predominately methane (~99 mol%), while thermogenic hydrates usually consist of a C_{2+} hydrocarbons mixture. Most methane hydrates occur in fine-grained silty and clayey sediments, where mineralogy and pore structure significantly impact their formation, stability, and storage capacity.

This study examines methane hydrate deposits in two key regions: the Black Sea and the Sea of Marmara (SoM). The Black Sea hosts extensive methane-dominant hydrates in clay-rich sediments, whereas the SoM, traversed by the North Anatolian Fault, contains thermogenic gas hydrates with complex compositions. Analysis of thermogenic gases from hydrate samples reveals a composition with primarily methane (66.1 mol%), with the highest recorded concentrations of propane (18.8 mol%) and isobutane (9.5 mol%) to date.[1] The SoM provides insights into gas composition effects on hydrate stability, while the Black Sea helps assess sedimentological controls on hydrate formation and methane storage.

To evaluate these factors, high-pressure volumetric and phase equilibrium (VLHE) experiments were conducted on binary, ternary, and multicomponent gas mixtures using site-collected and commercial analogs. Gas chromatography and Raman spectroscopy confirmed that propane and isobutane go preferentially into hydrates and that the multicomponent mixtures form sII hydrates.[2,3] Computational modeling using CSMGem[4] demonstrated how gas composition heterogeneity affects hydrate stability, explaining also SoM hydrate persistence despite high seafloor temperatures. Meanwhile, hydrate formation experiments in illite-rich clay/sand mixtures revealed that increasing clay content alters hydrate morphology from pore-filling to vein/fracture-filling structures.[5] Additionally, Raman spectroscopy analyses of hydrate samples showed that small cage occupancy decreases with higher clay content, indicating a reduction in methane storage capacity.[5]

Acknowledgments
The authors thank the different projects for their financial supports: DOORS by the EU Project number 101000518, Blame ANR-18-CE01-0007, Hydraclay ANR-22-CE29-0025-03 and the GDR2026 hydrates for the financial help.

References

1. L. Ruffine, J.-P. Donval, C. Croguennec, P. Burnard, H. Lu, Y. Germain, L. N. Legoix, L. Bignon, M. N. Çağatay, B. Marty, D. Madre, M. Pitel-Roudaut, P. Henry and L. Géli, *Deep Sea Research Part II: Topical Studies in Oceanography* 2018, **153**, 145-149.
2. C. Bourry, B. Chazallon, J. L. Charlou, J. P. Donval, L. Ruffine, P. Henry, L. Geli, M. N. Çagatay, S. Inan and M. Moreau, *Chem. Geol.* 2009, **264**, 197-206.
3. L. Ruffine, O. Fandino, J. Etoubleau, S. Chéron, J.-P. Donval, Y. Germain, E. Ponzevera, V. Guyader, B. Dennielou, G. Etiope, L. Gasperini, B. Giovanni, P. Henry, C. Grall, Ç. M. Namik, J. L. Charlou and L. Géli, in *Advances in Natural Gas Technology*, ed. H. A. Al-Megren, IntechOpen, 2012, pp. 29-56.
4. E. D. Sloan and C. A. Koh, *Clathrate hydrates of natural gases*, CRC, Third Edit edn., 2008.
5. A. C. Agnissan, C. Guimpier, M. Terzariol, O. Fandino, S. Chéron, V. Riboulot, A. Desmedt and L. Ruffine, *J. Geophys. Res. Solid Earth* 2023, **128**, e2023JB027333.

Measurements of the solubility of H_2S in CH_4 at cryogenic temperatures using optical microscopy

ORAL_O3.23 - Phase Equilibria and Fluid Properties

Mark T. J. Barwood[1,2], Rossen Sedev[1], Peter J. Metaxas[1], Peter E. Falloon[1] and Eric F. May[1,2*]

[1]*Fluid Science and Resources, The University of Western Australia, Crawley, Western Australia, Australia*
[2]*Future Energy Exports Cooperative Research Centre, Western Australia, Australia*

[*]*eric.may@uwa.edu.au*

Hydrogen sulphide, H_2S, is often found in natural gas reservoirs and can be present at concentrations of up to. This compound poses a range of issues during natural gas processing; it is highly toxic, can form acidic solutions with water, and also contributes to sulphide stress cracking. As a result, the concentration of H_2S in natural gas is often significantly reduced during a process called "gas sweetening", which is most commonly conducted using an amine-based absorbent. The presence of H_2S in natural gas can also create additional issues when the gas is liquefied as its triple point temperature (187.6 K) is above typical LNG production temperatures (~ 110 K). This means that solid phases of H_2S can be thermodynamically stable at LNG conditions, and that if H_2S is present at a sufficient concentration it can "freeze-out" and form a solid phase.
The formation of solid phases during LNG production can cause serious issues to the plant's operational integrity as they can block the main cryogenic heat exchanger. These blockages often require total plant shutdowns for remediation, which are not only costly but also contribute significantly to non-routine CO_2 emissions when inventory gas is flared. To accurately assess whether a freeze-out event can occur, it is necessary to understand the solubility limit of impurities in natural gas. Despite the prevalence of H_2S in natural gas, there are very few data which can be used to accurately assess its solubility in LNG.
To address this data gap, in this work we present a new synthetic visual apparatus capable of measuring solid-fluid equilibrium at high pressure and cryogenic temperatures. This system, based on an existing design first developed by Sampson *et al.*[1-5], combines a stereomicroscope, a liquid nitrogen cooling system, and a high-pressure measurement cell with optical access. The apparatus is housed in an enclosure to contain any leaks of potentially toxic H_2S-containing fluids. Measurements of solid H_2S solubility in CH_4, measured at three concentrations between (1000-5000) ppm H_2S, are used to tune a temperature-dependent H_2S-CH_4 solid-fluid equilibrium binary interaction parameter in the software tool ThermoFAST. These data and improvements to the model significantly improve the ability of LNG plant operators to estimate the solubility of H_2S in LNG.

Acknowledgements
The authors thank Mr. Craig Grimm for assistance with the enclosure design and for fabricating the apparatus. The authors also thank Profs. Markus Richter, J. P. Martin Trusler, and Rob Marriott for valuable discussions and advice.

References

1. C. C. Sampson, P. J. Metaxas, M. T. J. Barwood, P. L. Stanwix, M. L. Johns and E. F. May, *Langmuir* 2023, **39**, 4631-4641.
2. C. C. Sampson, P. J. Metaxas, M. T. J. Barwood, R. Sinclair-Adamson, P. E. Falloon, P. L. Stanwix, M. L. Johns and E. F. May, *AIChE Journal* 2023, **69**, e18001.
3. C. C. Sampson, P. J. Metaxas, A. Siahvashi, P. L. Stanwix, B. F. Graham, M. L. Johns and E. F. May, *Chemical Engineering Journal* 2021, **407**, 127086.
4. W. Wu, M. T. J. Barwood, P. J. Metaxas, P. E. Falloon and E. F. May, *Chemical Engineering Journal* 2025, 159804.
5. M. T. J. Barwood, P. J. Metaxas, P. E. Falloon, A. S. D. Milligan, W. Wu and E. F. May, *International Journal of Hydrogen Energy* 2024, **71**, 845-856.

Measurements and modelling of the solubility of solid methanol in liquid methane

ORAL_O3.24 - Phase Equilibria and Fluid Properties

Wanying Wu[1,2], Mark T. J. Barwood[1,2], Peter Fallon[1], Eric F. May[1,2,*]

[1]*Fluid Science & Resources, Department of Chemical Engineering, School of Engineering, University of Western Australia, Crawley, Western Australia, 6009, Australia*
[2]*Future Energy Exports Cooperative Research Centre, Perth, Western Australia, Australia*

[*]*eric.may@uwa.edu.au*

Methanol is commonly injected into natural gas during production to prevent gas hydrate formation. Removing methanol to trace amounts (at concentrations as low as parts-per-million) subsequently is necessary if that gas is destined for liquefied natural gas (LNG) production. Higher residual methanol levels can potentially freeze out at typical LNG conditions and possibly lead to blockages in downstream equipment, such as heat exchangers, causing safety and economic problems. Current engineering models are not capable of providing accurate predictions of the solid-fluid equilibrium (SFE) conditions at which methanol solids can form in liquid methane.

To improve the accuracy of current and future predictive models, relevant SFE data need to be acquired because for methanol-methane mixtures the data situation is relatively poor. To our knowledge, the only relevant measurements were conducted by Neumann and Mann[1], who reported solubilities (a total of 7 data points) for solid methanol in liquid methane ranging between (1 to 60) ppm at temperatures between (108 – 150) K.

This work uses high-resolution optical measurements to study methanol solubility in methane at methanol concentrations from (10 to 50) ppm at temperatures between (141 – 151) K. The newly measured data and the data reported by Neumann and Mann[1] are then compared with predictions made using thermodynamic models implemented in the software ThermoFAST. By adjusting the value of a binary interaction parameter in the equation of state for the fluid mixture, the accuracy of SFE predictions for the methanol-methane binary mixture could be improved by up to 37 K. Ultimately, this work should help LNG plant operators better characterize the process conditions under which methanol may cause a freeze-out risk.

References

1. A. Neumann and R. Mann, *Kaltetechnik-Klimatisierung* 1970, **22**, 182-183.

Cryogenic speed of sound of gaseous mixtures of mixed refrigerants employed for hydrogen liquefaction

ORAL_O3.25 - Phase Equilibria and Fluid Properties

Xiong Xiao,[1] J.P. Martin Trusler,[2] Eric F. May,[1,3] Paul L. Stanwix,[1*] and Saif ZS. Al Ghafri[1,2]

[1] *Fluid Science & Resources, Department of Chemical Engineering, School of Engineering, the University of Western Australia, Crawley, Western Australia, 6009, Australia*
[2] *Department of Chemical Engineering, Imperial College London, London SW7 2AZ, UK*
[3] *Future Energy Exports Cooperative Research Centre, Perth, Western Australia, Australia*

[*] *e-mail: paul.stanwix@uwa.edu.au*

Technologies that enable cost-effective hydrogen storage and distribution will be critical to developing domestic and global hydrogen supply chains. In this regard, liquid hydrogen (LH_2) has emerged as a viable option that offers advantages in certain contexts, particularly when extremely high purities are required in end- use applications such as fuel cells, and demonstrations of LH_2 production and shipping from Australia to Japan have recently been completed. The current liquefaction process, however, faces numerous technical hurdles, primarily the high energy consumption between (11.9 and 15.0) kWh/kgLH_2, and the high liquefaction cost between (2.5 and 3.0) US$/kg$LH_2$.

Alternative liquefaction cycles using mixed refrigerants, consisting of blends of hydrogen, helium, neon, and/or nitrogen, offer a promising avenue for reducing costs and energy consumption in hydrogen liquefaction processes. Nonetheless, the development of efficient refrigeration systems using these mixed refrigerants is impeded by the lack of thermophysical property data and reliable models, particularly at cryogenic temperatures below 77 K.

To address this critical gap, this research focuses on measuring the speeds of sound in binary mixtures of He and Ne under cryogenic conditions (down to 30 K) across a wide range of pressures with standard uncertainties within 0.2%. A modified cryostatic chamber housing a cylindrical acoustic resonator is used for the precise determination of experimental sound speeds. The chamber is cooled using an Advanced Research Systems (ARS) cryocooler consisting of an expander (DE-210) that operates on the Gifford-McMahon refrigeration cycle and a water-cooled helium compressor (ARS-10HW). Temperature is monitored using Cernox thin film resistance cryogenic sensors and controlled using a Lakeshore Cryotenics Model 336 temperature controller. The resonator is a thick-walled cylindrical fixed cavity resonator made from stainless steel 316, designed to excite standing waves using a piezoelectric disc (PZT) transducer. The cavity length was optimized with an 80 mm spacer to lower resonance frequencies and minimize structural noise interference.

The experimental speed of sound data for the (0.245 He + 0.755 Ne), (0.497 He + 0.503 Ne) and (0.745 He + 0.255 Ne) mixtures were conducted at temperatures from (40 to 100) K and pressures up to 10 MPa. The majority of the preliminary data revealed deviations of up to 2% from the predictions of the Helmholtz energy-based equation of state (EOS) proposed by Tkaczuk et al.[1]. While the discrepancies diminish as density approaches zero (i.e., under ideal gas conditions), they become more pronounced at higher pressures. This density-dependent trend suggests that the current EOS does not fully account for non-ideal intermolecular interactions between helium and neon at elevated pressures and low temperatures. The newly measured speed of sound data can be utilized to refine EOS models by providing high-accuracy constraints to optimize the pressure-density-temperature (p-ρ-T) relationships and isentropic compressibility predictions in the cryogenic regime. These valuable data could significantly enhance the predictive reliability of thermodynamic models, leading to more efficient design and operation of mixed-refrigerant hydrogen liquefaction cycles.

Reference

1. J. Tkaczuk, et al., *J. Phys. Chem. Ref. Data*. 2020, **49**, 023101.

Solubilities of refrigerants in surrogates for refrigeration oils using Raman spectroscopy

ORAL_O3.26 - Phase Equilibria and Fluid Properties

Fabian Luther[1,*], Julius H. Jander[2], Andreas P. Fröba[2], Markus Richter[1,3]

[1]*Professorship of Applied Thermodynamics, Chemnitz University of Technology, 09107 Chemnitz, Germany*
[2]*Institute of Advanced Optical Technologies Thermophysical Properties (AOT-TP), Department of Chemical and Biological Engineering (CBI) and Erlangen Graduate School in Advanced Optical Technologies (SAOT), Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Paul-Gordan-Straße 8, 91052 Erlangen, Germany*
[3]*Leibniz University Hannover, Institute of Thermodynamics, An der Universität 1, 30823 Garbsen, Germany*

[*]*Fabian.Luther@mb.tu-chemnitz.de*

The efficiency of compression refrigeration cycles can also be improved by optimizing the compressor performance, particularly by understanding the complex multiphase flow of the refrigeration oil/refrigerant mixture within the narrow gaps of the compressor's moving boundaries. To address this challenge, a collaborative research effort combining fluid dynamic experiments and simulations with thermophysical property measurements and modeling is being conducted within the Archimedes Research Unit, funded by the German Research Foundation.
This study focuses on gas solubility measurements of natural refrigerants, e.g., carbon dioxide and propane, in various surrogates for refrigeration oils, e.g., pentane, hexane, decane, and squalene. It should contribute to the development of methodologies including experimental methods for the characterization of technical relevant refrigeration oils in the future. As the chain length of the alkanes studied increases, the asymmetry between the oil and the refrigerant increases which is reflected by significant differences in molecular structures and critical properties.
To complement and extend existing vapor-liquid equilibrium data, an approach for gas solubility measurements based on the work of Lipinski and Richter[1] was further developed. In this work, the intensities of the Raman signatures of the solute are correlated with its partial density. This requires an initial calibration of the pure solute, e.g., carbon dioxide or propane, in the gas phase, which enables the calculation of the partial density of solute in the binary mixture. Using information on the density of the pure solvent at the investigated pressure and temperature, the composition of the liquid phase can be accessed from the partial densities of the solvent and solute in the mixture. This optical and contactless approach was initially validated for binary systems consisting of carbon dioxide and water, where good agreement with existing literature data was found.[1] In the present contribution, an improved methodology will be presented which has been further adapted for more complex Raman signals as given by the refrigeration oil/refrigerant mixtures. The revised methodology incorporates a refined correction approach to account for differences in the absolute intensities of the solute's Raman signature measured in the gas phase and when dissolved in a dense liquid.
The experimental data obtained by the improved methodology might serve as a basis for the development and refinement of models for description of thermophysical properties, which are emphasized in further subprojects of the Archimedes Research Unit. Ultimately, these models are intended to be integrated into fluid dynamic simulations of complex multiphase surge and gap flows in rotary positive displacement compressors.

Acknowledgements
We thank Deutsche Forschungsgemeinschaft (DFG) for funding our ongoing research within the Research Unit FOR 5595 Archimedes (Oil-refrigerant multiphase flows in gaps with moving boundaries - Novel microscopic and macroscopic approaches for experiment, modeling, and simulation) - project number 510921053.

References

1. G. Lipinski and M. Richter, *Physchem* 2021, **1**, 176-188.

Revisiting the static dielectric constant of hydrogen: Improved modeling at cryogenic conditions

ORAL_O3.27 - Phase Equilibria and Fluid Properties

Guinevere M. Sellner[1,*], Allan H. Harvey[2], Lewis Incerti[1], Paul L. Stanwix[1], Eric F. May[1]

[1]*Fluid Science & Resources, School of Engineering, University of Western Australia, 6009 WA, Australia*
[2]*Applied Chemicals and Materials Division, National Institute of Standards and Technology (NIST), CO, USA*

[*]*gwen.sellner@research.uwa.edu.au*

In the global shift towards clean energy alternatives, hydrogen has emerged as a promising candidate due to its low environmental impact and high energy density, particularly in liquid form. This has driven the demand for high-precision sensor technologies capable of quantifying hydrogen properties for efficient and safe process monitoring, especially at the cryogenic conditions that hydrogen liquefaction requires. However, many potential sensing technologies are limited by the accuracy of predictive models for hydrogen's properties. Dielectric permittivity, in particular, offers strong potential for cryogenic, online, and non-invasive hydrogen analysis and spin isomer (*ortho-para*) compositional measurement, as demonstrated in previous work.[1] Yet, existing correlations for hydrogen's static dielectric constant—most notably the model by Harvey & Lemmon[2] —were developed with natural gas applications in mind and so emphasize temperature ranges above 100 K. Consequently, they exhibit significant shortcomings when extrapolated to the hydrogen liquefaction relevant cryogenic regime (sub-50 K).

In this work, we identify and address limitations in prior dielectric constant models by deriving a revised expression for the first dielectric virial coefficient, A_ε, that is valid over a broader temperature range, 1 to 1000 K. This was achieved by combining high-accuracy ab-initio quantum chemical calculations for state-specific polarizabilities with a rigorous statistical mechanical treatment of rovibrational state populations, including proper treatment of *ortho*- and *para*-hydrogen spin isomers. The resulting low-density behaviour of the dielectric constant is then correlated with an empirical framework and validated against both historical and newly evaluated experimental data.[1] For a quantitative description of the full fluid range, the first dielectric virial coefficient must ultimately be augmented by terms of higher order in density. These can be determined empirically based on our measurements and data available in the literature.

Our findings provide a significantly improved representation of hydrogen's dielectric behaviour at cryogenic temperatures and establish a more reliable basis for its use in advanced sensing and cryogenic thermophysical modelling. These results underscore the importance of re-evaluating fundamental property correlations when extending their use to modern hydrogen technologies operating beyond their original design conditions.

References

1. M. Hopkins, *Advanced Microwave Sensors for Phase Equilibrium Studies*, PhD thesis, The University of Western Australia, 2022.
2. A.H. Harvey and E.W. Lemmon, *Int. J. Thermophys.* 2005, **26**, 31-46.

A benchmark of physical properties of the organic solid state for crystal structure prediction by COST Action BEST-CSP

Highlighted ORAL_HO4.1 - Organic Materials and Polymers

Ivo B. Rietveld[1,*]

[1]SMS Laboratory, University of Rouen Normandy

*ivo.rietveld@univ-rouen.fr

Crystal structure prediction has made considerable progress, and a number of academic groups and companies are capable of providing realistic crystal structure landscapes for organic materials. Deciding which of the predicted structures or polymorphs is experimentally relevant and which structure is the most stable is often more difficult to determine. One of the reasons is that the energy differences between polymorphs can be quite small, moreover, the forcefields or basis sets may not be optimal for the system under study, and it remains difficult to take temperature into account. However, how sure can we be about the accuracy of measured quantities? DSC is notorious for measurements that are too fast to result in equilibrium data. Is the temperature of the X-ray diffraction equipment at the sample really what we think it is? Therefore, a concerted effort to produce physical data of the molecular solid state is essential. If multiple labs measure the same property and the results are evaluated together, we will be able to determine the best possible physical data with a clear experimental error which will have more weight than uncoordinated separate measurements of physical data from single laboratories. It does not mean that experimental errors can be fully eliminated, but they can be minimized and clearly defined for a group of measurements for which we know how they are carried out. The resulting outcome provides theoreticians in crystal structure prediction of organic molecules with the maximum attainable experimental accuracy for a datapoint. The combined work should lead to a benchmark of physical data of the organic solid state. This is the main objective of the COST Action BEST-CSP and many European laboratories and companies participate in the BEST-CSP Action.
This presentation will discuss current progress of the benchmark of physical data that is being obtained of molecules such as benzophenone, metacetamol, sulfamerazine, phenylpiracetam, picolinamide, and 4-hydroxyacetophenone. Properties such as melting points, melting enthalpies, polymorph equilibrium temperatures and enthalpies and thermal expansion are measured for the benchmark as well as infrared and NMR spectra.

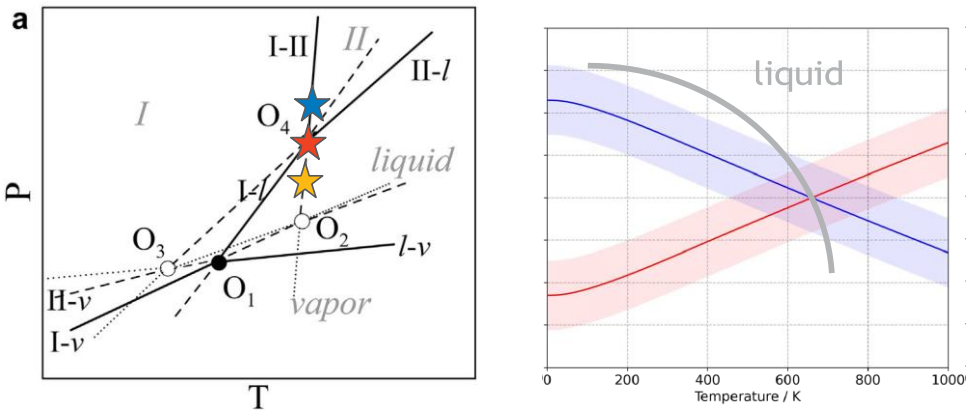


Figure 1: Comparison between experiment and calculation; Metacetamol I-II-L triple point at 0.7 GPa and 535 K.

Acknowledgments
This presentation is based upon work from COST Action BEST-CSP, CA22107, supported by COST (European Cooperation in Science and Technology). The author thanks J. v.d. Streek of Avant-garde Materials Simulation for the figures.

Phase equilibria and modeling involved in the CO_2-assisted recovery of terephthalic acid from PET upcycling

ORAL_O4.2 - Organic Materials and Polymers

Diego T. Melfi[1,2] and Aaron M. Scurto[1,2*]

[1]*University of Kansas, Department of Chemical & Petrol. Engineering*
[2]*Center for Environmentally-Benign Catalysis (CEBC)*

[*]*ascurto@ku.edu*

Alkaline decomposition of polyesters, like polyethylene terephthalate (PET), is often used for the chemical recycling (upcycling) for a circular polymer economy. PET is reacted with sodium hydroxide to produce ethylene glycol (EG) and disodium terephthalate (Na_2TPA) which is then reactively separated to terephthalic acid (TPA) with HCl or H_2SO_4. As a potentially more sustainable alternative to mineral acids, we have introduced the use of compressed carbon dioxide (CO_2) as a pH switch for the recovery of TPA from aqueous Na_2TPA. Gaseous CO_2 partially dissolves as aqueous CO_2 and simultaneously forms carbonic acid and dissociates to carbonate ions (HCO_3^- and/or CO_3^{-2}) and aqueous protons. From a solution of Na^+, H_3O^+, terephthalate, bicarbonate, and/or carbonate ions, TPA precipitation occurs. We have investigated the simultaneous phase and chemical equilibrium involved in this TPA recovery from Na_2TPA solutions using CO_2. Several binary and ternary systems of these electrolyte solutions were not available in the literature and were measured here experimentally. The equilibria of higher order systems were also investigated including actual NaOH-depolymerization product mixtures. A range of different process conditions (temperature, pressures to the vapor pressure or critical point of CO_2, initial loading, etc.) were experimentally investigated and modeled. The identity and quality of the produced terephthalic acid was verified by FTIR and NMR. TPA yields up to 94 % were verified. Lower temperatures, higher pressures, and lower Na_2TPA loadings favor the recovery of TPA. The presence of residual sodium hydroxide and ethylene glycol in solution would eventually decrease the recovery of TPA but would actually be minimal in practical or industrial conditions. Chemical and phase equilibrium modeling with the extended UNIQUAC (eUNIQUAC) activity coefficient model well correlates the experimental data.

Acknowledgements
This material is based upon work supported by the US National Science Foundation (NSF) under Grant No. OIA – 2119754.

Determination of the intramolecular hydrogen bonding strength in diols

ORAL_O4.3 - Organic Materials and Polymers

Riko Siewert[1,2,*], Sergey P. Verevkin[1,2], Karsten Müller[1,2]

[1]University of Rostock, Institute of Technical Thermodynamics, Germany
[2]University of Rostock, Competence center "CALOR at the Department Life, Light & Matter

[*]riko.siewert@uni-rostock.de

Hydrogen bonds have a significant influence on various properties of chemical compounds. Intermolecular hydrogen bonds lead to higher boiling temperatures and enthalpies of vaporization. In contrast, the formation of an intramolecular hydrogen bond leads to a lower enthalpy of vaporization, as the bonded conformation is stabilized in the vapor phase. Due to the lower strength of the intramolecular hydrogen bond compared to the intermolecular bond, quantification is a difficult task that is usually carried out using a combination of several methods. These include, infrared spectroscopy, quantum chemical calculations, homomorph schemes and group-contribution methods.[1] Despite the combination of these methods, exact quantification is still difficult because the definitions of intramolecular hydrogen bond strength differ slightly for every method. In the past, investigations using infrared spectroscopy have been carried out for diols in highly diluted solutions.[2] Therefore, the influence of the solvent must be taken into account. In quantum chemical calculations, the standard enthalpies of formation in the gas phase of intramolecularly bonded and non-bonded conformers are calculated and the enthalpy difference is interpreted as the strength of the bond. With this definition, the strength of the intramolecular hydrogen bond can be calculated with either the non-bonded cis or trans conformation (Figure 1), resulting in different bond strengths.

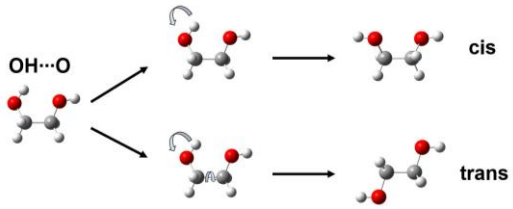


Figure 1: Intramolecularly bonded conformation (left side) and non-bonded conformations (right side) of 1,2-ethanediol.

The combination of group contributions and experimentally determined standard enthalpies of formation is also related to the gas phase, with increments from substances without intramolecular hydrogen bonding (Figure 2).

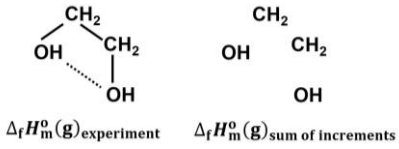


Figure 2: Experimentally determined enthalpy of formation in the gas phase with intramolecular hydrogen bonding (left side) and increment model without hydrogen bonding (right side).

Finally, homomorph schemes are based on vaporization enthalpies as a bridge between the liquid and the vapor phase, which is built by van der Waals interactions, intermolecular and intramolecular hydrogen bonds. In this work, it was shown that despite these various definitions with reference to different phases, it is possible to quantify the strength of intramolecular hydrogen bonds in diols.

References

1. R. Siewert, R. Ludwig and S. P. Verevkin, *Phys. Chem. Chem. Phys.* 2021, **23**, 25226-25238.
2. W. K. Busfield, M. P. Ennis and I. J. McEwen, *Spectrochim. Acta, Part A* 1973, **29**, 1259-1264.

Influence of pre-thermal treatment on the isothermal crystallization of isotactic polypropylene

ORAL_O4.4 - Organic Materials and Polymers

Yoshitomo Furushima[1,*], E. Billur Sevinis Ozbulut[1], Akihiko Toda[2], Mehmet Dinc[3], Benedikt Keitel[3], Boris Mizaikoff[3,4]

[1] *Toray Industries Europe GmbH, Toray Research Center Inc.*
[2] *Hiroshima University*
[3] *Hahn-Schickard, Ulm*
[4] *Institute of Analytical and Bioanalytical Chemistry, Ulm University*

[*] *Yoshitomo.furushima.x6@mail.toray*

By leveraging the precise temperature control of FSC, we investigated the effects of pre-annealing on the crystal structure and crystallization rate of isotactic polypropylene (iPP). Pre-nucleation annealing just below the glass transition temperature (−20˚C), following Tammann's two-stage nucleation approach, accelerated crystallization rates at all subsequent crystallization temperatures (40˚C, 90˚C, and 125˚C). In contrast, the crystal structure remained unaffected by low-temperature pre-annealing, with mesophase formation confirmed at 40˚C, regardless of pre-nucleation conditions. This finding suggests that nuclei formed at low temperatures lack the determining factors for α- or mesophase formation, which depends solely on crystallization temperature during growth.

Similarly, self-nucleation just above the melting point had no impact on either the crystal structure or crystallization rate. Additionally, we examined the influence of trace crystallization on subsequent crystallization behavior by performing preliminary crystallization at temperatures both higher and lower than the final crystallization temperature. Interestingly, the presence of a small amount of pre-crystallization alone did not alter subsequent crystallization rates; rather, crystallization rates increased only when the pre-annealing temperature was lower than the subsequent crystallization temperature. (Figure 1) WAXD confirmed mesophase formation at 40˚C, even in the presence of a small amount of pre-existing α-crystals.

Collectively, these results strongly suggest that polymorphism is determined solely by crystallization temperature, while nucleation rates are enhanced at lower temperatures. Pre-annealing at low temperatures promotes faster crystallization during subsequent high-temperature isothermal crystallization.

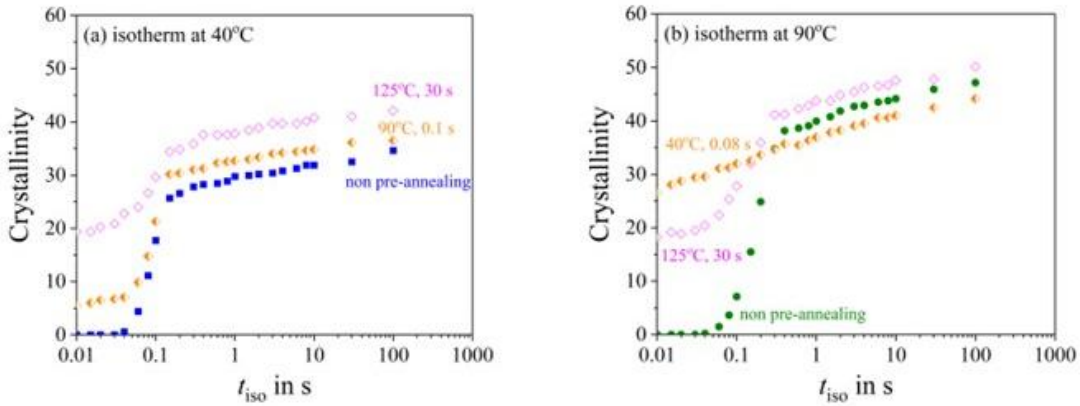


Figure 1: Isothermal crystallization of pre-crystallized iPP.

Acknowledgments
This work was financially supported by Toray Research Center, Inc., Japan. Y. F. wishes to offer special thanks to Ms. Hatsumi Yamamoto (Toray Research Center, Inc.) for her invaluable assistance. The WAXS experiments were performed at the BL03XU beamline of SPring-8 under the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2023A7212, 2023B7261).

References

1. Y. Furushima, A. Toda, M. Nakada, S. Konishi, H. Shioji, Y. Yoshida, E. B. Sevinis Ozbulut, M. Dinc, B. Keitel, and B. Mizaikoff, *Macromol. Chem. Phys.* 2024, **225**, 2400376.

Isothermal titration calorimetry applied to rare earth recovery process with functionalized polymeric particles

ORAL_O4.5 - Organic Materials and Polymers

Pedro A. Martínez-Montoya[1], Ángel J Morales-Ramírez[2,3], José M. el Río[4], Mónica Corea[1,*]

[1] *Instituto Politécnico Nacional, Escuela Superior de Ingeniería Química e Industrias Extractivas, , Laboratorio de Investigación en Polímeros y Nanomateriales, UPALM S/N Zacatenco, Gustavo A. Madero Cd. de México C.P. 07738, México.*
[2] *Instituto Politécnico Nacional, Escuela Superior de Ingeniería Química e Industrias Extractivas, , Departamento de Ingeniería Metalúrgica UPALM S/N Zacatenco, Gustavo A. Madero Cd. de México C.P. 07738, México.*
[3] *Instituto Politécnico Nacional, Centro de Investigación e Innovación Tecnológica, Cda. de CECATI, s/n, Santa Catarina, Azcapotzalco, C. P.02250, CDMX.*
[4] *Instituto Politécnico Nacional, Escuela Superior de Físico Matemáticas, UPALM S/N Zacatenco, Gustavo A. Madero Cd. de México C.P. 07738, México*

**mcorea@yahoo.com.mx; mcorea@ipn.mx*

Nowadays the potential of rare earth elements (REE) called "industrial gold" has been continuously explored in various fields, and some rare earth elements are considered very valuable additives in the areas of high technology.[1] They are of the most strategically important elements because they play a key role in many sophisticated technologies as the automotive industry, renewable energies, defense sectors, among others.[2] The last decade has seen new mechanisms developed for the extraction of rare earths[3], principally by using organic extractants. These materials are expensive and highly polluting, and their complete replacement by compounds, which are less polluting and more economical to improve the extraction and discharge efficiency, has not yet been achieved.[4] Currently, various adsorbents are used for rare earth ion recovery, such as activated carbon, ion exchange resins[5], organic and inorganic composite materials, and biomaterials[6] However, these materials often have low adsorption capacity and poor recyclability.
In this work the proposal is the use of some functional groups on a surface of polymeric particles, that they can function as a chelate agent, forming metal complex. For that a series of polymeric particles were synthesized by means of emulsion polymerization techniques. They were functionalized with acrylic acid, fumaramide and curcumine and used for recovery a series of REE. The particles showed excellent chelation capacity to trap rare earth ions, maintaining their morphology. The results of recover efficiency were confirmed by isothermal titration calorimetry, showing that the process are highly entropic.

References

1. Z. Chen, Z. Li, J. Chen, P. Kallem, F. Banat, and H. Qiu, *J. Environ. Chem. Eng.* 2022, **10**, 107104.
2. B. K. Pramanik, L. D. Nghiem, and F. I. Hai, *Water. Res.* 2020, **168**, 115149.
3. M. Traore, A. Gong, Y. Wang, L. Qiu, Y. Bai, W. Zhao, Y. Liu, Y. Chen. Y. Liu, H. Wu, S. Li, and Y. You. *J Rare Earths.* 2023, **41**, 182.
4. W. Hua, T. Zhang, M. Wang, Y. Zhu, X. Wang, *Chem Eng J.* 2019, **370**, 729.
5. Z. Chour, B. Laubie, J. L. Morel, Y. Tang, R. Qiu, M. O. Simonnot, L. Muhr, *Chem Eng Process Process Intensif.* 2018, **130**, 208.
6. M. Hisada, Y. Kawase, *J. Environ. Chem. Eng.* 2017, **5**, 6061.

Low-temperature heat capacities and absolute entropies of a variety of inorganic salts, oxides, and metals

Highlighted ORAL_HO5.1 - Inorganic Materials and Metals

Brian F. Woodfield[1,*]

[1] *Department of Chemistry and Biochemistry, Brigham Young University, Provo, Utah U.S.A*

**brian_woodfield@byu.edu*

When investigating the thermodynamic properties of modern inorganic materials and technologically relevant minerals, it is often desirable to calculate the formation energetics relative to the oxides, halides, sulphates, and other common salts. A thorough and detailed literature review has found that there are a surprising number of these basic oxides and salts missing from the literature, the thermodynamic data is incomplete, or just unreliable for a variety of reasons. We have begun a project to measure the heat capacities and calculate the absolute entropies for these missing oxides and salts. In this talk, we report the results from the initial phases of this project and show several surprising results.

Expanding aluminum salt-based recovery of PGMs from mixed spent automotive catalytic converters

ORAL_O5.2 - Inorganic Materials and Metals

Flavia N. Braga[1,2,3], Claúdia G. Silva[2,3], Filipe H. B. Sosa[1], Nicolas Schaeffer[1], João A.P. Coutinho[1], Helena Passos[2,3*]

[1]CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal
[2]LSRE-LCM – Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[3]ALiCE – Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

[*]hpassos@fe.up.pt

Over the past few decades, the fast increase in global vehicle production, combined with increasingly stringent environmental regulations, has led to the substantial accumulation of spent automotive catalytic converters (SACC). Although considered a critical secondary source of platinum group metal (PGM) - particularly Pt, Pd, and Rh - the recycling rate of SACC remains insufficient.[1,2] To address the environmental and safety concerns associated with conventional leaching using hazardous aqua regia, our previous work demonstrated the effectiveness of aluminium chloride and aluminium nitrate solutions as more sustainable alternatives for Pt recovery from diesel-derived SACC.[3] Here, this approach is extended to the extraction of Pt, Pd, and Rh from SACC mixtures originating from both gasoline and diesel vehicles, using aluminium-based leachates. Several pretreatment strategies were evaluated to determine their influence on metal availability and leaching efficiency. Although thermal treatment is commonly employed to eliminate organic residues, our findings suggest that it negatively affects the extraction process. To elucidate this phenomenon, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and X-Ray diffraction analysis (XRD) were carried out. In the leaching step, the use of combined SACC from different sources led to a marked improvement in metal recovery, indicating potential synergistic effects. Further investigation explored the chemical and structural interactions occurring between different catalyst compositions during leaching. Experiments using pure metals as reference materials helped clarify how the presence of distinct catalyst matrices influences redox conditions, solubility behaviour, and overall PGM dissolution mechanisms in mixed systems.

Acknowledgments
This work was financially supported by national funds through FCT – Fundação para a Ciência e a Tecnologia, I.P., within the scope of the project PlatILPlus (2022.04478.PTDC, DOI: 10.54499/2022.04478.PTDC). This work was further supported by national funds through FCT/MCTES (PIDDAC): LSRE-LCM, UIDB/50020/2020 (DOI: 10.54499/UIDB/50020/2020) and UIDP/50020/2020 (DOI: 10.54499/UIDP/50020/2020); ALiCE, LA/P/0045/2020 (DOI: 10.54499/LA/P/0045/2020); CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020. N.S. acknowledges the European Research Council (ERC) for the starting grant ERC-2023-StG-101116461. F.H.B. Sosa and F. Braga acknowledge FCT for the researcher contract CEECIND/07209/2022 and the Ph.D. grant 2023.01749.BD, respectively.

References

1. N. Bahaloo-Horeh and S. M. Mousavi, *J Hazard Mater* 2020, **400**, 123186.
2. IPA - International Platinum Group Metals Association, *On the Occasion of the IPA' s 25th Anniversary We Present : 25 Prominent and Promising Applications Using Platinum Group Metals*, 2012.
3. F. N. Braga, A. Coelho, A. R. F. Carreira, F. H. B. Sosa, N. Schaeffer, H. Passos and J. M. C. A. P. C. Coutinho, *(submitted for publication)*, 2025.

Thermodynamics of solvent extraction in Type V DES, an evolution or a revolution from conventional systems?

ORAL_O5.3 - Inorganic Materials and Metals

Nicolas Schaeffer[1,*], Inês C.M. Vaz[1,*], Margarida Bastos[2], Luís M.N.B.F. Santos[2] and João A.P. Coutinho[1]

[1] *CICECO, Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Portugal*
[2] *CIQUP, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal*

**nicolas.schaeffer@ua.pt; ines.vaz@ua.pt*

Hydrophobic Type V eutectic solvents (HES) offer a promising alternative to traditional organic phases in metal ion solvent extraction (SX), offering advantages such as eliminating the need for diluents and preventing the formation of a third phase. Due to their non-ideal nature, typically being constituted by a highly structured liquid phase and complex intercomponent interactions, it could be expected that the SX behavior of HES differs from ideal conventional extraction systems. However, contrary to expectations the general extraction tendencies for a given metal chelating agent diluted in an organic diluent or incorporated as a HES component do not significantly vary, warranting a deeper study of the underlying mechanisms.[1]

This study investigates the solvent extraction of lanthanides, focusing on the biphasic transfer of nitrato complexes of lanthanides ($[Ln(NO_3)_n]^{3-n}$) with tri-n-octylphosphine oxide (TOPO) as the extractant and hydrogen bond acceptor. In the system under analysis, the TOPO extractant is incorporated in a HES together with decanoic acid ($C_{10}OOH$) as a hydrogen bond donor. The partitioning of metal ions between this biphasic liquid system was studied at different temperatures. The results were rationalized by measuring the thermochemical signatures associated to the biphasic transfer of $[Ln(NO_3)_n]^{3-n}$ using isothermal titration calorimetry. For method validation and to highlight differences in thermodynamic behavior between HES and conventional systems, the results are then compared with a traditional SX system (described in the literature[2]) in which TOPO is diluted in toluene.

Acknowledgements
N.S. acknowledges the European Research Council (ERC) for the starting grant ERC-2023-StG- 101116461. I.C.M.V. acknowledges the PRR - Recovery and Resilience Plan for funding, through the scope of the Agenda for Business Innovation "New Generation Storage" (Project nº 58 with the application C644936001-00000045). This work was partially developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 (DOI:10.54499/UIDB/50011/2020), UIDP/50011/2020 (DOI:10.54499/UIDP/50011/2020) & LA/P/0006/2020 (DOI:10.54499/LA/P/0006/2020), financed by national funds through the FCT/MCTES (PIDDAC).

References

1. U.G. Favero, N. Schaeffer, H. Passos, K.A.M.L. Cruz, D. Ananias, S. Dourdain, M.C. Hespanhol, *Sep. Purif. Technol.* 2023, **314**, 123592.
2. T.S. Grimes, P.R. Zalupski, L.R. Martin; *J. Phys. Chem. B* 2014, **118**, 12725-12733.

Phase equilibria and thermophysical properties of ionic liquids or deep eutectic solvents with hydrofluorocarbon gases

Highlighted ORAL_HO6.1 - Ionic Fluids and Deep Eutectic Solvents

Karim S. Al-Barghouti, Saufishan Thalikkassery Akbar, Diego Melfi, Ana Colaco Morais, Mark B. Shiflett, and Aaron M. Scurto*

[1]*University of Kansas, Department of Chemical & Petrol. Engineering,* Lawrence, KS 66045 USA
[2]*NSF-ERC EARTH (Environmentally Applied Refrigerant Technology Hub)*
[3] Wonderful Institute for Sustainable Engineering

**ascurto@ku.edu*

Many hydrofluorocarbon (HFC) refrigerant gases have been scheduled for eventual phase-out in Europe, the US, etc. due to their generally high Global Warming Potential (GWP). Most refrigerants are actually azeotropic or near-azeotropic mixtures of HFCs, some of which will be phased out, while low GWP HFCs may be blended with the next generation of refrigerant gases, e.g. hydrofluoroolefins (HFOs). While conventional distillation cannot fully separate these mixtures, Ionic liquids (ILs) and Deep Eutectic Solvents (DESs) have been proposed as entrainers in novel extractive distillation technologies. The low volatility of ILs or many DESs allow efficient separation from the HFC gases. Design and optimization of extractive distillation engineering units require a comprehensive evaluation of a multitude of thermodynamic and transport properties of the pure components as well as the biphasic gas and IL or DES mixtures.

In this work, we have measured the vapor-liquid equilibrium and thermophysical properties of several imidazolium-based ILs and cholinium chloride based DESs saturated with the hydrofluorocarbon gases difluoromethane (R-32), and pentafluoroethane (R-125) to elevated pressures and temperatures. Investigated properties include phase equilibrium thermodynamics (solubility, density, and interfacial tension), and transport properties (viscosity, diffusivity, and thermal conductivity). Our results indicate highly non-ideal behavior across the different properties measured.

Many ILs and DESs have a high solubility of HFC gases at moderate temperatures and pressures. However, it is the difference in solubility, i.e. the selectivity, of the HFCs in the various entrainers that allows the circumvention of the azeotropic point. All systems investigated exhibit large negative excess molar volumes. The viscosity of both IL and DES systems exhibits a sharp decrease with even low loadings of the HFCs resulting from a general dilution effect with addition of the low viscosity HFCs. This is important for ILs and especially DESs which generally have higher viscosity that conventional absorption solvents. Fickian and self-diffusivities have been investigated using a microbalance and pulsed field gradient stimulated echo NMR technique at elevated pressures. Simple Stokes-Einstein relationships using measured mixture viscosity only approximately follow the experimental data. However, unlike the dilution effect found in viscosity (diffusivity), thermal conductivity remains dominated by that of the IL even to very high HFC loadings. The complex behavior in terms of the thermodynamic and transport properties on extractive distillation design are discussed.

Acknowledgments
This material is based upon work supported by the US National Science Foundation (NSF) under EEC-1852308, and EFRI-2029354 and ERC-2330175.

AI-enabled discovery of deep eutectic solvents based lubricants

ORAL_06.2 - Ionic Fluids and Deep Eutectic Solvents

João P. Santos,[1] Filipe H. B. Sosa,[1] Dinis O. Abranches,[1,*] João A. P. Coutinho[1]

[1] *CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193, Portugal*

**jdinis@ua.pt*

Deep eutectic solvents (DESs), binary liquid mixtures noted for their strong intermolecular interactions, have emerged as promising green alternatives to traditional organic solvents. The design of these novel solvents is complex, as their properties do not simply reflect the weighted average of their precursors. Incorporating low molecular weight compounds, such as water, to reduce viscosity or modulate other properties is a common practice. This leads to an overly complex and extensive DES design space, where the number, chemical nature, and relative composition of precursors must be carefully tuned. Machine learning (ML), with its innate ability to correlate variables, presents a promising alternative to trial-and-error approaches in the design of DESs. While most ML models require an exceedingly large number of data points to be properly trained, stochastic ML based on Gaussian processes (GPs) can fully capture the properties of organic and inorganic compounds with small and scarce datasets (common in the DES literature), using sigma profiles as molecular descriptors.

In this work, GPs were used to fit and predict several physicochemical properties of DESs, namely density, viscosity, and melting temperature. Experimental data was collected from the literature, including over 400 unique DES combinations and more than 4000 independent data points, covering most common families of organic compounds. Each dataset was carefully split into training, validation, and testing sets to determine the optimal GP architecture and hyperparameters for each physicochemical property. Coefficients of determination exceeding 0.95 were achieved for all studied properties, including viscosity, which spanned values over eight orders of magnitude, and melting temperature, which encompassed a range of nearly 700 K. Using the trained GP models, new DES-based lubricants were designed by exploring the sigma profile space of DESs. The GPs suggested novel combinations of precursors not present in the original database to achieve desired viscosities and melting temperatures. These novel DESs were experimentally prepared and characterized for the first time in this work. Viscosity and tribological properties were also measured, which surpassed common standards in the literature for low and high operational temperatures, effectively leading to DES formulations suitable for lubricant applications. Overall, this work highlights the efficacy of stochastic machine learning in navigating the vast DES chemical space and its potential to streamline solvent discovery while promoting sustainable chemical practices.

Acknowledgements
This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 (DOI 10.54499/UIDB/50011/2020), UIDP/50011/2020 (DOI 10.54499/UIDP/50011/2020) & LA/P/0006/2020 (DOI 10.54499/LA/P/0006/2020), financed by national funds through the FCT/MCTES (PIDDAC). Filipe Sosa acknowledges FCT (CEECIND/07209/2022).

Screening of high-temperature solvents for methanol separation

ORAL_06.3 - Ionic Fluids and Deep Eutectic Solvents

Murilo L. Alcantara[1*], João Fabian[1], Filipe H. B. Sosa[1], João Coutinho[1]

[1] *Universidade de Aveiro, CICECO – Aveiro Institute of Materials, Portugal*

**murilo.la@ua.pt*

The conversion of CO_2 into methanol is a crucial step in developing sustainable, decentralized energy storage systems. However, conventional methanol synthesis is limited by thermodynamic equilibrium, requiring high pressures and energy-intensive condensation steps for product separation. This study proposes a breakthrough approach by employing ionic liquid (IL)-based in situ sorption to selectively remove methanol and water from the reaction environment, thereby shifting equilibrium and enhancing conversion efficiency. In this study, we identify and validate ILs capable of operating in a trickle-bed reactor at 483–513 K, offering a robust and energy-efficient alternative to conventional separation methods [1].
Through COSMO-RS modeling, a comprehensive screening of over 15,000 ILs was performed to evaluate their affinity for methanol and water at the reactor's operational temperature. Infinite dilution activity coefficients were used to assess ILs interaction with solutes. Similar trends were found at 298K and 513K, and strong dependency was found for ILs' anions with high punctual charged sites.

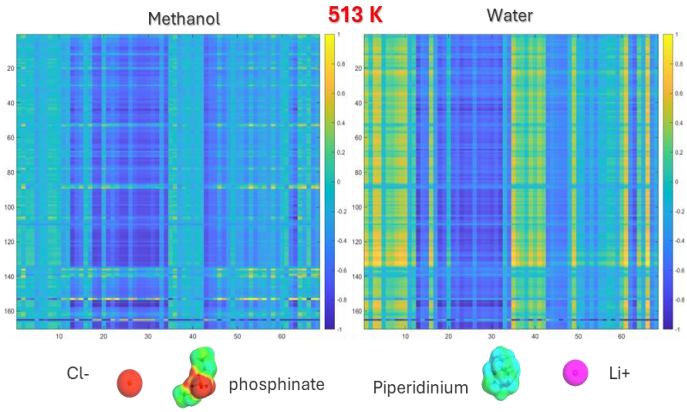


Figure 1: COSMO-RS screening through $\ln(\gamma^{\infty})$ results for methanol and water solubility at 513 K, and best ion candidates.

The thermal stability of the best candidates was evaluated by *ai4solvents* software [2] to assure these ILs could operate at the reacting temperature. The best ion candidates were chloride, and phosphinated anions, and piperidinium and Lithium cations. The proposed IL-based separation process could enable methanol production at a higher yield by shifting chemical equilibrium within the trickle bed reactor. Furthermore, these findings provide a viable pathway for scaling up IL-enhanced methanol synthesis, reducing the need for high-pressure operations.

Acknowledgments
This work was developed within the scope of the project CICECO Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MCTES (PIDDAC). This study also received financial support from Illimited project, financed by Horizon Europe agreement n° 101192964.

References

1. J. Reichert, S. Maerten, K. Meltzer, A. Tremel, M. Baldauf, P. Wasserscheid and J. Albert, *Sustain Energy Fuels* 2019, **3**, 3399-3405.
2. Z. Song, J. Chen, J. Cheng, G. Chen and Z. Qi, *Chem. Rev.* 2024, **124**, 248-317.

Enhancing the bioavailability of antimalarial drugs with natural excipients

ORAL_06.4 - Ionic Fluids and Deep Eutectic Solvents

Luan B. Corso[1,2*], Isabella W. Cordova[3], João A. P. Coutinho[3], Olga Ferreira[1], Simão P. Pinho[1], André Zuber[2], Mónia A. R. Martins[1]

[1]CIMO, LA SusTEC, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[2]Academic Department of Engineering, Federal University of Technology – Paraná, Francisco Beltrão-PR 85601-970, Brazil
[3]CICECO, Aveiro Institute of Materials,Complexo de Laboratórios Tecnológicos, University of Aveiro,3810-193 Aveiro, Portugal

[*]luancorso@gmail.com

Malaria remains a serious global public health problem, with 249 million cases reported in 2022 in 85 endemic countries, resulting in 608,000 deaths, mainly in Africa. To combat malaria, the World Health Organization recommends preventive measures that include vector control and chemoprevention. Key measures include the use of mosquito nets and insecticide spraying. In addition, vaccination and administration of antimalarials, such as artemisinin, play essential roles in preventing and controlling the disease. However, current treatments based on artemisinin combination therapies (ACTs) have faced significant challenges, mainly due to increasing parasite resistance, highlighting the need to develop new approaches to improve drug efficacy.[1] Furthermore, the low water solubility of artemisinin reduces its bioavailability, compromising oral absorption and increasing the required dosage.

Artemisinin is typically extracted from the Chinese plant *Artemisia annua L.*, however, the process employs toxic solvents, such as hexane and petroleum ether, which harm the environment and human health. As an alternative, recent research has explored green solvents, such as ionic liquids and natural deep eutectic solvents, which provide efficient and sustainable extraction.[2] Due to the large number of available options, computational methods such as the COnductor like Screening MOdel for Realistic Solvents (COSMO-RS) are typically used to optimize solvent selection by narrowing down the choices to the most effective options.[3]

In this work, COSMO-RS is used to evaluate the interaction between different families of solvents and antimalarial compounds including artemisinin, quinine, quinidine, tetracycline, artemether, dapsone, and pyrimethamine. The best natural-based excipients are then used to perform the extraction of antimalarial compounds from their natural sources. The goal is to improve drugs solubility and, consequently, enhance their therapeutic efficacy while applying more environmentally friendly extraction methods.

Among the 7791 options evaluated using COSMO-RS, mixtures involving formic acid, heptane, pentane, and triethylamine stand out. According to the criteria established by the International Council for Harmonization of Technical Requirements for Pharmaceuticals for Human Use, these compounds are considered less toxic and of less risk to human health. Furthermore, within the terpene family, thymol, carvacrol, and eugenol also stand out, both in their pure form and in equimolar mixtures with other compounds.

Acknowledgements
This work was supported by national funds through FCT/MCTES (PIDDAC): CIMO, UIDB/00690/2020 (DOI: 10.54499/UIDB/00690/2020) and UIDP/00690/2020 (DOI: 10.54499/UIDP/00690/2020); and SusTEC, LA/P/0007/2020 (DOI: 10.54499/LA/P/0007/2020). This work is also part of the "Artemisinin bioavailability enhancement through eutectic formation with natural excipients" project financed by PhosAgro/UNESCO/IUPAC Partnership in Green Chemistry for Life (contract number 4500513457).

References

1. World Health Organization, WHO guidelines for malaria, 30 November 2024, World Health Organization, 2024.
2. A. M. Ferreira, I. Sales, S. A. O. Santos, T. Santos, F. Nogueira, S. Mattedi, S. P. Pinho, J. A. P. Coutinho and M. G. Freire, *Chem & Bio Engineering* 2024, **1**, 44-52.
3. C. Fan, Y. Shan, L. Wen and X. Cao, *Sustain Chem Pharm* 2023, **33**, 101096.

Stepwise conformational disorder in an ionic plastic crystal

ORAL_06.5 - Ionic Fluids and Deep Eutectic Solvents

Letícia A. Souza[1,*], Thamires A. Lima[2], Vitor H. Paschoal[3], Luke L. Daemen[4], YZ[5], Abner M. Sampaio[1], Mauro C. C. Ribeiro[1,*]

[1]Laboratório de Espectroscopia Molecular, Instituto de Química, Universidade de São Paulo, SP, Brazil, [2]Chemical and Biological Engineering Department, Drexel University, Philadelphia, PA 19104, [3]Faculty of Chemistry, Wrocław University of Science and Technology, Wrocław, Poland, [4]Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA, [5]Department of Nuclear Engineering and Radiological Science, University of Michigan, Michigan, USA

**leticia_souza@usp.br, mccribei@iq.usp.br*

Thermal properties of ionic liquids (ILs) often involve complex phase transitions beyond simple crystallization and melting.[1] Some ILs also exhibit plastic crystal phases, where translational order coexists with rotational disorder of polyatomic ions.[2] Vibrational spectroscopy (Raman and infrared) is an essential tool for correlating macroscopic properties with molecular structure.[3] However, spectroscopic measurements and physicochemical properties do not always reflect the same system state, as phase transitions depend on the material's thermal history. In this work, we investigated the phase transitions of the IL choline bis(trifluoromethanesulfonyl)imide [Chol][NTf_2] using Raman and infrared spectroscopy with simultaneous thermal measurements. Raman bands probed different cation and anion conformations. The ν(CN) stretching mode of $[Chol]^+$ appears at 765 cm^{-1} or 716 cm^{-1}, for the *anti* or *gauche* conformation, respectively (Figure 1). Meanwhile, the SO_2 rocking mode of [NTf_2] appears at 326 cm^{-1} for the *cisoid* and 340 cm^{-1} for the *transoid* conformation. Phase behavior revealed two solid-solid transitions before melting. Simultaneous Raman and calorimetric data acquisition enabled the observation of synchronized conformational changes in $[Chol]^+$, confirming these events as solid-solid transitions rather than melting. After the first transition, the system enters a disordered plastic crystal phase, where $[Chol]^+$ gains conformational flexibility while [NTf_2] retains its *trans* conformation. The anion undergoes conformational changes only upon melting, leading to a stepwise conformational disorder in the system.

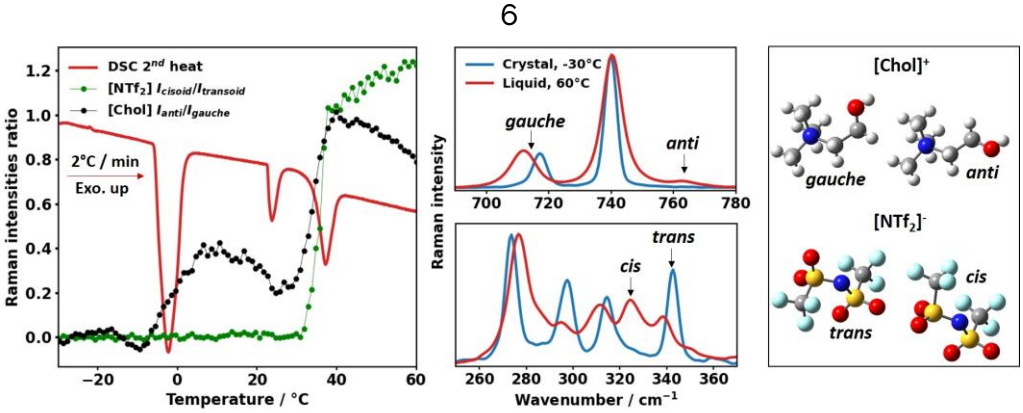


Figure 1: Left: Temperature dependence of the Raman intensity ratio for [Chol] (765 cm^{-1}/716 cm^{-1}, black symbols) and [NTf_2] (326 cm^{-1}/340 cm^{-1}, green symbols). The red line represents the DSC heating curve. Right: Raman spectra of the low-temperature crystal (-30 °C, blue) and liquid (60 °C, red), highlighting bands that monitor conformational changes during DSC measurements.

Acknowledgments
FAPESP (2022/11983-4, 2023/16685-4) and CNPq.

References

1. C. P. Fredlake, J. M. Crosthwaite, D. G. Hert, S. Aki and J. F. Brennecke, *J. Chem. Eng. Data* 2004, **49**, 954-964.
2. U. A. Rana, M. Forsyth, D. R. MacFarlane and J. M. Pringle, *Electrochim. Acta* 2012, **84**, 213-222.
3. V. H. Paschoal, L. F. O. Faria and M. C. C. Ribeiro, *Chem. Rev.* 2017, **117**, 7053-7112.

Phase equilibria of binary and ternary deep eutectic solvents

ORAL_O6.6 - Ionic Fluids and Deep Eutectic Solvents

Lucas Pandolphi Zini[1,2,*], Gabriel Teixeira[2], Jean-Philippe Harvey[1], João A. P. Coutinho[2], Christian Robelin[1]

[1]*Centre for Research in Computational Thermochemistry (CRCT), Department of Chemical Engineering, Polytechnique Montréal, Box 6079, Station Downtown, Montréal, Quebec, H3C 3A7, Canada*
[2]*CICECO, Aveiro Institute of Materials, Complexo de Laboratórios Tecnológicos, University of Aveiro, Campus Universitário de Santiago, Aveiro, Portugal*

[*]*lucas.pandolphi-zini@polymtl.ca*

Deep eutectic solvents (DESs) have gained significant attention due to their potential applications in electrochemistry, organic synthesis, and separation processes.[1] Although phase diagrams of several binary DESs have been measured, the phase behavior of ternary systems remains largely unexplored, limiting their optimized utilization[2] since adding a third component may tune the physicochemical properties of DESs. It would be valuable to model phase equilibria of ternary systems, which would allow the selection of ternary compositions with values of the liquidus temperature within a specific range, thus avoiding a tedious and costly trial-and-error experimental approach.[3]
The CALculation of PHAse Diagrams (CALPHAD) method is a valuable tool for obtaining the parameters of a thermodynamic model by means of critical evaluation and optimization of available experimental data for binary and ternary systems. The Modified Quasichemical Model in the Quadruplet Approximation (MQMQA) was developed at the Centre for Research in Computational Thermochemistry (CRCT) to describe the thermodynamic properties of inorganic systems using the CALPHAD approach[4] and is implemented in FactSage®, an integrated thermochemical software and database package. The MQMQA has not yet been applied to represent the behavior of systems with organic compounds. The main objective of this work is to develop a thermodynamic model for binary and ternary DESs using the powerful CALPHAD method for the first time. Various ternary systems of the type HBA-HBA-HBD and HBA-HBD-HBD, where HBA = Hydrogen Bond Acceptor and HBD = Hydrogen Bond Donor, are being investigated. Focus is being made on three HBAs (choline chloride ChCl, $ZnCl_2$, and a chloride ionic liquid) and two HBDs (urea and a monocarboxylic acid). All available experimental data from the literature was collected, and relevant binary and ternary phase diagrams (for which data are lacking) are being measured by differential scanning calorimetry (DSC) and visual method (using a melting-point apparatus). The ChCl-$ZnCl_2$-urea ternary system was selected as a prototype system since it received early attention and there was enough phase diagram data in the literature to model the three binary subsystems (including ChCl-urea, which is well documented). According to newly measured phase equilibria, for some of the published binary data, there may have been water contamination, and the formation of intermediate compounds (i.e. cocrystals) may have been neglected.
This work provides new phase equilibrium data for binary and ternary DESs, and thermodynamic modelling is in progress. Various ternary systems are being considered, and this will enable the rational design of DESs for targeted applications.

Acknowledgments
The modelling part of this project is supported by the Natural Sciences and Engineering Research Council of Canada (NSERC) (Discovery Grant RGPIN 3901-2021). Lucas Pandolphi Zini acknowledges a MITACS Globalink Research Award for his experimental internship at CICECO – Aveiro Institute of Materials.

References

1. Q. Zhang, K. O. Vigier, S. Royera and F. Jérôme, *Chem. Soc. Rev.* 2012, **41**, 7108-7146.
2. E. A. Crespo, L. P. Silva, M. A. R. Martins, L. Fernandez, J. Ortega, O. Ferreira, G. Sadowski, C. Held, S. P. Pinho and J. A. P. Coutinho, *Ind. Eng. Chem. Res.* 2017, **56**, 12192-12202.
3. B. B. Hansen, S. Spittle, B. Chen, D. Poe, Y. Zhang, J. M. Klein, A. Horton, L. Adhikari, T. Zelovich, B. W. Doherty, B. Gurkan, E. J. Maginn, A. Ragauskas, M. Dadmun, T. A. Zawodzinski, G. A. Baker, M. E. Tuckerman, R. F. Savinell and J. R. Sangoro, *Chem. Rev.* 2021, **121**, 1232-1285.
4. A. D. Pelton, Phase Diagrams and Thermodynamic Modeling of Solutions, Elsevier, Amsterdam, 2019.

Anion chain length effect on the thermodynamic properties of bis(fluoroalkylsulfonyl)imide-based ionic liquids

ORAL_06.7 - Ionic Fluids and Deep Eutectic Solvents

Rodrigo M. A. Silva[1,*], Ana I. M. C. Lobo Ferreira[1], Daniel Rauber[2], Luís M. N. B. F. Santos[1]

[1]*Centro de Investigação em Química (CIQUP), Institute of Molecular Sciences (IMS), Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua Campo Alegre s/n, 4169-007 Porto, Portugal*
[2] *Department of Chemistry, Saarland University, Campus B 2.2, 66123 Saarbrücken, Germany*

**rodrigo.m.a.silva98@gmail.com*

In this work we aimed to investigate and understand the effect of the fluorinated chain size in bis(fluoroalkylsufonyl)imide-based anions on the thermodynamic properties of ionic liquids (ILs). For this we investigated four different 1-ethyl-3-methylimidazolium-based ionic liquids, whose anions bear fluoroalkyl chains of different lengths (n = 0, 1, 2 and 4; [FSI], [NTf_2], [BETI] and [Nona], respectively). The structures of the IL pairs are presented in Figure 1.

Figure 1: Structure of the studied ionic liquid pairs.

Differential scanning calorimetry (DSC) was used to investigate the phase behavior of these ILs. The results reveal that the melting point of the ILs increases as the fluoroalkyl chains become larger. The melting enthalpy and entropy, however, don't follow this monotonic trend, revealing a complex enthalpy-entropy balance. Furthermore, polymorphism was detected for the larger anions. Studies of thermogravimetric analysis (TGA) show that the [FSI]-based IL has a significantly lower thermal stability than the other bis(fluoroalkylsufonyl)imide-based anions, which have a thermal stability similar to the [NTf_2]-based IL. The study of the heat capacity was done at T = 298.15 K, and as a function of temperature between T = 283 K and T = 333 K, using, respectively, drop calorimetry[1] and differential scanning microcalorimetry[2]. This allowed the estimation of the contribution of the difluoromethylene group, –CF_2–, to the heat capacity of the liquid phase at T = 298.15 K, which was found to be similar to that found in previous studies with fluoroalkyl-based ILs. The volatility of the ILs was determined through Knudsen effusion method coupled with quartz crystal microbalance (KEQCM)[3]. The ILs bearing the larger [BETI] and [Nona] anions were found to be more volatile than that based on the [NTf_2] anion, but also to have larger enthalpies of vaporization. The increase in volatility was correlated with a large increase in entropy of vaporization, which overcomes the enthalpic contribution.

Acknowledgements
This work was supported by the Fundação para a Ciência e Tecnologia (FCT) (funded by national funds through the FCT/MCTES (PIDDAC)) to CIQUP, Faculty of Science, University of Porto (Project UIDB/00081/2020), IMS-Institute of Molecular Sciences (LA/P/0056/2020). RMAS is grateful to FCT for the award of his PhD grant (U1/BD/153093/2022). AIMCLF is also financed by national funds through the FCT-I.P., in the framework of the execution of the program contract provided in paragraphs 4, 5 and 6 of art. 23 of Law no. 57/2016 of 29 August, as amended by Law no. 57/2017 of 19 July.

References

1. L. Santos *et al. J. Chem. Thermodyn.* 2011, **43**, 1818-1823.
2. R. Silva *et al. J. Phys. Chem. B* 2024, **128**, 3742-3754.
3. L. Santos *et al. J. Chem. Thermodyn.* 2018, **126**, 171-186.

Thermodynamic speed of sound in ionic liquids

Highlighted ORAL_HO6.8 - Ionic Fluids and Deep Eutectic Solvents

Marzena Dzida*

University of Silesia in Katowice, Institute of Chemistry, Szkolna 9, 40-006 Katowice

**marzena.dzida@us.edu.pl*

Ionic liquids are interesting systems with many fascinating properties and many potential applications. However, due to ionic character, their properties are different from the properties of molecular liquids. Ionic liquids are dissipative systems because of their two-three orders of magnitude larger viscosity than those of typical molecular organic solvents at room temperature. Therefore, the shear contribution can be appeared in ultrasonic wave propagation. The acoustic method has found acceptance as a precise tool for the determination of thermodynamic properties of liquids at atmospheric and high pressures provided fulfill two conditions. The speed of sound is the thermodynamic equilibrium property (*i.e.* it can be used in the Laplace-Newton equation) at low frequencies, where the speed of sound does not depend on frequency as well as when the effects of absorption on the speed of sound are small *i.e.* the dissipative processes are neglected.[1] Some ionic liquids exhibit dispersive effects at relatively low frequency range. Thus, the speed of sound measured with available equipment is a non-thermodynamic one and cannot be used for determining thermodynamic properties. IUPAC recommended "*…the interpretation of speed-of-sound values and their usability for the determination of related thermodynamic properties can only be done when the absorption coefficient or relaxation regions are known…*" [2] based on our work[1] as "*Good Research Practice because it may require additional measurements for complete characterization of the system.*"[2] The classical absorption coefficient can be calculated and the ultrasound absorption coefficient of aprotic ionic liquids can be estimated at the low frequency range using viscosity, density and speed of sound.[1] It allows to select measurement method and conditions in order to obtain thermodynamic speed of sound.

References:

1. M. Dzida, E. Zorębski, M. Zorębski, M. Żarska, M. Geppert-Rybczyńska, M. Chorążewski, J. Jacquemin, I. Cibulka, *Chem. Rev.* 2017, **117**, 3883-3929.
2. A. Bazyleva, J. Abildskov, A. Anderko, O. Baudouin, Y. Chernyak, J.-C. de Hemptinne, V. Diky, R. Dohrn, J. R. Elliott, J. Jacquemin, J.-N. Jaubert, K. G. Joback, U. R. Kattner, G. M. Kontogeorgis, H. Loria, P. M. Mathias, J. P. O'Connell, W. Schröer, G. J. Smith, A. Soto, S. Wang, R. D. Weir, *Pure Appl. Chem.* 2021, **93**, 253-272.

Quest to find the holy grail of ionanofluids. Brief story on isobaric heat capacity of ionanofluids

ORAL_06.9 - Ionic Fluids and Deep Eutectic Solvents

Krzysztof Cwynar[1,*], Anna Kolanowska[1], Katarzyna Kaczmarek[1], Sławomir Boncel[2,3], Marzena Dzida[1]

[1]*Institute of Chemistry, University of Silesia in Katowice, Szkolna 9, 40-006 Katowice, Poland*
[2]*Faculty of Chemistry, Department of Organic Chemistry, Bioorganic Chemistry and Biotechnology, NanoCarbonGroup, Silesian University of Technology, Krzywoustego4, 44-100 Gliwice, Poland*
[3]*Centre for Organic and Nanohybrid Electronics, Silesian University of Technology, Konarskiego 22B, 44-100 Gliwice, Poland*

[*]*krzysztof.cwynar@us.edu.pl*

Ionanofluids (INFs) are defined as a stable dispersion of nanoparticles in ionic liquids (ILs). The addition of nanoparticles, such as multi-walled carbon nanotubes (MWCNTs), indisputably leads to increased thermal conductivity and viscosity of INFs. The research focused on the isobaric heat capacity of INFs does not provide a definite answer about the effect of nanostructures on this property.
To explore this phenomenon, we performed a state-of-the-art review of the literature data, with consideration to sample purity, apparatus used, and experimental conditions. Unfortunately, a self-contradictory landscape emerged with many examples of outright contradictory data.
We conducted experimental determination of the isobaric heat capacity of INFs with various ILs, such as 1-ethyl-3-methylimidazolium thiocyanate, and different types of MWCNTs for more than 60 INFs using high precision differential scanning calorimeter.[1] Our results show that the effect of the addition of MWCNTs to ILs does not alter the isobaric heat capacity of INFs significantly. Absolute changes were not greater than 3.0% at 298.15 K. The model describing the isobaric heat capacity of INFs considering the existence of nanolayer on the surface of nanoparticles[2] was taken under examination based on the experimental data. The results suggest that nanolayer cannot have any significant effect on the isobaric heat capacity of INFs.[1]

Acknowledgments
This work was financially supported by the National Science Centre (Poland) Grant No. 2021/41/B/ ST5/00892.

References

1. K. Cwynar, J. Dziadosz, Ł. Scheller, E. Zorębski, R. Jędrysiak, A. Kolanowska, A. Blacha, S. Boncel, M. Dzida, *J. Mol. Liq.* 2023, **387**, 122535.
2. R. Hentschke, *Nanoscale Res. Lett.* 2016, **11**, 88.

Absorption of hydrofluorocarbons in fluorine-based eutectic solvents: Insights from molecular modeling

ORAL_O6.10 - Ionic Fluids and Deep Eutectic Solvents

B. González-Barramuño[1,*], E. Cea-Klapp[1], H. Quinteros-Lama[2], J. M. Garrido[1]

[1]*Departamento de Ingeniería Química, Universidad de Concepción, Edmundo Larenas 219, Concepción, Chile.*
[2]*Departamento de Ingenierías Industriales, Facultad de Ingeniería, Universidad de Talca, Merced 437, Curicó, Chile.*

[*]*basgonzalez@udec.cl*

In the coming years, ambitious goals have been set to achieve the phase-out of fluorinated greenhouse gases, especially hydrofluorocarbons (HFC), to combat climate change and global warming. A circular economy framework for these compounds offers advantages over the current linear model, fueling the search for effective methods for their capture and recycling. Eutectic solvents have emerged as promising alternatives due to their tunable characteristics, allowing the design of novel solvents for highly specific tasks.
Fluorinated functionalization in liquids has proven effective for capturing fluorinated gases.[1] In particular, perfluoropentanoic acid (PFPA) forms eutectic mixtures with specific fluorinated salts, also showing potential for the absorption of HFC.[2] However, complex chemical structures and highly associative environments hinder the theoretical characterization of solvents of this kind, posing challenges for fast and effective development in their design. Thus, increasingly predictive approaches, combining molecular detail and thermodynamic accuracy, are becoming a progressively valuable tool.
In this work, the thermophysical properties of PFPA-based eutectic solvents are studied from a molecular perspective. Within a predictive approach, molecular dynamics (MD) simulations and the COSMO-RS model are used to analyze the deviation from ideal solution behavior and the absorption of HFC, as shown in Figure 1. In addition, MD simulations provided insights into the solvation mechanism and estimations of transport properties in the liquid phase. These findings offer valuable insight into HFC absorption in complex solvent environments, providing a basis for further research in an application of industrial interest.

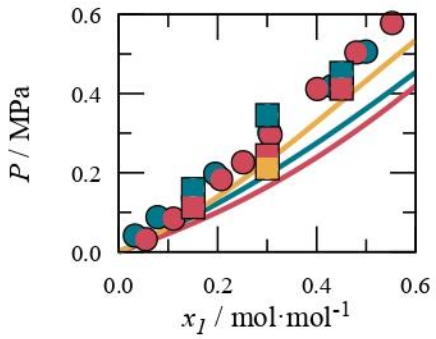


Figure 1: Absorption isotherms for R134a (1) in three different PFPA-based eutectic solvents. MD results (squares), COSMO-RS predictions (solid lines) and available experimental data values[2] (circles) are presented.

Acknowledgments
This research was supported by FONDECYT, Chile (Project 1230236 and 1240765) and FOVI220054. B. González-Barramuño's work was funded by the National Agency for Research and Development (ANID) / Scholarship Program / DOCTORADO BECA NACIONAL / 2023-21230318.

References

1. J. E. Sosa, R. P. Ribeiro, P. J. Castro, J. P. Mota, J. M. Araújo and A. B. Pereiro, *Ind. & Eng. Chem. Res* 2019, **58**, 20769-20778.
2. P. J. Castro, A. E. Redondo, J. E. Sosa, M. E. Zakrzewska, A. V. Nunes, J. M. Araújo and A. B. Pereiro, *Ind. & Eng. Chem. Res.* 2020, **59**, 13246-13259.

Polyol-based deep eutectic solvents: A comparative study of betaine and choline chloride as hydrogen bond acceptors

ORAL_O6.11 - Ionic Fluids and Deep Eutectic Solvents

Gabriel Teixeira [1,*], Olga Ferreira [2,3], João A. P. Coutinho [1]

[1]*CICECO, Aveiro Institute of Materials, Complexo de Laboratórios Tecnológicos, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal*
[2]*Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal*
[3]*Laboratório para a Sustentabilidade e Tecnologia em Regiões de Montanha, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal*

[*]*gabriel.teixeira@ua.pt*

Deep eutectic solvents (DES) are receiving significant attention as sustainable alternatives to conventional solvents in many applications, with choline chloride (ChCl) emerging as the most widely studied hydrogen bond acceptor (HBA) [1,2] due to its low toxicity,[3] biodegradability, and low melting enthalpy (4.3 kJ·mol^{-1}).[4] However, ChCl-based DES are not halogen-free, which limits their applicability in specific environmentally sensitive contexts. Recently, betaine, a biodegradable and halogen-free zwitterion derived from renewable sources, has been proposed as a promising alternative to ChCl.[5] Betaine's molecular structure, characterized by a strong anionic carboxylate moiety and partially shielded ammonium groups, hindering strong self-association interactions, rendering it a viable HBA candidate. Nevertheless, betaine exhibits a higher melting enthalpy (17.98 kJ·mol^{-1})[6] and, like ChCl, undergoes thermal degradation upon melting.[4,6]
This study investigates the potential of betaine as a sustainable substitute for ChCl in DES by constructing solid-liquid equilibrium (SLE) phase diagrams. Polyols were selected as hydrogen bond donors (HBD) due to their structural diversity and compatibility with betaine. Experimental SLE phase diagrams revealed that betaine consistently demonstrated negative deviations from ideality, while most polyols exhibited near ideal behavior. However, the complete composition range was constrained by the thermal degradation of betaine and the high viscosity or boiling points of certain polyols. COSMO-RS predictions were also employed to model the interactions within these systems. Initial predictions overestimated cross-interactions between betaine and polyols, resulting in underestimated melting temperatures. This discrepancy was attributed to the selection of conformers that prioritized intermolecular interactions over intramolecular stabilization. By refining the conformer selection process to better represent intramolecular interactions, the accuracy of the predictions improved significantly.
This work highlights the potential of betaine as an alternative HBA to be considered in designing innovative DES while providing critical insights into the thermodynamic behaviour and molecular interactions present in these mixtures.

Acknowledgements
This work was developed within the scope of the projects: CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 and LA/P/0006/2020, and CIMO-Mountain Research Center, UIDB/00690/2020 and LA/P/0007/2020, financed by national funds through the Portuguese Foundation for Science and Technology/MCTES; Artemisinin bioavailability enhancement through eutectic formation with natural excipients funded by UNESCO/IUPAC - PhosAgro/UNESCO/IUPAC. Gabriel Teixeira thanks FCT for his Ph.D. grant (UI/BD/151114/2021).

References

1. E. L. Smith, A. P. Abbott and K. S. Ryder, *Chem Rev* 2014, **114**, 11060-11082.
2. D. Rente, M. Cvjetko Bubalo, M. Panić, A. Paiva, B. Caprin, I. Radojčić Redovniković and A. R. C. Duarte, *J Clean Prod* 2022, **380**, 135147.
3. M. Marchel, H. Cieśliński and G. Boczkaj, *Ind Eng Chem Res* 2022, **61**, 11288-11300.
4. L. Fernandez, L. P. Silva, M. A. R. Martins, O. Ferreira, J. Ortega, S. P. Pinho and J. A. P. Coutinho, *Fluid Phase Equilib* 2017, **448**, 9-14.
5. D. O. Abranches, L. P. Silva, M. A. R. Martins, S. P. Pinho and J. A. P. Coutinho, *ChemSusChem* 2020, **13**, 4916-4921.
6. S. Wang, Y. Zhang and J. Wang, *J Chem Eng Data* 2014, **59**, 2511-2516.

Eutectic solvents as sustainable dye baths for cotton dyeing

ORAL_O6.12 - Ionic Fluids and Deep Eutectic Solvents

Alexandre M. S. Jorge[1*], Helena F. Ribeiro[1], and Jorge F. B. Pereira[1]

[1]*CERES, FCTUC, Department of Chemical Engineering, University of Coimbra, Rua Sílvio Lima, Pólo II - Pinhal de Marrocos, 3030-790 Coimbra, Portugal*

**alexandrej@eq.uc.pt*

The textile industry is a major source of global wastewater, mainly due to inefficient dyeing processes that discharge synthetic dyes and toxic chemicals into freshwater bodies.[1] Recently, eutectic solvents (ES) have attracted attention as greener alternatives for textile dyeing, offering advantages such as low vapor pressure, non-volatility, non-flammability, and strong thermal and chemical stability.[2,3] This study explores the dyeing performance and color properties of three eutectic solvents – cholinium chloride/glycerol (ChCl/Gly), cholinium chloride/urea (ChCl/U), and glycerol/urea (Gly/U). Among these, Gly/U was identified as the most economical and resource-efficient ES. The optimized Gly/U system (1:1 molar ratio with 20% water) demonstrated a highly efficient dye bath, achieving 30% curcumin exhaustion and a color difference (ΔE) of 24.0 over five consecutive dyeing cycles. Additionally, the system enhanced colorfastness compared to conventional dye baths. This process proved to be reproducible across the five cycles, maintaining stable colorimetric values and colorfastness. The findings propose a sustainable cotton dyeing process that minimizes the use of harmful chemicals, lowers energy consumption, and reduces wastewater generation, promoting a more environmentally friendly approach to textile processing.

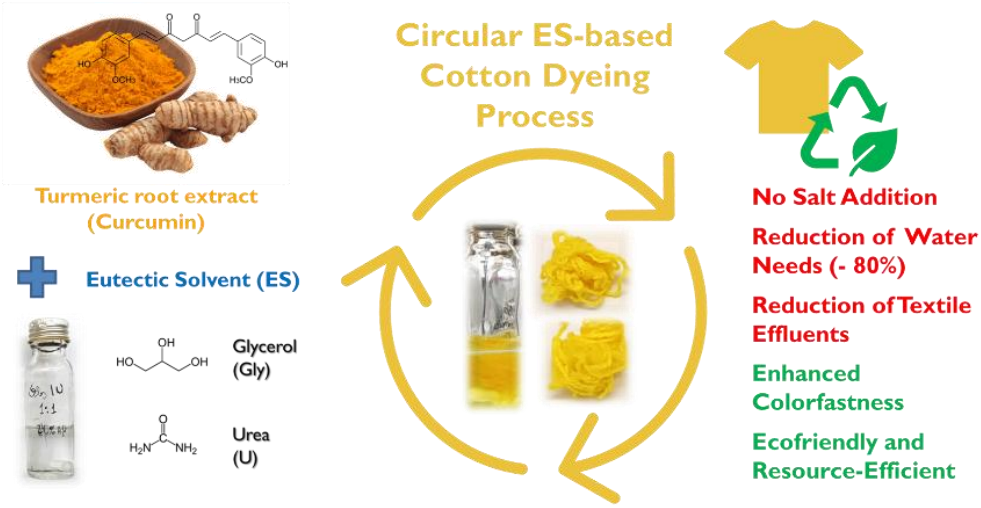


Figure 1. Scheme of the circular and sustainable ES-based cotton dyeing process designed.

Acknowledgments
CERES is supported by the Fundação para a Ciência e a Tecnologia (FCT) through the projects UIDB/ EQU/00102/2020 and UIDP/EQU/00102/2020. J.F.B. Pereira and A. M. S. Jorge acknowledge FCT for funding the project DRI/India/0044/2020 (DOI: 10.54499/DRI/India/0044/2020) and Fundação Calouste Gulbenkian for funding the project "DyeLoop". H. F. Ribeiro acknowledges FCT for PhD Grant (UI/BD/150909/2021).

References

1. A. M. S. Jorge, K. K. Athira, M. B. Alves, R. L. Gardas and J. F. B. Pereira, *Journal of Water Process Engineering* 2023, **55**, 104125.
2. A. M. S. Jorge, H. F. Ribeiro and J. F. B. Pereira, *J Environ Chem Eng* 2025, **13**, 115553.
3. C. Mouro, A. P. Gomes, R. V. Costa, F. Moghtader and I. C. Gouveia, *Gels* 2023, **9**, 800.

Pressurized hot water and deep eutectic solvents as additives for extracting cannabinoids from *Cannabis sativa* L.

ORAL_O6.13 - Ionic Fluids and Deep Eutectic Solvents

Joana Barroca Dias[1,2,*], Kristof Stagel[2], Renate Paltram[3], Heidi Halbwirth[3], Jorge F.B. Pereira[1], Katharina Bica-Schröder[2]

[1] *CERES, FCTUC, Department of Chemical Engineering, University of Coimbra, Coimbra, Portugal*
[2] *Institute of Applied Synthetic Chemistry, TU Wien, Vienna, Austria*
[3] *Institute of Chemical, Environmental and Bioscience Engineering, TU Wien, Vienna, Austria*

[*] *jmbarrocadias@gmail.com*

Cannabinoid extraction from *Cannabis sativa* L. is essential for medical applications.[1] Traditional methods often depend on large volumes of organic solvents, raising concerns about environmental impact and safety.[2] An alternative approach, pressurized hot water extraction (PHWE), utilizes high temperature and pressure to alter the chemical and physical properties of water, enhancing its ability to dissolve cannabinoids and making it a more sustainable option.[3] Further improvements can be achieved by incorporating specific additives into the process. This research examines how integrating deep eutectic solvent (DES) components into PHWE can optimize the extraction of cannabinoids, in particular cannabidiol (CBD), while maintaining an environmentally responsible approach.

Experiments were conducted using a multi-cellular reactor, subjecting *Cannabis sativa* L. samples to PHWE at temperatures between 100°C and 200°C and pressures from 10 to 40 bar. At certain PHWE operating conditions, an *in situ* selective decarboxylation of cannabinoids occurred. The addition of choline chloride-based DES significantly enhanced cannabinoid extraction efficiency. Specifically, the combination of choline chloride and glycerol improved the solubility and recovery of CBD and THC, increasing yields by 50% compared to PHWE at the optimum conditions. This combined technique preserves the environmental benefits of PHWE while delivering superior performance.

The findings suggest that incorporating additives, particularly choline chloride-based compounds, into PHWE provides a more effective and sustainable method for extracting cannabinoids. This approach holds promise for industrial-scale applications, offering both high efficiency and reduced environmental impact.

Acknowledgements

CERES is supported by the Fundação para a Ciência e a Tecnologia (FCT) through the projects UIDB/EQU/00102/2020 (https://doi.org/10.54499/UIDB/00102/2020) and UIDP/EQU/00102/2020 (https://doi.org/10.54499/UIDP/00102/2020). This research was developed in the ambit of Erasmus+ program. Joana M. B. Dias and Jorge F. B. Pereira acknowledge the Fundação Calouste Gulbenkian for funding project DYELOOP.

References

1. S. Pisanti, A. M. Malfitano, E. Ciaglia, A. Lamberti, R. Ranieri, G. Cuomo, M. Abate, G. Faggiana, M. C. Proto, D. Fiore, C. Laezza, and M. Bifulco, *Pharmacology and Therapeutics* 2017, **175**, 133-150.
2. J. Azmir, I. S. M. Zaidul, M. M. Rahman, K. M. Sharif, A. Mohamed, F. Sahena, M. H. A. Jahurul, K. Ghafoor, N. A. N. Norulaini and A. K. M. Omar, *Journal of Food Engineering* 2013, **117**, 426-436.
3. M. Plaza and C. Turner, *TrAC Trends in Analytical Chemistry* 2015, **71**, 39-54.

Predicting heat capacity in deep eutectic solvents using machine learning for sustainable design

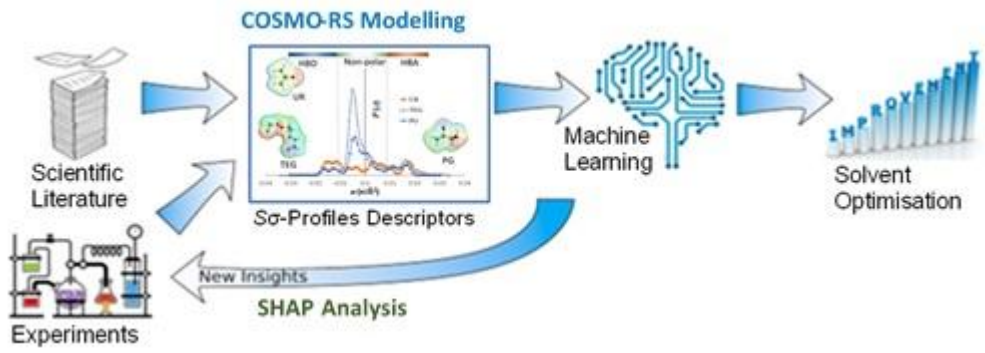
ORAL_O6.14 - Ionic Fluids and Deep Eutectic Solvents

M. Natália D.S. Cordeiro[1,*], Elisabete S.C. Ferreira[1], Amit K. Halder[1]

[1] *LAQV-REQUIMTE, Dept. Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre s/n, Porto, Portugal*

**ncordeir@fc.up.pt*

Deep eutectic solvents (DES) are gaining recognition as environmentally friendly alternatives across a range of industries due to their unique properties. Among these, heat capacity is a key parameter influencing DES performance in applications such as energy storage, chemical synthesis, and thermal regulation. Traditional methods for determining heat capacity are often time-consuming and resource-intensive, driving the need for more efficient predictive approaches. In this communication, we unveil the outcomes of our efforts in developing and validating machine learning (ML) models tailored for predicting the heat capacity of binary deep eutectic solvents. Leveraging descriptors generated from the Conductor-like Screening Model for Real Solvents (COSMO-RS), our dataset comprises 530 isobaric heat capacity measurements across a wide temperature range (278.15 to 423.15 K) for thirty distinct binary DES (see Scheme 1). Among the four supervised ML regression models evaluated, the Multilayer Perceptron (MLP) achieved the best performance, yielding an absolute average relative deviation (AADR%) of just 1.7% across all data points. The MLP model also significantly outperforms previous approaches[1-3] and demonstrates strong generalisability, showing promising predictive accuracy even for unseen data like ternary DES. This underscores the power of integrating quantum-chemical descriptors with advanced machine learning techniques for accurate prediction of DES properties. Additionally, a SHAP (SHapley Additive exPlanations) analysis revealed the most impactful features influencing DES heat capacity, offering valuable insights for the rational design and selection of new DES formulations tailored to specific needs.



Scheme 1: General workflow followed.

Acknowledgements
This work received financial support from FCT/MCTES (UIDB/50006/2020 DOI 10.54499/UIDB/50006/2020) through national funds.

References

1. M. Taherzadeh, R. Haghbakhsh, A.R.C. Duarte and S. Raeissi, *J. Mol. Liq*. 2020, **307**, 112940.
2. A. Bagherzadeh, N. Shahini, D. Saber, P. Yousefi, S.M.S. Alizadeh, S. Ahmadi and F. T. Shahdost, *Measurement* 2022, **188**, 110630.
3. A.S. Darwish, R.A. Alwan, A. Boublia, T. Lemaoui, Y. Benguerba, I.M. AlNashef and F. Banat, *Fuel* 2025, **381**, 133278.

Towards compartmentalized micelles: How the phobicity between hydrogenated and fluorinated chains determines organization

Highlighted ORAL_HO7.1 - Soft Matter, Colloids, and Complex Fluids

Tiago M. Eusébio, José Santos Pereira, Gonçalo M. C. Silva, Pedro Morgado, Eduardo J. M. Filipe*

Centro de Química Estrutural – Institute of Molecular Sciences, Instituto Superior Técnico, Universidade de Lisboa

**efilipe@tecnico.ulisboa.pt*

The mutual phobicity between hydrogenated and fluorinated chains is at the origin of intriguing anomalies in the properties of fluids. We have recently shown that aqueous solutions of mixed hydrogenated and fluorinated ionic surfactants exhibit intramicellar segregation[1], displaying hydrogen-rich and fluorine-rich domains, demonstrating the formation of compartmentalized micelles.

Compartmentalization within these nanoaggregates is a fascinating topic. The ability to solubilize solutes of different natures in different compartments is potentially important in areas ranging from detergency to drug delivery. Understanding of the self-assembly process is obviously crucial for the design of those compartmentalized supramolecular structures.

In this work, the self-assembly of different types of systems is studied, both experimentally and computationally. Mixtures of ionic hydrogenated and fluorinated surfactants (of the 1-alkyl-3-methylimidazolium family) were studied, as well as partially fluorinated ionic surfactants. Aqueous mixtures of fluorinated and hydrogenated alcohols were also investigated. Atomistic Molecular Dynamics simulations were used to obtain the structure of the different compartmentalized micelles, showing that intramicellar segregation occurs in all cases.

In the case of the mixture of alcohols, the longer fluorinated alcohol forms the "core" of the micelle, while the smaller ethanol molecules form a hydrogenated corona at the interface with water (Figure 1a). As for the partially fluorinated surfactants, again, the fluorinated segments form the "core" of the micelle, while the hydrogenated parts and ionic heads rest on the outer layer, indicating radial segregation (Figure 1b). In the case of the mixed surfactants, lateral segregation is observed (Figure 1c). Different types of domains and morphologies of compartmentalized micelles are thus formed. The influence of chain length, degree of fluorination, and composition was studied. The solubilization of different solutes was also tested.

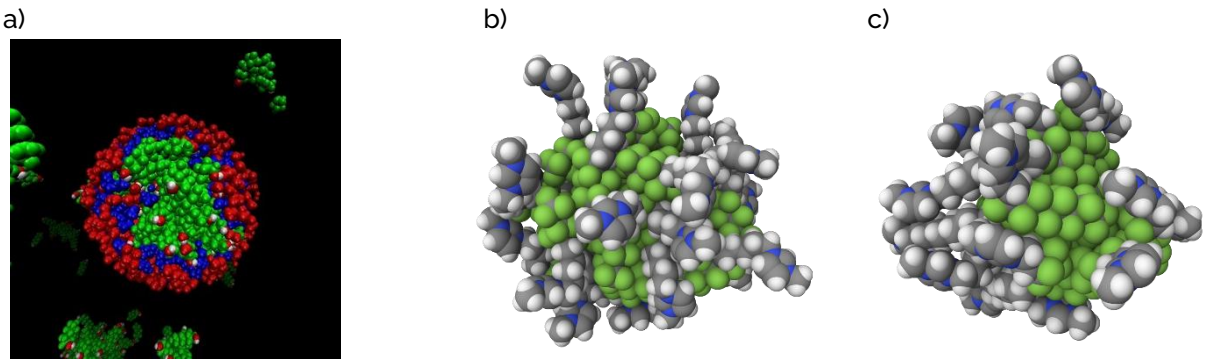


Figure 1. MD simulation snapshots of compartmentalized micelles: a) (perfluoroheptanol+ ethanol+ water) micelle; b) Partially fluorinated cationic micelle; c) Mixed hydrogenated and fluorinated cationic micelle. Colour scheme: ethanol molecules – blue, water molecules – red; C atoms - grey, N atoms - blue, H - white, F atoms - green.

References

1. G. M. C. Silva, P. Morgado, E. J. M. Filipe, *Journal of Colloid and Interface Science* 2024, **654**, 906-914.

Inversely coupled thermogelation: designing a polymer/surfactant hydrogel for smart topical delivery

ORAL_O7.2 - Soft Matter, Colloids, and Complex Fluids

Rui L. Machado[1], Elsa C. Loureiro[1], Sandra G. Silva[2], Eduardo F. Marques[1,*]

[1]*CIQUP (Centre of Research in Chemistry), IMS (Institute of Molecular Sciences), Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre, 4169-007 Porto, Portugal*

[2]*LAQV-REQUIMTE (Associated Laboratory for Green Chemistry of the Network of Chemistry and Technology), Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre, 4169-007 Porto, Portugal*

[*]*efmarque@fc.up.pt*

Hydrogels are highly versatile tridimensional networks widely used in biomedicine for their biocompatibility, tunability, and similarity to the extracellular matrix.[1] Recently, they've served as scaffolds for drug delivery nanovehicles (micelles, vesicles, tubes), creating effective therapeutic systems.[2] In this work, we developed a thermo-responsive hybrid gel for topical drug delivery by combining a triblock copolymer matrix with a surfactant tube network. The tubes arise from the self-assembly of lysine-based surfactants (developed in-house)[3], while the polymeric matrix is based on Pluronic F127, which undergoes thermally induced gelation. Imaging, calorimetric, and rheological studies provide extensive insight into the structural composition and functional properties of the hybrid gel. With increasing temperature, the system undergoes complex microstructural alterations, evolving from a tube network, that disassembles into either micelles or vesicles (depending on the surfactant used), to a polymeric liquid-crystal that entraps the surfactant nanostructures. At skin temperature, the gel is capable of self-healing, is easily spreadable, and has adequate strength for topical use. It also exhibits slow, sustained release of a fluorescent probe (carboxyfluorescein), along with high biocompatibility and improved cellular internalization compared to neat F127. This platform has great potential for long-term topical drug delivery.

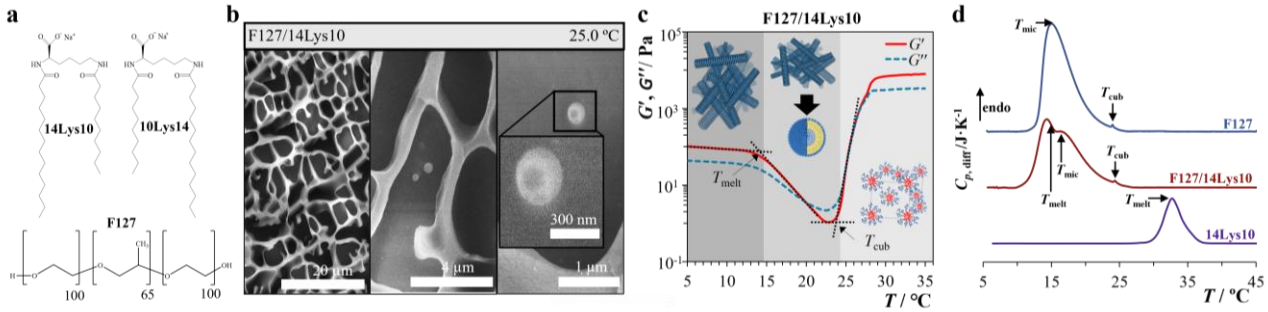


Figure 1: Thermal behavior of the hybrid gels. **a.** molecular structure of the gels' components; **b.** microstructure as observed by cryo-SEM imaging; **c.** rheological properties with increasing temperature; **d.** DSC thermogram with phase transition peaks.

Acknowledgements
Financial support from Fundação para a Ciência e Tecnologia (FCT) through project 2022.05543.PTDC-Smart4Vir, through CIQUP via grant UID/QUI/0081/2020 (https://doi.org/10.54499/UIDB/00081/2020) and IMS via grant LA/P/0056/2020 (https://doi.org/10.54499/LA/P/0056/2020). Elsa C. Loureiro acknowledges support through a research scholarship from project 2022.05543.PTDC-Smart4Vir.

References

1. J. Li and D. J. Mooney, *Nat. Rev. Mater.* 2016, **1**, 16071.
2. R. L. Machado, A. C. Gomes and E. F. Marques, *J. Mol. Liq.* 2024, **416**, 126453.
3. I. S. Oliveira, R. L. Machado, M. J. Araujo, A. C. Gomes and E. F. Marques, *Chem. Eur. J.* 2021, **27**, 692-704.

Identification of various crystalline phases of the thermotropic liquid crystal OHMBBA by DSC-XRD and DSC-Raman spectroscopy

ORAL_O7.3 - Soft Matter, Colloids, and Complex Fluids

Ami Hayashi[1], Kosuke Shido[2,4], Mariko Noguchi[1,*], Atsushi Nagoe[3], Hiroki Fujimori[1,2]

[1]*College of Humanities and Sciences, Nihon University, Tokyo, 156-8550, Japan*
[2]*Graduate School of Integrated Basic Sciences, Nihon University, Tokyo, 156-8550, Japan*
[3]*School of Science and Engineering, Kokushikan University, Tokyo, 154-8515, Japan*
[4]Present Address: *Lithium Resources Research Organization, Hirosaki University, Aomori, 036-8561, Japan*

[*]*noguchi.mariko@nihon-u.ac.jp*

Differential scanning calorimetry (DSC) is a thermal analysis method that can obtain thermodynamic information such as phase transition temperatures and transition entropy of materials DSC is useful for analyzing various phase transition behaviors, including metastable phases formed under specific conditions, because it allows precise temperature control easily. Simultaneous measurement of DSC and diffraction or spectroscopy can be a more powerful method for identifying each phase than DSC, because microscopic information from the structure of each phase can be obtained in addition to macroscopic information from DSC.

In this work, we performed DSC and simultaneous measurements of DSC-X-ray diffraction (XRD) and DSC-Raman spectroscopy of *N*-(2-hydroxy-4-methoxybenzylidene)-4'-*n*-butylaniline (OHMBBA) to investigate the effect of precooling treatments on phase behaviors.[1] OHMBBA is one of the most famous thermotropic liquid crystals that form a glassy liquid crystal state by quenching.[2] In this research, we found that OHMBBA forms various solid phases depending on the cooling conditions, crystalline phases, glassy-liquid-crystal states, or a mixture of both. We performed the DSC measurements of OHMBBA before melting and after melting with different precooling treatments, and the different DSC heating curves were obtained. On 1st heating before melting, endothermic peaks were observed at 317 K and 337 K. These results suggest that the stable crystalline phase C_I was maintained in the 1st cooling and that the phase transitions from the C_I phase to N phase at 317 K and from the N phase to I phase occurred at 337 K in the 1st heating. In the heating process after cooling with the rate of 100 K min^{-1}, a glass transition was observed at 209 K, indicating that the glassy N phase (N_G) was formed by quenching. At 245 K, the supercooled N phase was transformed into the C_{II} phase through the cold crystallization. On further heating, the exothermic peak was observed at 271 K, which is due to the solid-solid phase transition from the C_{II} to the C_I phases. The endothermic peaks at 317 K and 337 K were observed, corresponding to due to the C_I-N transition and the N-I transition respectively. These results with previous studies.[2] Interestingly, the DSC heating curve changed continuously as the cooling rate was slowed down. As the cooling rate decreased, the glass transition at 209 K and the exothermic peak around 245 K due to the N-C_{II} transition became smaller. In the sample cooled at 10 K min^{-1}, these anomalies disappeared, and two new endothermic peaks appeared at 220 K and 228 K. The simultaneous measurements of DSC-XRD and DSC-Raman spectroscopy were used to examine the phase behavior. DSC-XRD measurements perfectly captured that the melted OHMBBA crystallizes into a new metastable crystalline phase C_{II}' when cooled at 10 K min^{-1}, and that it transitions to the stable crystalline phase C_I and finally melts into the N phase during the heating process. Moreover, the simultaneous measurements of DSC-Raman spectroscopy revealed that the phase behaviors of OHMBBA after cooling rapidly (above 100 K min^{-1}) and normally (at 10 K min^{-1}). We distinguished two different metastable phases, C_{II} and C_{II}' at 230-270 K by analyzing wavy DSC curves observed in the DSC-Raman spectroscopy. In the Raman spectra, the positions of a peak due to the stretching vibration of C=C in the phenyl ring exhibited that OHMBBA formed into different solid states at low temperatures after cooling rapidly (N_G) and normally (C_{IV}).

References

1. K. Shido, M. Noguchi, A. Hayashi, A. Nagoe and H. Fujimori, *J. Therm. Anal. Calorim.* 2024, **149**, 453-462.
2. M. Sorai and S. Seki, *Mol. Cryst. Liq. Cryst.* 1973, **23**, 29-327.

Approximation for determining the effective nanolayer thickness in nanofluids of spherical nanoparticles through permittivity

ORAL_O7.4 - Soft Matter, Colloids, and Complex Fluids

T. P. Iglesias[1,*], A. Queirós[1,2], M. F. Coelho[2]

[1] *Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Vigo, 36310 Vigo, Spain*
[2] *Politécnico do Porto, Instituto Superior de Engenharia do Porto, 4200-072 Porto, Portugal*

**tpigles@uvigo.gal*

In this study, a novel approach is introduced to determine nanolayer thickness, knowing nanofluid permittivity. The nanoparticles are assumed to be spherical, and the generalized Maxwell Garnett model for spherical inclusions with a single layer is applied under the hypothesis that nanolayer permittivity is significantly higher than that of both the nanoparticles and the base fluid. It is shown that the equation derived from the generalized Maxwell Garnett model coincides with that from the Steeman-Maurer model, despite the fact that the two models are based on different premises. The proposed approximation is tested on alumina (15nm or 40 nm) + water nanofluid. The hypothesis is deemed highly plausible, supported by the findings of both Leong et al.'s model (when translated into permittivity) and the generalized Maxwell Garnett model for the nanofluids studied. Results show that nanolayer thickness decreases as nanoparticle concentration increases and increases with rising temperature. Building upon this, the nanolayer density is calculated following Iglesias et al.'s model.[1] It is observed that this increases with increasing temperature and decreases with increasing nanoparticle concentration. Furthermore, the nanolayer density is smaller or greater than that of the base fluid, depending on whether the molar volume of mixing is positive or negative. These findings lead to the hypothesis that a positive increment of nanofluid density (or a negative molar volume of mixing) could provide insights into the stability of nanofluids prepared without surfactants.

Acknowledgments
This work was funded by the European Union H2020-MSCA-RISE- 2019 PEPSA-MATE (872233) and Consellería de Cultura, Educación e Universidade, Xunta de Galicia, Spain (Grant ED431B 2024/27).

References

1. T.P. Iglesias, A. Queiros and M.F. Coelho, *J. Mol. Liq*. 2024, **393**, 123537.

Electron correlation mechanism to make glassy state of phonons in organic charge transfer complexes

ORAL_O7.5 - Soft Matter, Colloids, and Complex Fluids

Y. Nakazawa[1,*], H. Manabe[1], V. C. Arthurs[1], T. Nomoto[2], S. Yamashita[1], H. Akutsu[1]

[1]*Dept. of Chemistry, Graduate School of Science, Osaka University*
[2]*RIKEN*

[*]*nakazawa@chem.sci.osaka-u.ac.jp*

A charge-glass (CG) state is considered as a metastable electronic state driven by electron correlations typically emerging in molecular charge transfer complexes. It appears in 1/4 filling electronic states of p-electron band with strong electron correlations in typically in M_2X compounds where M denotes electron doner/acceptor molecules and X is monovalent counter ions. In this electron filling, owing to the inter-site Coulomb repulsion *V* which tends to form a charge ordering state with electron-rich or electron-poor sites, charge ordering (CO) appears with superlattice periodicity. This is a kind of Wigner lattice state of electrons. However, if the molecular stacking in the electron donor/acceptor layer has frustration which disturbs formation of suitable charge ordering pattern, the glassy freezing of electron density manifest itself in low temperature region. BEDT-TTF (bis(ethylenedithio)tetrathiafulvalene) based charge-transfer salts with a q-type donor arrangement is a typical material which shows such CG states.

We have developed a new apparatus to measure accurate heat capacity and thermal conductivity of tiny single crystal samples of molecular compounds and performed detail and systematic thermodynamic studies of these materials. Temperature dependences of the heat capacity of q-(BEDT-TTF)$_2$CsZn(SCN)$_4$, slowly cooled q-(BEDT-TTF)$_2$RbZn(SCN)$_4$ and q-(BEDT-TTF)$_2$RbCo(SCN)$_4$ are shown in Figure 1.No drastic peak appears in the temperature dependence of the heat capacity in the former two compounds which means that the material do not show any long range ordering in the whole temperature range. However, drastic change of lattice heat capacity has been observed in the q-(BEDT-TTF)$_2$RbCo(SCN)$_4$. and CO order is realized and makes the lattice robust at low temperature. In the case of q-(BEDT-TTF)$_2$CsZn(SCN)$_4$ in which charge glass state is realized, the low temperature heat capacity has drastic peak in its C_pT^{-3} vs T plot reminiscent of formation of phonon glasses.[1] In addition, at around 100 K, which is the characteristic temperature range where charge glass occurs, there is a slight structure in the temperature dependence of the heat capacity due to glass formation.[2-3] We will discuss the dynamics of charge glass and the characteristics of the lattice heat capacity due to phonons related to it, based on the temperature and frequency dependence of the AC heat capacity. This seems to be a new mechanism to make disordered phonon structure in regular lattice in molecular crystals and demonstrates strong coupling of electronic freedom with lattice degrees of freedom in molecular crystals. We also discuss cooling rate dependence of q-(BEDT-TTF)$_2$RbZn(SCN)$_4$ and investigate drastic difference of lattice state between well- ordered CO state and glassy state.

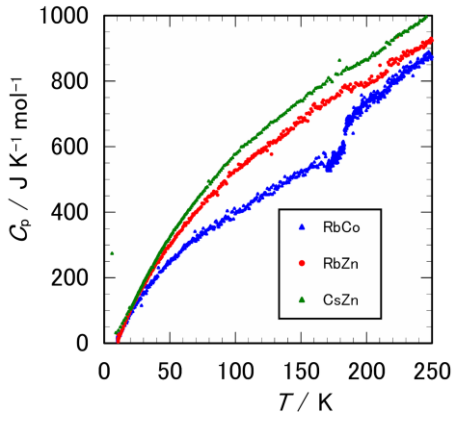


Figure 1: Temperature dependence of the heat capacity of three q-(BEDT-TTF)$_2$ X compounds obtained by single crystal measurement.

References

1. R. Yoshimoto et al. *Physica B* 2014, **449**, 19-24.
2. T. Nomoto and Y. Nakazawa et al. *J. Phys. Soc. Jpn.* 2019, **88**, 073601 1-4.
3. T. Nomoto and Y. Nakazawa et al. *Phys. Rev.* B 2023, **107**, 124803 1-7.

Derivative thermodynamic properties of confined fluids based on density functional theory

Highlighted ORAL_HO8.1 - Surfaces, Interfaces, and Confinement

Gennady Gor,[1,*] Geordy Jomon,[1] Andrei Kolesnikov[1]

[1]*New Jersey Institute of Technology*

[*]*gor@njit.edu*

Thermodynamic properties of fluids confined in nanopores differ from the properties of the same fluids in bulk.[1] Most prominent examples of such differences include shifts of the phase transitions - capillary condensation or freezing in the pores. Recent experimental and molecular simulation studies showed that isothermal compressibility of a fluid confined in a nanopore differs from the compressibility of the same fluid in bulk.[2] Density functional theory (DFT) has been widely used for modeling thermodynamics of confined fluids and e.g. is capable of quantitatively predicting capillary condensation for simple fluids, such as argon or nitrogen, in nanopores.[3-5] However, the same DFT models failed to reproduce compressibility for even bulk fluids.[6]

Here we use a rather simple DFT model for argon based on the Percus-Yevick equation and consider the temperature at which the vapor and liquid densities match the experimental values. We show that the isothermal compressibility of bulk liquid argon at this temperature matches the experimental value as well. We performed the calculations of compressibility of argon confined in carbon slit pores of various sizes and demonstrated that the compressibility of argon in confinement is lower than that in bulk. The bulk modulus (1/compressibility) appears to be a linear function of the 1/pore size, consistent with the molecular simulation results.[2] In addition to isothermal compressibility, we calculated another derivative thermodynamic property - thermal expansion coefficient of confined argon. Our calculations showed that it behaves similar to compressibility - it is always lower than the bulk value and gradually increases for the smaller pore sizes. Our study contributes to the fundamental knowledge in thermodynamics of confined fluids. It also demonstrates the potential of DFT for calculation of properties which are very challenging to calculate using molecular simulations.

Acknowledgments
The work was supported by the National Science Foundation, grant CBET-2344923.

References

1. R. An, R. Le, K. E. Gubbins, M. Sliwinska-Bartkowiak, and M. Thommes, *Adsorption* 2025, **31**, 69.
2. C. D. Dobrzanski, B. Gurevich, and G. Y. Gor, *Appl. Phys. Rev.* 2021, **8**, 021317.
3. P. I. Ravikovitch, A. Vishnyakov, and A. V. Neimark, *Phys. Rev. E* 2001, **64**, 011602.
4. J. Landers, G. Y. Gor, and A. V. Neimark, *Coll. Surf. A* 2013, **437**, 3.
5. V. de Morais Sermoud, A. de Freitas Gonçalves, A. G. Barreto Jr, L. F. M. Franco, F. W. Tavares, and M. Castier, *Fluid Phase Equilib.* 2024, **586**, 114177.
6. G. Y. Gor, *Poromechanics VI* 2017, 465.

Quantifying the uncertainty of force field selection on adsorption predictions in metal-organic framework materials

ORAL_O8.2 - Surfaces, Interfaces, and Confinement

C. McCready[1], K. Asif[1], J. R. B. Gomes[2], A. J. Fletcher[1], M. Jorge[1,*]

[1]*Department of Chemical and Process Engineering, University of Strathclyde, 75 Montrose Street, Glasgow G1 1XJ, United Kingdom*
[2] *CICECO - Aveiro Institute of Materials, University of Aveiro, Aveiro, Portugal*

**Miguel.jorge@strath.ac.uk*

Molecular simulation of adsorption is a powerful tool to screen large databases of porous materials (e.g. MOFs) and guide experiments towards the best performing materials. However, comparisons between simulated and experimental adsorption isotherms in MOFs are still fraught with challenges. On the experimental side, there is significant variation between isotherms measured on the same system, with a significant percentage (~20%) of published data being considered outliers.[1] On the simulation side, force fields are often chosen "off-the-shelf" with little or no validation. In this work, we address this problem by systematically testing a variety of force fields and computing an adsorption "consensus isotherm", including a quantification of parametric uncertainty based on ensemble averaging.[2] This is compared against a similarly generated consensus experimental isotherm constructed from a manually curated set of data from literature. Our study focuses on methane and carbon dioxide adsorption, two of the most relevant greenhouse gases, on a series of prototypical materials that represent the most widely studied MOF "families. Our results show that the uncertainty in simulated isotherms arising from force field selection can be as large as 15%, while the experimental variability can reach 20%, even after outlier removal.[3] We also show that standard "generic" force fields can provide reliable predictions for some systems but can fail dramatically for others, highlighting systematic shortcomings in those models. In many cases these disagreements can be explained by the presence of defects in the experimental sample (as for UiO-66)[3] or by specific interactions with open metal sites, which cannot be accurately predicted using standard force fields[4]. Based on these results, we offer recommendations for future simulation studies of adsorption, including high-throughput computational screening of MOFs.

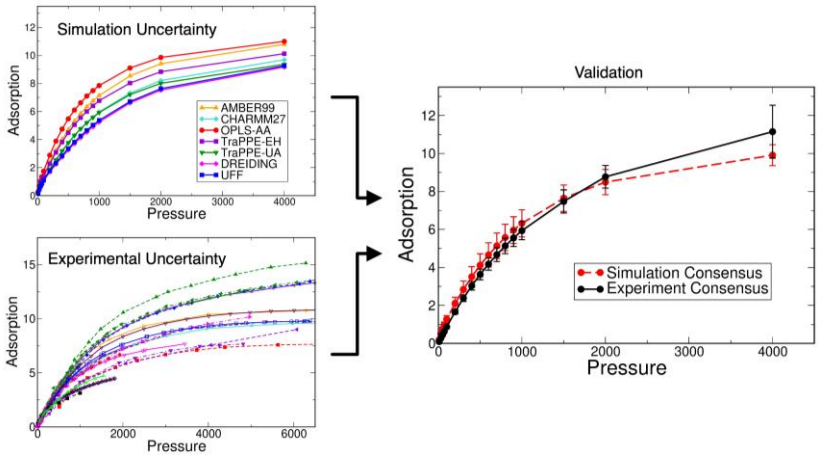


Figure 1: The uncertainty arising from force field selection (top left) and experimental data (bottom left) are quantified to allow for a rigorous comparison between simulated and experimental adsorption isotherms (right).

References

1. J. Park, J. D. Howe, D. S. Sholl, *Chem. Mater.* 2017, **29**, 10487–10495.
2. M. Vassaux, S. Wan, W. Edeling, P. V. Coveney, *J. Chem. Theory Comput.* 2021, **17**, 5187-5197.
3. C. McCready et al, *J. Chem. Theory Comput.* 2024, **20**, 4869-4884.
4. C. Campbell, J. R. B. Gomes, M. Fischer, M. Jorge, *J. Phys. Chem. Lett.* 2018, **9**, 3544-3553.

Water vapor sorption of salt nanoparticles in porous silica: experimental insights and thermodynamic modelling

ORAL_O8.3 - Surfaces, Interfaces, and Confinement

Shaoheng Wang*, Michael Steiger

Department of Chemistry, University of Hamburg, Hamburg, Germany

**shaoheng.wang@uni-hamburg.de*

The water vapor sorption of salt particles in porous media has attracted significant attention due to its application in thermal energy storage, gas drying, and its distinct sorption behavior compared to the bulk phase.[1-3] Studies using various methods have reported that the deliquescence relative humidity (DRH) of the salt nanoparticles in porous media is lower than that of bulk crystals.[1,3] In hydrophilic porous silica, the DRHs shift is attributed to a combination of solubility changes and vapor pressure drop.[1] The solubility is influenced by the interfacial energy of nanocrystals and the Laplace pressure induced by the curvature of solution-air interface, which manifest as salt–in and salt–out effect, respectively.[1]

In this study, the water vapor sorption curves of several salt nanoparticles ($CaCl_2$, $MgCl_2$, KCl, $NaClO_4$, $Mg(ClO_4)_2$) confined in porous silica (SBA–15 and MCM–41) with pore sizes ranging from 3 to 20 nm were measured using a Vapor Sorption Analyzer. As illustrated by the KCl sorption curve in Figure 1, a distinct downward shift in DRH within nanopore is observed. The water vapor sorption process occurs in three stages: deliquescence, curvature filling, and dilution. A thermodynamic model incorporating Pitzer theory, the Kelvin equation, and Laplace pressure was employed to calculate the water vapor sorption curves and assess the influence of pore size on the deliquescent equilibrium. Additionally, the determination of salt–solution interfacial energy (γ_{sl}) and the solubility of salt nanoparticles in porous silica will be discussed.

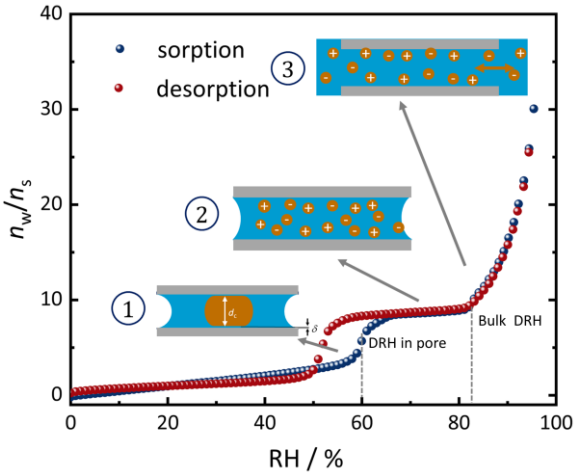


Figure 1. Water vapor sorption curve of the KCl nanoparticle in 7.0 nm SBA-15.

References

1. T Talreja-Muthreja et al. *Langmuir* 2022 **38**, 10963-10974.
2. T.S Yan et al. *J. Heat Mass Trans.* 2019, **139**, 990-999.
3. I.V. Ponomarenko et al. *Microp. Mesop. Mater.* 2010, **129**, 243-250.

Tailoring morphology and wetting behavior of films of ionic liquid mixtures with varied alkyl chain lengths

ORAL_O8.4 - Surfaces, Interfaces, and Confinement

Soraia R. M. R. Silva[1,*], Rita M. Carvalho[1], Margarida Bastos[1], Luís M. N. B. F. Santos[1], and José C. S. Costa[1]

[1]*CIQUP, Institute of Molecular Sciences (IMS), Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Portugal*

[*]*soraiareis21@gmail.com*

Extensive research has focused on films formed by pure ionic liquids (ILs).[1-3] However, growing interest in IL mixtures and their synergistic properties presents new opportunities for targeted applications and fundamental scientific investigations.[4] This study explores the morphology of films composed of mixtures of two ILs, $[C_2C_1im][OTf]$ and $[C_8C_1im][OTf]$, co-deposited via physical vapor deposition (PVD)/vacuum thermal evaporation (Figure 1). The primary objective was understanding how varying the IL ratio influences droplet formation, surface coverage, and overall film structure.[5]

Thin-film growth was examined on glass substrates coated with indium tin oxide (ITO) and ITO/glass surfaces coated with metallic films (Au and Ag). Film morphology was characterized using optical and high-resolution scanning electron microscopy (SEM), while elemental composition was analyzed via X-ray photoelectron spectroscopy (XPS). The results show that IL mixture morphology is strongly influenced by both IL composition and substrate type. Increasing $[C_8C_1im][OTf]$ content led to larger microstructures due to improved wetting, particularly on Au surfaces, resulting in nearly fully coalesced films. Metallic surfaces near ITO significantly impacted droplet behavior, with ILs exhibiting a strong affinity for metals, especially when the long-chain IL dominated the mixture.[5]

The IL-assisted crystallization of rubrene, a high-performance organic semiconductor (OSC) that typically exhibits poor crystallinity when deposited via PVD, highlights the potential of IL mixtures to enhance organic film quality. X-ray diffraction (XRD) confirmed that $[C_2C_1im][OTf]$ and $[C_8C_1im][OTf]$ mixtures significantly improved rubrene crystallinity, demonstrating their potential to create an optimal environment for OSC solubility and crystallization.[5]

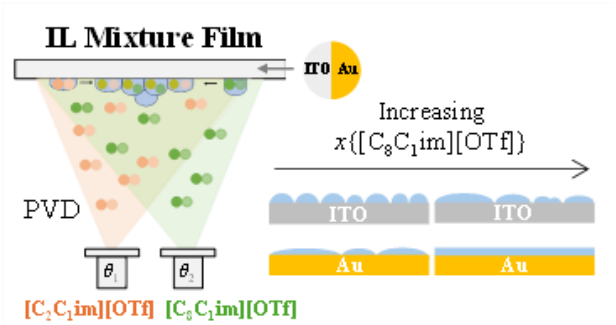


Figure 1: Schematic representation of the deposition of ionic liquid (IL) mixture films by PVD.

Acknowledgments

The authors thank the Portuguese Foundation for Science and Technology (FCT) for the financial support to CIQUP, Faculty of Science, University of Porto (Project UIDB/00081/2020: DOI 10.54499/UIDP/00081/2020), and IMS-Institute of Molecular Sciences (Grant LA/P/0056/2020), Faculty of Science, University of Porto. The research was partially funded by ASCENT+ Access to European Infra-structure for Nanoelectronics (EU Horizon 2020 Programme Grant 871130).

References

1. Y. Matsumoto, *Molecules* 2023, **28**, 1991.
2. J. Costa, A. Alves, M. Bastos and L. Santos, *Phys. Chem. Chem. Phys* 2022, **24**, 13343.
3. M. Teixeira, L. Santos and J. Costa, *Colloids Interfaces* 2022, **6**, 46.
4. H. Niedermeyer, J. Hallett, I. Garcia, P. Hunt and T. Welton, *Chem. Soc. Rev* 2012, **41**, 7780-7802.
5. S. Silva, R. Carvalho, O. Bondarchuk, G. Oliveira, J. Araújo, M. Bastos, L. Santos, and J. Costa, *Langmuir* 2025, **41**, 9086-9099.

Surface cleaning procedure using gas for contact angle measurement

ORAL_O8.5 - Surfaces, Interfaces, and Confinement

Eva Mühlegger, Kai Langenbach*

TU Dortmund, Dortmund, Germany

**kai.langenbach@tu-dortmund.de*

Contact angles describe the wetting behavior of fluids on surfaces. In process design, this is a decisive parameter for the design and development of packings in columns to gain information of the size of the interfacial area for the mass transport. Contact angles are also important in product design e.g. for synthetic materials, as they describe the printability but also surface properties.
Contact angles are a property depending on the material pairing only, however, they are challenging to measure as the results show only low reproducibility. In defined measurement set ups with a controlled atmosphere and a strict cleaning procedure based on liquids, higher reproducibility is achievable, but the thermodynamically true contact angle will be still unknown. This is due to the strong influence of the adsorbate layer on top of any technical surface. Heier et al.[1]could show that the composition and the thickness of the adsorbate layer mainly influence the contact angle measurement.
The chemical composition of the adsorbate layer strongly depends on the history and the surrounding of the surface. Usually, solid samples for the contact angle measurement are cleaned with easily evaporable solvents, e.g. iso-propanol before the measurement. This can lead to thick adsorbate layers on top of the sample, which have a strong impact on the contact angle measurements, even after drying[2]. It is shown that the gas cleaning method can reduce the thickness of the adsorbate layer.
In the proposed experimental procedure, both the history of the surface itself and the measuring environment are well defined and therefore, the adsorbate layer on the sample is a controlled variable. By controlling this key variable, the contact angle can be measured with higher reproducibility. In this work, the development of the gas cleaning method with partial factorial analysis as well as results for water on stainless steel and water on aluminum are presented. The standard deviation of the contact angle measurements can be reduced with the proposed gas cleaning method to a third of the standard deviation without gas cleaning.

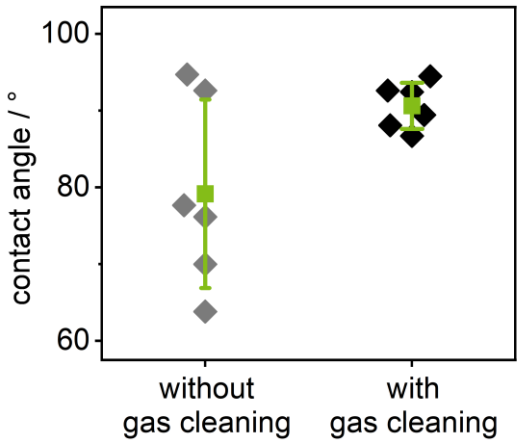


Figure 1: Contact angles of H_2O on stainless steel without and with the gas cleaning procedure.

References

1. M. Heier, R. Merz, S. Becker, K. Langenbach, M. Kopnarski and H. Hasse, *Adsorpt. Sci. Technol.* 2021, **2021**, 1-11.
2. M. Heier, S. Stephan, F. Diewald, R. Müller, K. Langenbach and H. Hasse, *Langmuir* 2021, **37**, 7405-7419.

Giant crystalline film growth of organic semiconductors on engineered ionic liquid surfaces in vacuum

ORAL_O8.6 - Surfaces, Interfaces, and Confinement

Artur F. M. Farinha[1,*], Luís M. N. B. F. Santos[1], and José C. S. Costa[1]

[1]*CIQUP/Institute of Molecular Sciences (IMS), Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre s/n, 4169–007 Porto, Portugal*

[*]*up201506214@fc.up.pt*

We investigated how the chemical nature, shape, and size of alkylimidazolium-based ionic liquids (ILs) influence the crystallization behavior of organic semiconductors (OSCs) under vacuum deposition conditions. The length of the IL alkyl chains affects both wettability and thin-film morphology[1], making IL-assisted vapor deposition a promising strategy to enhance organic film crystallinity[2].

This work examined two OSCs: a carbazole derivative (TCB) and a phenylamine derivative (TDAB), building upon previous studies that explored other OSCs, like pentacene or perylene[2,3]. TCB exhibits a molecular structure analogous to TDAB but differs in the additional chemical bonds between the phenyl groups in the carbazolyl unit. This structural variation significantly influences key thermodynamic properties of these OSCs, including the glass-forming ability and crystallization tendency[4,5]. Vapor deposition techniques by thermal evaporation were utilized, with various deposition strategies employed: sequential depositions (IL over OSCs), inverted sequential depositions (OSCs over IL), and simultaneous depositions[4].

In the absence of IL, TCB exhibited minimal crystallization, while interaction with IL deposited above it resulted in small TCB crystal growth in the nanometer range. In inverted sequential and simultaneous depositions, TCB crystals displayed significantly larger growth (Figure 1). Prior to IL deposition, TDAB exhibited well-defined pillar-shaped crystals. During sequential depositions, IL did not affect the morphology of the crystalline microstructures of TDAB, with IL accumulating atop them. However, argon plasma treatment induced the collapse of the IL structures, resulting in a thin IL coating on the TDAB pillars. Additionally, in inverted sequential depositions, TDAB crystalline filaments showed preferential growth inside IL droplets. Morphological analysis using SEM and crystallinity evaluation through XRD provided insights into film formation dynamics, elucidating the influence of IL on OSC film growth[4].

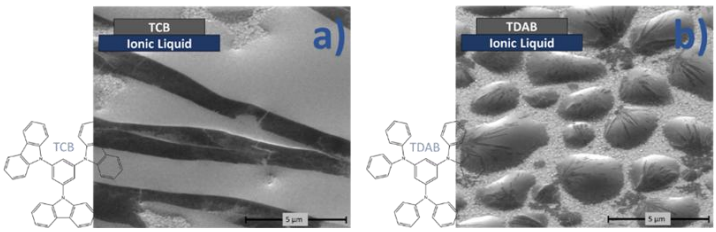


Figure 1: SEM micrographs exhibiting OSCs' crystalline growths when deposited over ionic liquids. a) 1,3,5-Tris(N-carbazolyl)benzene (TCB) deposited over $[C_8C_1Im][NTf_2]$, b) 1,3,5-Tris(diphenylamino)benzene (TDAB) deposited over $[C_8C_1Im][NTf_2]$.

Acknowledgments

This work was supported by the Fundacão para a Ciência e Tecnologia (FCT) (funded by national funds through the FCT/MCTES (PIDDAC)) to CIQUP, Faculty of Science, University of Porto (Project UIDB/00081/2020: DOI 10.54499/UIDP/00081/2020), and IMS-Institute of Molecular Sciences (LA/P/0056/2020). A.F.M. Farinha also thanks the FCT and the European Social Fund (ESF) for the award of a Ph.D. Research Grant (ref. 2022.11342.BD: DOI 10.54499/2022.11342.BD).

References

1. J.C.S. Costa, A. Alves, M. Bastos, L.M.N.B.F. Santos, *Physical Chemistry Chemical Physics* 2022, **24**, 13343-13355.
2. J.C.S. Costa, R.M. Campos, Â.C.M. Castro, A.F.M. Farinha, G.N.P. Oliveira, J.P. Araújo, L.M.N.B.F. Santos, *CrystEngComm* 2024, **25**, 913-924.
3. R.M. Campos, A.C.P.M. Alves, M.A.L. Lima, A.F.M. Farinha, J.P.S. Cardoso, A. Mendes, J.C.S. Costa, L.M.N.B.F. Santos, *ChemPhysChem* 2020, **21**, 1814-1825.
4. A.F.M.Farinha, G.N.P. Oliveira, J.P.Araújo, L.M.N.B.F. Santos, J.C.S. Costa, *Crystal Growth & Design* 2025, **25**, 612-623.
5. J.C.S. Costa, M.A.L. Lima, A. Mendes, L.M.N.B.F. Santos, *RSC Advances* 2020, **10**, 11766-11776.

Antioxidant efficiency in tween and cyclodextrin-stabilized emulsions

ORAL_O8.7 - Surfaces, Interfaces, and Confinement

Sonia Losada-Barreiro[1,*], Tamara Martínez-Senra[1], Fátima Paiva-Martins[2], Carlos Bravo-Díaz[1]

[1] *Universidade de Vigo, Departamento de Química Física, 36310, Vigo, Spain*

[2]*REQUIMTE/LAQV, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Campo Alegre 687, Porto, Portugal*

[*]*sonia@uvigo.es*

The oxidation of lipids is one of the causes of quality in many types of food, leading to nutrient losses. It generates compounds with undesirable sensory characteristics and even gives rise to toxic compounds that could negatively affect human health. Controlling interfacial properties in multiphasic systems is a fundamental question in colloid chemistry and in unsolved problems in the food industry.
Here we have evaluated the physical and oxidative stability of emulsions prepared using stripped soybean oil and stabilized by Tween 20 and β-cyclodextrins (β-CD). δ-tocopherol (TOC) was employed as a representative antioxidant. Its antioxidant efficiency in these emulsions was evaluated by determining the kinetics of the formation of primary oxidation products (conjugated dienes, CDs) according to the AOCS Official Method Ti 1a 64.
We have also determined the effects of increasing temperature (T) and emulsifier concentration (ΦI) on the distribution of TOC in Tween-based emulsions. TOC is an essentially oil-insoluble antioxidant (AO), and only one partition constant, that between the oil and interfacial region POI, is needed to describe its distribution in emulsions.
The results obtained should provide basic information on the factors controlling antioxidant distributions and efficiencies and permit a more rational selection of antioxidants and emulsifiers in food stabilization.

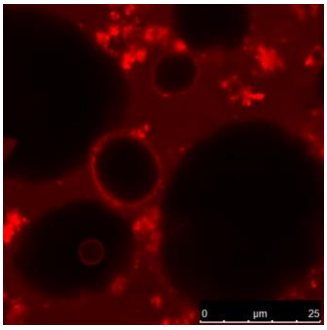


Figure 1: Confocal laser scanning microscope image of soybean oil emulsion stabilized by β-CD.

Acknowledgments
Financial support of the following institutions is acknowledged:
MICIU/AEI/Grant PID 2022-136443OB-I00 and "ERDF/EU", Universidade de Vigo.
T. M.-S. thanks Spain-Ministry of Science and Innovation for a FPU research training grant.

Detailed simulation of a liquid H_2 plant including ortho-para hydrogen conversion

Highlighted ORAL_HO9.1 - Modelling and Simulation

Fuyu Jiao[1,*], Saif Al Ghafri[1], Xiong Xiao[1], Eric May[1] and Michael Johns[1]

[1]*Fluid Science & Resources, University of Western Australia, Perth, WA, 6009, Australia*

[*]*fuyu.jiao@uwa.edu.au*

Liquid hydrogen (LH_2) plays a crucial role in emerging energy and transportation systems, particularly for hydrogen storage, distribution, and aerospace applications. However, the energy-intensive liquefaction process remains a significant challenge, necessitating advanced process optimisation to improve efficiency and reduce costs. This work presents the design and simulation of a large-scale hydrogen liquefaction process with a production capacity of 450 tonnes per day (TPD) using ASPEN HYSYS. The simulation uniquely incorporates quantitative reaction kinetics for the required ortho-para hydrogen conversion (OPC) and has been validated against multiple literature models. A detailed optimisation process was conducted to determine the optimal placement of heat exchanger-reactor combinations, leading to a final simulation case with a specific energy consumption (SEC) of 7.64 kWh/kg and an exergy efficiency of 29.99%. The SEC can be further reduced to 6 kWh/kg if adiabatic efficiencies exceed 85%. Catalyst-filled plate-fin heat exchangers (PFHX) are recommended for continuous OPC due to their ease of fabrication and catalyst loading compared to shell-and-tube or coil-wound designs. Simulation results indicate that heat exchanger sizing is primarily constrained by heat transfer limitations rather than reaction kinetics, assuming existing literature OPC data remains valid. The total pressure drop across the catalyst packings is less than 3 bar, with a negligible impact on overall system performance. Additionally, the study examines impurity removal strategies for methane, nitrogen, water, oxygen, carbon dioxide, argon, and helium from upstream green hydrogen electrolysis and estimates the adsorption capacity required. These findings provide valuable insights for optimizing large-scale hydrogen liquefaction systems.

Investigating air-nanobubbles stability in water using a classical thermodynamic model for dispersed nanophase

ORAL_09.2 - Modelling and Simulation

Ashish Verma[1], Himanshu Paliwal[2], Navin Gopinathan[1,*]

[1]*Indian Institute of Technology Ropar, India*
[2]*Reliance Industries Limited, Mumbai, India*

[*]*navin.gopinathan@iitrpr.ac.in*

An understanding of the theoretical fundamentals of nanophase stability is increasingly essential in order to facilitate the control and manipulation of their properties. Bulk nanobubbles serve as a prime example of dispersed nanophase and exhibit unique characteristics with significant potential for sustainable, clean, green, and yield enhancement applications. A chemical equilibrium thermodynamic framework is developed in this work to investigate nanophase stability[1]. This framework is utilized to evaluate Gibbs free energy as a function of size and effective surface tension (γ^{eff}) and estimate key thermodynamic properties, including pressure, temperature, and gas composition of nanobubble, for a typical air-water nanobubble system. Our findings highlight the critical role of the curved nano-interface in nanobubble stability. Results confirm that nanobubbles in water at normal saturation exhibit negative Gibbs free energy minimum for all nanobubble radii investigated, indicating thermodynamic stability[1]. An observed Gibbs energy minimum at a specific effective surface tension links to the spontaneous formation and long-term stability. Notably, gas molecules are confined at extreme pressures (~1100 atm) within the nanobubble, even when the bulk pressure remains at 1 atm, while maintaining high surface area and reactivity. We establish a thermodynamic and mathematical basis for strong interfacial interactions at the nanobubble surface, hypothesized to be primarily Coulombic in nature. However, the exact mechanism by which these interactions create strong molecular traps remains unknown, necessitating further investigation. The lack of experimental probes capable of measuring charge distributions on the Stern layer of a nanobubble, its internal pressure, temperature, and composition presents a significant challenge in validating the classical thermodynamic model. To address this issue, we employ molecular dynamics (MD) simulations as an alternative methodology, successfully obtaining a stable oxygen nanobubble in water, thereby reinforcing the classical thermodynamic framework. For the first time, considering all the interfacial interactions, this study reports nanobubble pressure and molecular composition inside nanobubbles, progressing the nanobubble research and emphasizing the necessity for experimental validation, refinement of thermodynamic modeling using the advanced equation of state and a deeper understanding of interfacial interaction existing at curved nano-interface.

Keywords: Gibbs energy minima, Bulk nanobubble, Curved nano-interface, Thermodynamic stability of nanophase, Chemical equilibrium

References

1. A. Verma, H. Paliwal, N. Gopinathan, *Ind. Eng. Chem. Res.* 2024, **63**, 18120-18133

The challenge of reliable property data in process modelling

ORAL_09.3 - Modelling and Simulation

José M. S. Fonseca[1,*], María Francisco Casal[2]

[1]AVEVA, R&D, Applications - Simulation & Learning,
920 Memorial City Way, Suite 1200 Houston, TX 77024, United States
[2]Lonza Biologics, Engineering and facilities, 36410 O Porriño, Pontevedra, Spain

[*]jose.fonseca@aveva.com

The importance of reliable physical property data in process modelling is widely recognized, both in process development and in process optimization. But the scale of the consequences of using wrong data is not always fully understood.
In this work we delve into some industrial examples to see just how significant the impact of wrong data in the results of a model can be, and how it can influence the design of a new chemical process.
We also discuss examples of bad data, some retrieved from respectful databases, and see how practical consistency tests can support spotting problematic data sets.
Finally, we touch on pure component data regression, and how the equation selection can influence the results of the simulation, especially in the case of extrapolations.

Acknowledgements
The authors would like to thank Ralf Dohrn for the inspiration and Seiya Hirohama for the fruitful discussions.

Advancing molecular force fields of organic molecules for molecular dynamics simulations from ab initio calculations, single crystal data, and sublimation enthalpies

ORAL_O9.4 - Modelling and Simulation

Carlos E. S. Bernardes*, Inês O. Feliciano, M. Fátima M. Piedade

Centro de Química Estrutural, Institute of Molecular Sciences, Departamento de Química e Bioquímica, Faculdade de Ciencias, Universidade de Lisboa, Lisboa 1749-016, Portugal

* *cebernardes@fc.ul.pt*

Molecular dynamics (MD) simulation is a powerful tool for investigating various problems related to solid materials, particularly pharmaceuticals. These include rationalizing the stability order of different crystal forms (polymorphs), probing solid-solid phase transitions under varying temperatures and pressures, examining crystallization from solutions, and assessing drug solubility. The accuracy of MD simulations depends heavily on the force fields (FF) employed, which consist of potential functions describing atomic interactions.[1] However, most existing models are primarily designed for studying liquids and solutions, prioritizing transferability across molecules. As a result, they often fail to accurately reproduce key properties of solid materials, such as lattice enthalpy (enthalpy of sublimation) and crystal unit cell parameters.[2]
In this work, we present an approach that integrates density functional theory (DFT), AI-based evolutionary algorithms, and experimental data to develop molecule-specific FFs—implemented in the EVOFF program (Figure 1). The accuracy of these models will be discussed against experimental data from single-crystal structures of organic compounds (in particular, co-crystals) and the corresponding enthalpies of sublimation, both determined in this work.

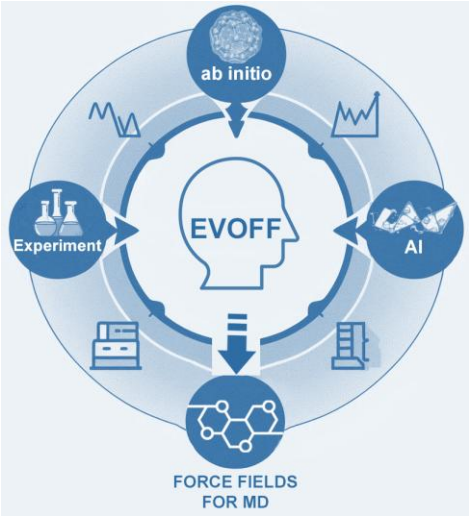


Figure 1: Schematic representation of the program EVOFF for the generation of molecular force fields.

Acknowledgments
We acknowledge the funding by Fundação para a Ciência e Tecnologia (FCT) through projects 2023.12474.PEX (https://doi.org/10.54499/2023.12474.PEX), UIDB/00100/2025 (https://doi.org/10.54499/UIDB/00100/2020) and UIDP/00100/2025 (https://doi.org/10.54499/UIDP/00100/2020), and LA/P/0056/2020. I. Feliciano gratefully acknowledge the FCT grant 2021.04637.BD.

References

1. C. E. S. Bernardes, *J. Chem. Inf. Model.* 2022, **62**, 1471-1478.
2. C. E. S. Bernardes and A. Joseph, *J. Phys. Chem. A* 2015, **119**, 3023-3034.

Fast and furious: Accelerating OpenCOSMO-RS with graph convolutional networks

ORAL_O9.5 - Modelling and Simulation

Dinis O. Abranches[1,*], Simon Müller[2], Irina Smirnova[2], João A. P. Coutinho[1]

[1] *CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193, Portugal*
[2] *Institute of Thermal Separation Processes, Hamburg University of Technology, Hamburg, 21073, Germany*

**jdinis@ua.pt*

The accurate characterization of phase equilibria in mixtures, solvents, and materials is crucial for the design of various unit operations in chemical engineering, including distillation, evaporation, crystallization, absorption, solubilization, and liquid-liquid extraction. Phase equilibria behaviour can be modelled and predicted using activity coefficients, which are closely related to excess chemical potentials and describe the thermodynamic non-ideality of liquid mixtures. These coefficients are governed by the differences in intermolecular interactions among mixture components and are a popular choice to describe vapor-liquid equilibrium, liquid-liquid equilibrium, and solid-liquid equilibrium. Other key applications of activity coefficients include adsorption, diffusion in multicomponent systems, chemical equilibrium constants, membrane transport, and life-cycle assessments (e.g., atmosphere and water partition coefficients of organic compounds).

Activity coefficients can be estimated with excess Gibbs energy models such as COSMO-RS,[1] or its open-source alternative openCOSMO-RS.[2] This statistical thermodynamic model relies on sigma profiles, which are quantum chemistry descriptors of molecules, to determine pair-wise interactions among mixture components. Although openCOSMO-RS can predict activity coefficients without the need for any experimental data, the generation of sigma profiles through computationally intensive quantum chemistry calculations, which can take several hours for a single compound, remains a major bottleneck of this approach.

The objective of this work is to leverage machine learning (ML) to significantly reduce the computational cost associated with openCOSMO-RS. To do so, a comprehensive database of sigma profiles, encompassing over 12,000 different molecules and 700 ions, was constructed using the software package ORCA. This database was used to train a graph convolutional network (GCN), with an initial architecture based on previous work[3] and further optimized here, that uses MMFF atom types as node-level features to boost accuracy and generalizability. This GCN attained coefficients of determination for sigma profiles and structural volumes over 0.96 and 0.99, respectively.

Using GCN predicted sigma profiles, the openCOSMO-RS model was reparametrized. This new version of openCOSMO-RS achieved a predictive performance comparable to that of quantum chemistry derived sigma profiles at a fraction of the cost. This allowed for the construction of a full software pipeline, enabling users to input the SMILES of mixture components and obtain their activity coefficients within milliseconds in a personal computer. Finally, several examples of phase equilibria modelling were explored as case studies.

Acknowledgements

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 (DOI 10.54499/UIDB/50011/2020), UIDP/50011/2020 (DOI 10.54499/UIDP/50011/2020) & LA/P/0006/2020 (DOI 10.54499/LA/P/0006/2020), financed by national funds through the FCT/MCTES (PIDDAC). DOA acknowledges the Universidade de Aveiro for the allocation of travel funds under the ECIU Mobility programme.

References

1. A. Klamt, V. Jonas, T. Bürger, and J. C. W. Lohrenz, *J. Phys. Chem. A* 1998, **102**, 5074-5085.
2. S. Müller, T. Nevolianis, M. Garcia-Ratés, C. Riplinger, K. Leonhard, and I. Smirnova, *Fluid Ph. Equilib.* 2025, **589**, 114250.
3. D. O. Abranches, E. J. Maginn, and Y. J. Colón, *J. Chem. Theory Comput.* 2023, **19**, 9318-9328.

Characterization of reactive working fluids by Monte Carlo simulations

Highlighted ORAL_09.6 - Modelling and Simulation

Julien Joliat[1,*], Silvia Lasala[1], Thijs J.H. Vlugt[2]

[1] *Université de Lorraine, CNRS, LRGP, F-54000 Nancy, France*
[2] *Engineering Thermodynamics, Process & Energy Department, Faculty of Mechanical, Maritime and Materials Engineering, Delft University of Technology, Leeghwaterstraat 39, Delft 2628CB, The Netherlands*

[*] *julien.joliat@univ-lorraine.fr*

The use of reactive fluids in thermodynamic cycles, typically Brayton and Rankine cycles, represents an unexploited and promising source of energy compared to traditional inert fluids, improving their efficiency.[1] These fluids use reversible chemical reactions that dynamically adapt their thermodynamic properties to temperature and pressure variations within the cycle. This behaviour allows the incorporation of chemical energy into thermodynamic transformations, with significant potential for improving the energy performance of systems. Preliminary theoretical studies indicate that these fluids could enhance cycle efficiency by more than 30% compared to conventional fluids such as water, ammonia, helium or carbon dioxide.[1] However, their absence in industry is due to the limited availability of sufficiently rapid and stable reversible reactions for practical applications.

The ERC REACHER project[2] aims to theorize and characterize new reactive fluids, such as those based on the chemical equilibrium of the type $A_2 \rightleftharpoons 2A$. These fluids, often novel in the literature, require theoretical approaches to predict their properties in the absence of experimental data. Thus, a multiscale methodology has been established, combining quantum chemistry calculations, predictions of thermodynamic properties based on Machine Learning methods, Monte Carlo simulations based on Lennard-Jones force fields, and numerical resolutions of predictive equations of state.

This methodology has been validated on well-known systems in the literature, such as the $N_2O_4 \rightleftharpoons 2NO_2$ reaction, where it demonstrated a remarkable ability to predict critical properties, phase equilibrium and system kinetics.[3] Monte Carlo simulations in the Gibbs ensemble (GEMC) and the isobaric-isothermal ensemble (NPT) have been used to determine the properties of monomers and dimers, while the reactive ensemble (REMC) has been used to accurately characterize the reaction equilibrium. This work shows that the thermodynamic properties of reactive fluids, including their critical properties and reaction characteristics, can be reliably characterized at the molecular scale.

The presentation will discuss the preliminary results obtained within the REACHER project, focusing on the $N_2O_4 \rightleftharpoons 2NO_2$ system and other conceptualized fluids. It will also highlight the importance of multiscale approaches in the design and evaluation of these fluids, paving the way for their future adoption in industry.

Acknowledgments
This work has received funding from the European Research Council (ERC) under the European Union's Horizon Europe research and innovation program (grant agreement No. 101040994). Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or European Research Council. Neither the European Union nor the granting authority can be held responsible for them.

References

1. S. Lasala, R. Privat, O. Herbinet, P. Arpentinier, D. Bonalumi and J.-N. Jaubert, *Energy Conversion and Management* 2021, **229**, 113685.
2. S. Lasala, *Project Repository Journal* 2022, **13**, 102-105.
3. S. Lasala, K. Samukov, H. Mert Polat, V. Lachet, O. Herbinet, R. Privat, J.-N. Jaubert, O. A. Moultos, K. De Ras and T. J. H. Vlugt, *Chemical Engineering Journal* 2024, **483**, 148961.

Polarization-consistent force fields to predict solvation and dielectric properties of mixtures

ORAL_09.7 - Modelling and Simulation

Zoe McPherson[1], Maria Cecilia Barrera[1], Leo Lue[1], José R. B. Gomes[2], Miguel Jorge[5,*]

[1]*Department of Chemical and Process Engineering, University of Strathclyde, 75 Montrose Street, Glasgow G1 1XJ, United Kingdom*
[2] *CICECO - Aveiro Institute of Materials, University of Aveiro, Aveiro, Portugal*

[*]*Miguel.jorge@strath.ac.uk*

Classical non-polarizable models, normally based on simple Lennard-Jones (LJ) sites and point charges, are extensively used to model thermodynamic properties of pure fluids, solutions and mixtures. An important shortcoming of this class of models is the lack of explicit polarization effects - i.e. a description of how the electron density responds to changes in the molecular environment. Instead, polarization is implicitly included, in a mean-field sense, into the parameters of the model, usually by fitting to pure liquid properties (e.g. density). Problems arise when trying to describe thermodynamic properties that involve a change of phase (e.g. enthalpy of vaporization), solutions/mixtures (e.g. solvation free energies), or that directly depend on the electronic response of the medium (e.g. dielectric constant). In this work, we demonstrate a new approach based on applying *post facto* corrections to properties computed by non-polarizable models in order to account for the effects of polarization.[1,2] This idea allows us to systematically improve prediction accuracy while maintaining computational efficiency. Our main aim is to obtain a force field that is able to predict properties of both pure liquids and solutions/mixtures with a high degree of accuracy. We have applied our new Polarization-Consistent Approach (PolCA) to develop new atomistic models for alkanes, alcohols and ketones[3,4], and are currently extending it to other classes of molecules. In comparison with state-of-the-art non-polarizable models, PolCA not only yields better predictions of pure liquid properties (e.g. density, self-diffusion, enthalpy of vaporization), but also leads to much more accurate predictions of solvation free energies in heterogeneous systems, for example, when polar molecules are solvated in non-polar solvents like alkanes (Figure 1). This significantly improves the transferability of the model with practically negligible computational overhead. We also demonstrate that our approach is able to dramatically improve predictions of the dielectric constant, both for pure fluids and for mixtures[5,6]. These improvements arise from a theoretically grounded consideration of the realistic effects of polarization in the liquid state, which relies on an accurate estimation of the molecular dipole moment in the liquid state. In this context, we also describe the recently developed Self-Consistent Electrostatic Embedding method that is able to predict realistic liquid phase dipole moments with a reasonable computational cost[7,8]. Overall, the PolCA framework and associated toolkit paves the way for a paradigm change in force field development.

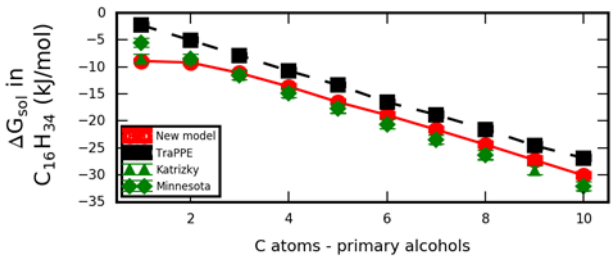


Figure 1: The PolCA model shows improved predictions for the solvation of alcohols in alkane solvents.

References

1. M. Jorge, *J. Chem. Phys.* 2024, **161**, 180901.
2. M. Jorge, M. C. Barrera, A. W. Milne, C. Ringrose, D. J. Cole, *J. Chem. Theory Comput.* 2023, **19**, 1790-1804.
3. M. C. Barrera, M. Jorge, *J. Chem. Inf. Model.* 2020, **60**, 1352.
4. M. C. Barrera, J. Cree, J. R. B. Gomes, M. Jorge, *J. Mol. Liq.* 2023, **383**, 122070.
5. M. Jorge, L. Lue, *J. Chem. Phys.* 2019, **150**, 084108.
6. J. Cardona, M. Jorge, L. Lue, *Phys. Chem. Chem. Phys.* 2020, **22**, 21741-21749.
7. M. Jorge, J. R. B. Gomes, A. W. Milne, *J. Mol. Liq.* 2021, **322**, 114550.
8. M. Jorge, J. R. B. Gomes, M. C. Barrera, *J. Mol. Liq.* 2022, **356**, 119033.

Molecular analyses of mass transport phenomena in polymer electrolyte fuel cell

ORAL_09.8 - Modelling and Simulation

T. Tokumasu[1,*]

[1]*Institute of Fluid Science, Tohoku University*

[*]*tokumasu@ifs.tohoku.ac.jp*

Polymer Electrolyte Fuel Cells (PEFC) are expected to be as one of next-generation power supply systems due to its low environmental damage, high efficiency, and availability for dispersed power systems and emergency use. Transport resistance of reactant and product materials such as proton, oxygen and water is the determining factor of their efficiency and therefore it is necessary to analyze the transport phenomena of proton, oxygen and water in PEFC as fast as possible to increase their performance and efficiency. A Membrane Electrode Assembly (MEA) of PEFC, however, consists of Gas Diffusion Layers (GDL), Micro Porous Layers (MPL), Catalyst Layers (CL), and a Polymer Electrolyte Membrane (PEM), where many nanoscale structures are constructed. In such flow fields, the characteristics of transport phenomena in MEA cannot be analyzed at the macroscopic point of view. Molecular simulation is a powerful tool to analyze these phenomena. In this study these nanoscale transport phenomena are analyzed by large scale Molecular Dynamics (MD) simulations[1,2] and the relation between the nanoscale structures and the transport phenomena is analyzed in detail. Especially, the transport phenomena of proton in PEM which has highly anisotropic water structures, oxygen permeability, oxygen scattering and proton diffusivity of ionomer in CL were simulated.

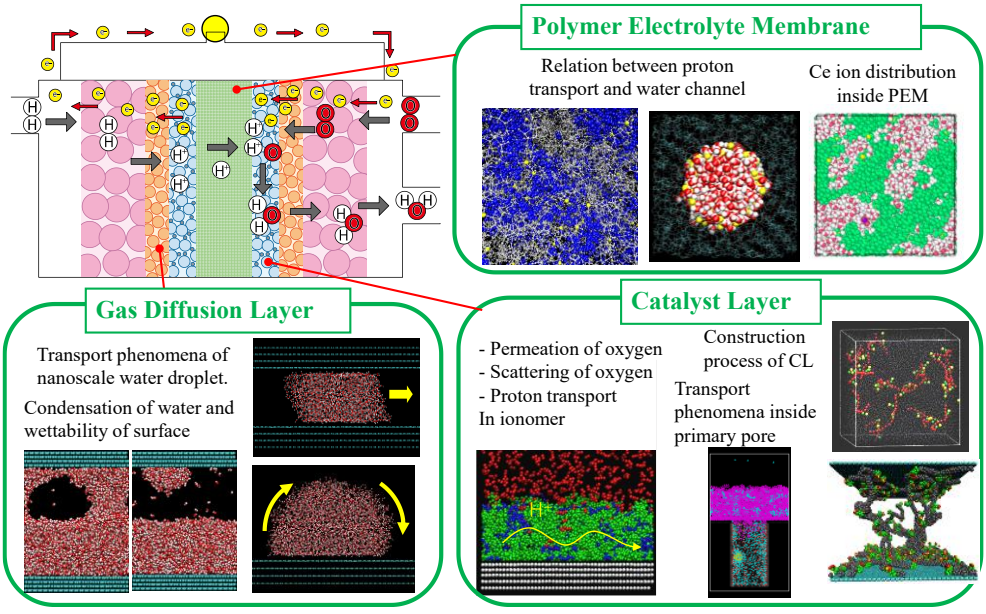


Figure 1: Large-scale molecular dynamics simulations of transport and structure characteristics of polymer electrolyte fuel cell.

Acknowledgments

The authors would like to thank the New Energy and Industrial Technology Development Organization (NEDO) of Japan (NPJP20003) for their financial support, and the calculations in this study were performed using the supercomputer, AFI-NITY, at the Institute of Fluid Science, Tohoku University. We would like to express our deep gratitude to all the parties involved.

References

1. Y. Kurihara, T. Mabuchi, and T. Tokumasu, *J. Electrochem. Soc.* 2017, **164**, F638.
2. Y. Kurihara, T. Mabuchi, and T. Tokumasu, *J. Power Sources* 2019, **414**, 268.

Unraveling the role of mixing entropy in equilibrated nano-confined reactions by statistical-thermodynamics modelling

ORAL_09.9 - Modelling and Simulation

Micha Polak[1,*], Leonid Rubinovich[1]

[1]*Department of Chemistry, Ben-Gurion University of the Negev, Beer-Sheva 8410500, Israel*

**mpolak@bgu.ac.il*

Given the limited current understanding of the mixing-entropy impact on equilibrium states of nano-confined reactions, the issue is addressed by incorporating statistical-mechanical averaging over fluctuating reaction extents. Thus, based on the canonical partition function, the interplay between mixing entropy and the fluctuations is unraveled while maintaining consistency with macroscopic behavior. Modeling the nano-system size dependence of the mixing entropy, the reaction extent, and a concept termed "reaction extent entropy" will be introduced for the combination reactions $A + B \leftrightarrow 2C$ and the specific case of $H_2 + I_2 \leftrightarrow 2HI$. A distinct inverse correlation is found between the first two properties, revealing consistency with the nanoconfinement entropic effect on chemical equilibrium (NCECE[1,2]). To acquire the time dependence of the instantaneous mixing entropy and extent following equilibration, the Stochastic Simulation (Gillespie) Algorithm is employed. In particular, the smallest nano-systems exhibit a step-like behavior associated with the discrete probability distribution of the reaction extent. It deviates significantly from the smooth mean values and may affect certain experimental measurements. As illustrated further for molecular adsorption and spin polarization, the newly introduced approach can be extended beyond nano-reactions to other confined systems consisting of small numbers of species.

References

1. M. Polak and L. Rubinovich, *Nano Letters* 2008, **8**, 3543.
2. L. Rubinovich and M. Polak, *Nano Letters* 2013, **13**, 2247.

Optimizing QM workflows for drug solubility prediction: The impact of conformer generation methods

ORAL_O9.10 - Modelling and Simulation

André M. M. Gomes[1,2,*], Paulo J. Costa[1], José F. O. Granjo[2]

[1] *BioISI - Instituto de Biosistemas e Ciências Integrativas and Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa*
[2]*Hovione R&D, Hovione FarmaCiência, Estrada do Paço do Lumiar, 1649-038 Lisbon, Portugal*

[*]*amgomes@ciencias.ulisboa.pt*

The pharmaceutical industry is evolving rapidly, driven by the need for efficiency, cost reduction, and faster drug development. A major challenge in early drug formulation is predicting key physicochemical properties such as solubility and stability. Quantum mechanics (QM)-based computational methods provide valuable molecular insights, reducing reliance on costly experimental testing. Despite these advantages, QM adoption in the pharmaceutical industry remains limited due to expertise requirements, computational cost, and the need for accurate molecular conformations. Poorly chosen conformers can impact solubility predictions, affecting drug development reliability. Ensuring relevant conformers is essential for maximizing predictive accuracy.[1]

To address this, we evaluated how different conformer generation approaches influence QM-based solubility and Gibbs solvation free energy (ΔG_{solv}) predictions. We compared multiple strategies to balance accuracy and computational cost while automating workflows for efficiency. By integrating these approaches, we streamlined QM calculations, minimizing manual intervention and bridging the gap between computational tools and industry applications. We compiled a dataset of 130 commercially available molecules with experimentally determined solubility across 25 solvents. A subset also included experimental ΔG_{solv} data. To assess QM-based calculations and the impact of conformer generation, we developed automated workflows incorporating four distinct approaches: (1) RDKit conformer generation with Merck molecular force field (MMFF) optimization; (2) RDKit + MMFF followed by DFT/BP86/def2-TZVPD optimization; (3) a basin-hopping-inspired method with GFN2-xTB[2] and DFT optimization; and (4) a COSMO-RS conformer generation workflow featuring three consecutive optimization steps. Each workflow used the SMILES code as input to determine the lowest energy conformation. The lowest energy conformers underwent Single Point calculations (DFT/BP86/def2-TZVPD) to extract molecular features for thermodynamic predictions, including solubility via COSMO-RS. The sigma profile was directly extracted from QM calculations to compute activity coefficients and compare predicted solubility with experimental data.[3,4]

Our preliminary results demonstrate promising solubility prediction performance with comparable accuracy across workflows. Notably, simpler methods like RDKit-based workflow (1) achieved similar accuracy while offering significant computational efficiency. This suggests that, despite initial conformations being a source of error, fast and accessible methods can provide reliable predictions.

Overall, this QM-based automated approach offers a robust framework for predicting key molecular properties, refining predictive models, and accelerating drug discovery, particularly when experimental data is limited. These workflows hold potential for broader applications in predicting thermodynamic and molecular properties using QM calculations, and optimizing pharmaceutical industry processes.

Acknowledgments
The authors thank Fundação para a Ciência e a Tecnologia (FCT), Portugal, for grant 024.05026.BDANA (AMMG), and projects UIDB/04046/2020-UIDB/04046/2020 (DOI: 10.54499/UIDB/04046/2020 and 10.54499/UIDP/04046/2020) to BioISI.

References

1. Wang et al., *J. Phys. Chem. A* 2005, **109**, 11285-11294.
2. Bannwarth et al., *WIREs Comput. Mol. Sci.* 2021, **11**, e1493.
3. E. A. Müller, D. B. Espinoza and F. J. Blas, *Fluid Phase Equilib.* 2025, **589**, 114250.
4. I. Udvarhelyi, G. Jójárt and G. Ferenczy, *J. Comput.-Aided Mol. Des.* 2021, **35**, 399-415.

Phonon-boundary scattering and boundary conditions: Application to the heat transfer in thin nanowires

Highlighted ORAL_HO9.11 - Modelling and Simulation

A. Sellitto

Department of Industrial Engineering, University of Salerno, Italy

asellitto@unisa.it

At the nanoscale, several conceptual questions still remain unanswered; some of them are sometimes fervently debated. It is, however, currently well-known that in nanosystems, the phonons always undergo different scattering mechanisms during heat propagation. The particular regime of heat transfer, instead, strictly depends on the ratio between the phonon mean free path and the characteristic size of the system, i.e., the so-called Knudsen number.

Among the aforementioned open questions, the role played by the phonon-boundary scattering, for different values of the Knudsen number, in particular is an interesting research playground.[1]

In this talk, therefore, an enhanced model of boundary conditions will be proposed in order to suitably address the problem of correct tackling of the phonon-boundary scattering when a heat flux is flowing in a thin nanowire.

References

1. I. Bochicchio, A. Sellitto, C. F. Munafò, *Journal of Thermal Stresses* 2025, DOI: 10.1080/01495739.2025.2458724

Molecular design, thermochemical and kinetics characterization of reactive working fluids

ORAL_O9.12 - Modelling and Simulation

Rachid Hadjadj[1,*], Julien Joliat[1], Sérgio Vilas-Boas[1], Olivier Herbinet[1], Silvia Lasala[1]

[1] *Université de Lorraine, CNRS, LRGP, F-54000 Nancy, France*

**rachid.hadjadj@univ-lorraine.fr*

Developing performant and sustainable energy conversion technologies, such as performant thermal power plants for waste heat recovery and industrial heat pumps, is crucial to face the increasing energy demands and environmental concerns. One of the promising approaches to improve the efficiency of these systems is to act on the working fluid of the thermodynamic cycles underlying their operation. Current technologies rely on pure fluids and inert mixtures. In the research project REACHER[1], we are investigating the impact of using reactive working fluids[2,3], instead of inert ones. More specifically, these fluids undergo reversible and fast dimerization chemical reactions ($A_2 \rightleftarrows 2A$) along the thermodynamic transformations occurring in thermodynamic cycles.

In this work, an innovative approach is proposed to design, characterize, rank and preliminary select these reactive fluids as working fluids for thermodynamic cycles. To achieve this goal, a Fortran script has been developed to generate all possible monomer/dimer molecules ($2A/A_2$) from a preselected set of 9 atoms (C, N, O, P, S, B, F, Cl, Br).

Overall, 263 reactions have been generated (i.e., 263 couples of dimers A_2 / monomers A). The thermochemical properties, the kinetics and the molecular stability of these reactions have then been characterized by Quantum Chemistry calculations, using the CBS-QB3 method[4] as implemented in the Gaussian 09 program package. After this characterization step, 106 dimers appeared to be stable; the further kinetic analysis showed that only 70 reactions, over these 106 stable systems, can be considered as being reversible and sufficiently for adequate for the applications of our interest. Figure 1 shows a map presenting the 106 designed reactions, according to their calculated enthalpy and entropy of reactions, and the 70 fast and reversible ones. The theoretical results have been validated and have been judged to be satisfactory. This work will introduce this reaction design and characterization methodology.

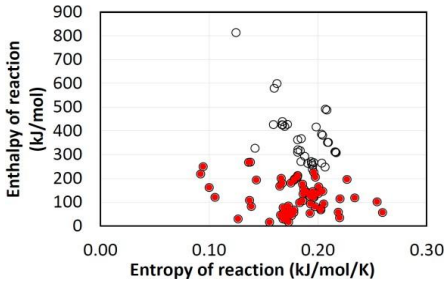


Figure 1: Enthalpy and entropy map of the designed chemical reactions (○: 106 stable reactive fluids; ● 70 stable and fast reversible reactions).

Acknowledgments
This work has received funding from the European Research Council (ERC) under the European Union's Horizon Europe research and innovation program (grant agreement No. 101040994).

References

1. REACHER Project, https://www.univ-lorraine.fr/erc-reacher/.
2. S. Lasala, R. Privat, O. Herbinet, P. Arpentinier, D. Bonalumi, and J.-N. Jaubert, *Energy Convers. Manag.* 2021, **229**, 113685.
3. A. Barakat, S. Lasala, P. Arpentinier, and J.-N. Jaubert, *Chem. Eng. J. Adv.* 2022, **12**, 100400.
4. J. A. Montgomery Jr., M. J. Frisch, J. W. Ochterski, and G. A. Petersson, *J. Chem. Phys.* 2000, **112**, 6532-6542.

Strain-induced morphological transitions in amphiphilic polymer conetwork bulk melts: A computational thermodynamic study

ORAL_09.13 - Modelling and Simulation

Konstantinos Andronikou[1], Costas S. Patrickios[1,*]

[1]*Department of Chemistry, University of Cyprus, 1 University Avenue, 2109 Aglanjia, Nicosia, Cyprus*

[*]*costasp@ucy.ac.cy*

Herein we present a computational thermodynamic study showing that externally-imposed tensile and compressive deformations can impart morphological phase transitions on amphiphilic polymer conetwork (APCN) bulk melts.[1,2] We observe primarily that APCN extension favors the formation of // transformation into normal lamellae, whereas APCN compression leads to the formation of, initially, parallel lamellae and, subsequently, normal cylinders. These changes are due to the fact that the interfacial area is reduced when a normal lamella is extended and when a parallel lamella or a normal cylinder are compressed. The extension result is consistent with a recent dissipative particle dynamics (DPD) simulations study which indicated that APCNs of all compositions were transformed to normal lamellae when sufficiently extended.[3] The presently-obtained morphology phase diagram with axes the deformation ratio and polymer composition shows that normal lamellae dominate for all polymer compositions provided that the deformation ratio is higher than 1 – 2. It also shows that normal cylinders dominate for all polymer compositions when the deformation ratio is between 0.1 and 1.0. The results of this work would be useful for exploring new APCN applications in technology (gel or solid polymer electrolytes in lithium ion batteries) and biomedicine (drug delivery and tissue engineering).

References

1. *Amphiphilic Polymer Co-Networks: Synthesis, Properties, Modelling and Applications*, ed. C. S. Patrickios, Royal Society of Chemistry, Cambridge, UK, 2020.
2. C. S. Patrickios and K. Matyjaszewski, *Polym. Int.* 2021, **70**, 10-13.
3. D. G. Tsalikis, M. Ciobanu, C. S. Patrickios, Y. Higuchi, *Macromolecules* 2023, **56**, 9299-9311.

Thermochemistry analysis of solid-electrolyte interfaces using neural network forcefields

ORAL_O9.14 - Modelling and Simulation

Martín Otero-Lema[1,2,*], Hadrián Montes-Campos[1,2], Trinidad Méndez-Morales[1,2], Luis M. Varela[1,2]

[1]*Grupo de Nanomaterias, Fotónica e Materia Branda, departamento de Física de Partículas, Universidade de Santiago de Compostela, Santiago de Compostela, Spain*
[2]*Instituto de Materiais (iMATUS), Universidade de Santiago de Compostela, Santiago de Compostela, Spain*
[*]*martin.oterolema@usc.es*

The solid-electrolyte interface (SEI) is a protective coating that naturally forms between the electrolyte and the electrode in metal-ion batteries during the first charge-discharge cycles.[1] This complex layer allows for ion transport, while acting as a barrier between the electrolyte and the electrode, thus preventing the further decomposition of the former. Therefore, the composition and thermochemical properties of the SEI, both its inner crystalline regions and its outer organic domains is of crucial importance for the development of safe and high performing electrochemical devices.

In this contribution we focus on the outer layers of the SEI, thought to be organic in nature and formed by the products of redox reactions that take place near the electrode during the first charge-discharge cycles. Using molecular dynamics simulations in combination with a neural network forcefield, we study the different chemical reactions that take place in a model SEI composed of carbonate ions, neutral carbonate molecules and different metallic ions (lithium, sodium and potassium). We observe decomposition reactions that drive the systems towards equilibrium compositions, which can vary depending on the nature of the metal cation. We find that the presence of lithium enables recombination reactions that do not take place in the presence of the other metals, leading to the formation of more complex molecules.

Acknowledgments
This work was funded by the Xunta de Galicia (GRC ED431C 2024/06). M. O. L. thanks the Xunta de Galicia for his Axudas de apoio á etapa predoutoral" grant (ED481A 2022/236). This work was done within the framework of project HI_MOV – "Corredor Tecnológico Transfronterizo de Movilidad con Hidrógeno Renovable", with reference 0160_HI_MOV_1_E, co-financed by the European Regional Development fund (ERDF), in the scope of Interreg VI A Spain – Portugal Cooperation Program (POCTEP) 2021-2027. This publication and the contract of T. M. M. are part of the grant RYC2022-036679-I, funded by MCIN/AEI/10.13039/501100011033 and FSE+. This work is part of the project CNS2023-144785, funded by MICIU/AEI /10.13039/501100011033 and the European Union "NextGenerationEU"/PRTR.

References

1. B. Li, Y. Chao, M. Li, Y. Xiao, R. Li, K. Yang, et. al. & J. Zhang, *Electrochemical Energy Reviews* 2023, **6**, 7.

Water dissociation and proton transport in ionic liquids

ORAL_09.15 - Modelling and Simulation

Luis M. Varela[1,2,*] Alejandro Rivera-Pousa[1,2], Martín Otero-Lema[1,2], Raúl Lois-Cuns[1,2], Pablo Martínez-Crespo[1,2], Hadrián Montes-Campos[1,2], Trinidad Méndez-Morales[1,2]

[1]Grupo de Nanomateriales, Fotónica y Materia Branda, Departamento de Física de Partículas. Universidade de Santiago de Compostela, Santiago de Compostela, Spain.
[2]Instituto de Materiais (iMATUS), Universidade de Santiago de Compostela, Santiago de Compostela, Spain

[*]luismiguel.varela@usc.es

We present a combined density functional theory (DFT) and classical molecular dynamics (MD) study to explore the molecular mechanisms governing hydrogen solvation in various ionic liquids. Structural analyses of bulk systems[1] reveal that, under high temperature and pressure conditions, hydrogen interacts weakly with the ionic liquid components, showing a slight preference for localization in apolar domains. Additionally, we investigate the gas uptake mechanism of hydrogen molecules nanoconfined within carbon nanotubes filled with ionic liquids, focusing on their impact on gas capture efficiency and spatial distribution within the nanotubes. These results are compared with those obtained for nitrogen. Our findings[2] indicate that nitrogen generally exhibits a higher absorption capacity than hydrogen. Aprotic ionic liquids demonstrate superior gas confinement performance, as hydrogen storage primarily depends on the availability of free volume, whereas nitrogen solvation is also influenced by energetic contributions. Finally, we report on simulations of water dissociation and proton transport in the studied mixtures together with a theoretical model of the thermodynamics of the process.

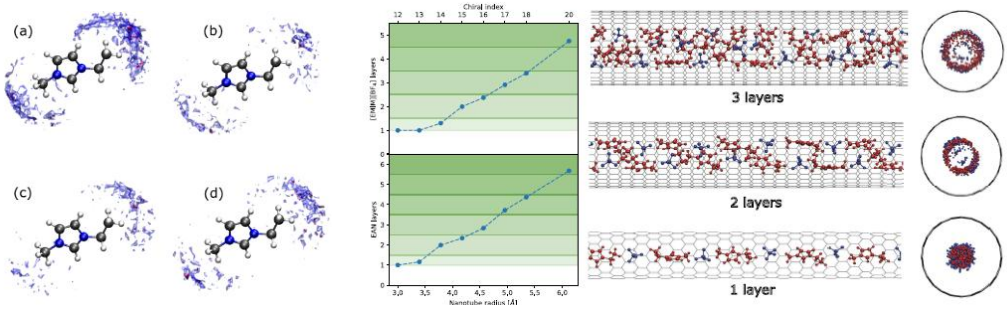


Fig.1 Left. Spatial distribution functions of H2 molecules around IL cations for different anion choices: (a) [NO3] , (b) [BF4] , (c)[B(CN)4] , and (d) [TFSI]– (Ref. 1). Number of ionic layers formed under confinement by [EMIM][BF4] (top) and EAN (bottom) as a function of the CNTs internal radii and their chiral index (Ref. 2).

Acknowledgements
The financial support of the Spanish Ministry of Science and Innovation (PID2021-126148NA-I00 funded by MICIU/AEI/10.13039/501100011033/FEDER, UE) is gratefully acknowledged. Moreover, this work was funded by the Xunta de Galicia (GRC ED431C 2024/06) and by Interreg PCTEP 0160_HI_MOV_1_E. A. R. P. thanks the Spanish Ministry of Education for his FPU18/01597 grant. M.O.L. and P.M.C. thank the Xunta de Galicia for his ``Axuda de apoio á etapa predoutoral" grant (ED481A 2022/236). This work and the contract of T. M. M. are part of the grant RYC2022-036679-I, funded by MICIU/AEI/10.13039/501100011033 and FSE+. This work is part of the project CNS2023-144785, funded by MAETD and the European Union "NextGenerationEU"/PRTR. R.L.C. acknowledges his Predoctoral Contract under the framework of the project PID2021-126148NA-I00 funded by MICIU/AEI/10.13039/501100011033/FEDER, UE.

References

1. A.Rivera-Pousa, R. Lois-Cuns, M. Otero-Lema, H. Montes-Campos, T. Méndez-Morales, and L. M. Varela, *J. Chem. Inf. Mod.* 2023, **64**,164-177.
2. M. Otero-Lema, R. Lois-Cuns, P. Martínez-Crespo, A. Rivera-Pousa, H. Montes-Campos, T. Méndez-Morales, L. M. Varela, *J Mol. Liq.* 2024, **405**, 124909.

Development of a differential scanning calorimeter equipped with a shearing system

Highlighted ORAL_HO10.1 - Instrumentation and Methods

Taro Yamamoto, Yuki Nagae, Hal Suzuki*

Department of Chemistry, Kindai University, Higashiosaka, Osaka 577-8502, Japan

** h_suzuki@chem.kindai.ac.jp*

The viscoelastic properties of liquid crystals and colloidal systems are known to change under shear stress, which can be explained by alterations in mesoscale molecular aggregation. Such changes sometimes induce phase transitions, known as shear-induced transitions (SIT), and the mechanism behind these transitions has attracted significant attention.

In this study, to explore the mechanism of SIT from a thermodynamic perspective, we developed a differential scanning calorimeter equipped with a shearing system (Shear-DSC) (Figure 1 (a)). Using this system, we investigated the thermotropic liquid crystal 4'-*n*-octyl-4-cyano-biphenyl (8CB).[1] The intrinsic heat flow curves associated with the transitions were successfully obtained by subtracting the contribution of shear heating, which was evaluated separately through viscosity measurements (Figure 1 (b) and (c)). Under shear, the smectic-to-nematic transition peak was found to broaden, and its transition temperature slightly decreased with increasing shear rate (Fig. 1 (d)). In contrast, the nematic-to-isotropic liquid transition remained unaffected by shear.

We also examined the transition from crystal to the rod-like micellar phase in an aqueous cetyltrimethylammonium bromide (CTAB) surfactant solution.[2] The transition was found to be influenced by the shear rate, which was attributed to the orientational ordering of micelles as well as the fracturing of crystallites. In both systems, the changes in transition entropy were found to be small.

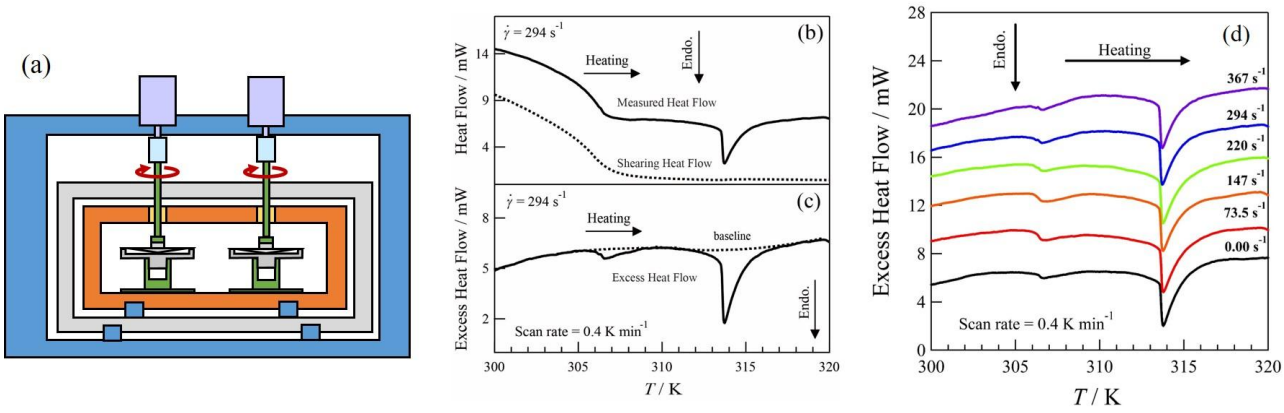


Figure 1: (a) Schematic of Shear-DSC. (b), (c), and (d) Results of Shear-DSC measurement for 8CB

References

1. T. Yamamoto, Y. Nagae, T. Wakabayashi, T. Kamiyama, H. Suzuki, *Soft Matter* 2023, **19**, 1492-1498.
2. T. Yamamoto, T. Wakabayashi, T. Kamiyama, H. Suzuki, *Thermochim. Acta* 2023, **730**, 179629.

Chemical thermodynamics as data-driven science/technology

ORAL_O10.2 - Instrumentation and Methods

Kazuya Saito*

Research Center for Thermal and Entropic Science, Graduate School of Science, Osaka University

Center For Computational Sciences, University of Tsukuba

**kazuya@chem.tsukuba.ac.jp*

It is well known that thermodynamics matured during the Industrial Revolution. The significant ingredient of thermodynamics at that time was the establishment of the independence of the ultimate efficiency of engines from working materials. However, it also implied precise relations among thermodynamic quantities of different materials, which is the essential basis of chemical thermodynamics. This aspect was pursued mainly in the petroleum industry, resulting in extensive efforts to measure, collect, and evaluate thermodynamic quantities of many compounds. In this regard, chemical thermodynamics is one of the first fields of data-driven science/technology. Enormous computational difficulty suffered in the initial period has now been resolved by the remarkable progress in computational power. Thus, computers can change thermodynamics from "should work" (in other words, "should be useful") to "practically useful" if we have reliable data. The need for significant data closely resembles the growing AI-based technology. Upon such a moment, it seems valuable to clarify how chemical thermodynamics is different from and similar to data-driven science/technology based on machine learning (ML). This contribution intends to trigger such consideration in the community.

Although both chemical thermodynamics and ML-based technology require large data sets, there is an essential difference between them. In the latter, analyses generally attempt to find not a (hidden yet true) relationship but a correlation among parameters, which may be specified artificially or distilled by an analysis method itself. Such a correlation is sufficient and incredibly useful for application purposes. Moreover, this property stems from the incompleteness of the input data, such as imprecise data and noise, and the unawareness of the users about the parameters that correctly control the phenomenon. On the other hand, chemical thermodynamics a priori knows the precise theory, thermodynamics, that any correct thermodynamic quantities should fulfill through the relation among state functions. Even a data point outside the experimental inaccuracy implies thermodynamic inconsistencies within the considered thermodynamic network. In this regard, chemical thermodynamics is at a different stage. In fact, however, any experimental quantities are incomplete and suffer from inaccuracies. Here, data analysis shows a resemblance between chemical thermodynamics and ML-based technology.

Thermodynamics requests data from the outside by its abstract nature. In this respect, the experimental input is crucial for chemical thermodynamics (using computational input such as the first-principles ones needs other considerations). On the other hand, the number of laboratories specializing in experimental thermodynamics has been decreasing worldwide in recent years. This is undoubtedly because achievements in experimental thermodynamics look old-fashioned and descriptive. These characteristics are scarcely appealing not only to funding agencies but also to young generations. To proceed with healthy progress, a collaboration between experimentalists and database creators/maintainers can play a significant role. Periodic, such as annual, announcements of target data from the database side with a somewhat detailed background (probably for data scientific merits) can accelerate the growth of the thermodynamic data network to maximize its practical utility. The supplied background facilitates the preparation of papers and funding applications by experimentalists. Significantly, such activity changes the role of the database creator/maintainer from a mere collector/evaluator of thermodynamic data to an active contributor to experimental thermodynamics.

Acoustic resonator for sound speed measurements in light gases at high pressures

ORAL_O10.3 - Instrumentation and Methods

Lu Ai[1], J. P. Martin Trusler[1,*]

[1]*Department of Chemical Engineering, Imperial College London, London SW7 2AZ, UK*

[*]*m.trusler@imperial.ac.uk*

Speed of sound measurements are highly valuable in the development of equations of state for both pure fluids and mixtures. Acoustic resonators are generally regarded as the best means of making such measurements in gases at low or moderate densities, while pulse-echo methods are more appropriate for liquids. The two techniques overlap somewhat for dense gases; resonators being limited as density increases by increasing coupling between gas and shell vibrations, and pulse-echo devices being limited at decreasing densities by poor pulse transmission.

Hydrogen and mixtures of hydrogen with inert gases are of increasing interest, as hydrogen is set to play an expanding role in the energy transition and the mixtures may be used as refrigerants in hydrogen liquefaction. New experimental data would be very useful to help improve equations of state for these systems. The technical interest in hydrogen extends to pressures of at least 70 MPa and hydrogen has the highest sound speed of any gas. Measuring the speed of sound in pure hydrogen or in hydrogen-helium mixtures present special challenges. Recently, some useful results were obtained for hydrogen using a combination of an acoustic resonator for pressures up to 10 MPa and a dual-path pulse-echo apparatus for pressures from 20 MPa to 100 MPa.[1] Overlap between the two techniques was not achieved and the objective of the current work is to optimize an acoustic resonator to achieve this.

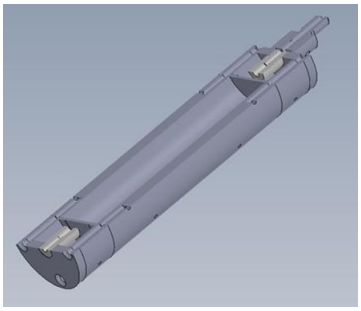


Figure 1: Cut-away visualization of the cylindrical resonator.

A new cylindrical resonator, as illustrated in Fig. 1, will be described. The shell of this resonator was fabricated from a beryllium-aluminum alloy which exhibits an exceptionally-high longitudinal sound speed, placing resonances frequencies of the shell well above the gas resonances of interest. The mounting of the resonator was designed to minimize damping of shell vibrations and a model for shell motion was developed. This model allows for flexing of the resonator end plates and stretching vibrations of the whole cylinder, both associated with damping coefficients. Helium was used for purposes of calibration and validation. The calibration step determined the acoustic pathlength, the compliance of the end plates and the damping coefficients for both end-plate vibration and the shell stretching mode. Measurements on pure hydrogen showed good agreement with previous work at pressures up to 30 MPa. The apparatus is designed for operation in the temperature range from 200 K to 370 K at pressures potentially up to 100 MPa.

References

1. T.-T.-G. Nguyen, C Wedler, S. Pohl, D. Penn, R Span, J. P. M. Trusler, M. Thol, *J. Chem. Thermodyn.* 2024, **198**, 107341.

Advancing two-phase isothermal calorimetry: ITC for metal extraction with eutectic solvents

ORAL_O10.4 - Instrumentation and Methods

Inês C. M. Vaz[1*], Nicolas Schaeffer[1], Margarida Bastos[2], Luís M. N. B. F. Santos[2] and João A. P. Coutinho[1]

[1] *CICECO, Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Portugal*
[2] *CIQUP, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Portugal*

**ines.vaz@ua.pt*

The growing demand for metals in modern lifestyles and low-carbon technologies requires the development of more efficient and sustainable extraction methods. Solvent extraction (SX) is widely used for metal recovery through selective ion partitioning between immiscible phases. The enthalpy of extraction, which quantifies the energetic balance between these partitions, is often the focus of attention in attempts to enhance separation efficiency[1]. Even in scenarios where enthalpy of extraction is not the primary driving force, the accurate determination of this property is crucial for correctly determining the entropic contribution to the metal partitioning at different temperatures.

Calorimetric techniques are the techniques to measure heat. Early studies employed isoperibol calorimeters, but required complex methodologies with multiple experimental steps[2]. In 1982, a pioneering approach enabled direct two-phase measurements[3], which subsequently evolved into the actual methodologies employed with isothermal titration calorimetry (ITC)[1,4]. These approaches were nevertheless developed to study enthalpy of extraction of a metal from an aqueous phase to an organic phase being constituted by a neat extractant or, more commonly, an extractant diluted in an "inert" solvent (e.g. dodecane, toluene). Nowadays, hydrophobic eutectic solvents (HES) present a promising alternative to conventional organic phases in SX, eliminating the need for diluents and mitigating third-phase formation[5].

In this study, we have built upon previous calorimetric methodologies to investigate the biphasic transfer of trisnitrato complexes of lanthanides ($M(NO_3)_3$) using tri-n-octylphosphine oxide (TOPO) as the extractant, incorporated within a hydrophobic eutectic solvent (HES) with decanoic acid as a phase former, using ITC. The experimental setup was optimized to ensure an efficient phase contact to attain a reaction equilibrium, without requiring extensive energies for phase agitation. Experiments involving the titration of aqueous metal solution of different concentrations, as well as, different aqueous to organic ratios were performed, leading to consistent results. Additionally, a performance test (water + propanol mixing) was conducted to confirm the calorimeter's sensitivity within the experiment's heat range, ensuring the absence of potential deviations due to the low thermal powers involved (as noticed by Lars Wadso[6]).

Overall, this study provides an accurate methodology to give valuable insights into the enthalpic contributions that drive metal ion partitioning and therefore on the extraction mechanisms of metal complexes in eutectic solvents. Furthermore, by advancing calorimetric methodologies for SX analysis, this work aims to support a robust framework for designing efficient and sustainable metal recovery processes with minimal waste generation.

Acknowledgments
N.S. acknowledges the European Research Council (ERC) for the starting grant ERC-2023-StG- 101116461. I.C.M.V. acknowledges the PRR - Recovery and Resilience Plan for funding through the scope of the Agenda for Business Innovation "New Generation Storage" (Project nº 58 with the application C644936001-00000045). This work was partially developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 (DOI:10.54499/UIDB/50011/2020), UIDP/50011/2020 (DOI:10.54499/UIDP/50011/2020) & LA/P/0006/2020 (DOI:10.54499/LA/P/0006/2020), financed by national funds through the FCT/MCTES (PIDDAC).

References
[1] *P. R. Zalupski, K. L. Nash*, *Solvent Extr. Ion Exch.*, 2008, **26**, 514-533; [2] Y. Marcus, Z. Kolaiik, *J. Chem. Eng. Data,* 1973, **18**, 155–163; [3] T. Sato, T. Nakamura, M. Kuwahara, *Chem. Lett.*, 1982, **11**, 731-732;[4] T. S. Grimes, P. R. Zalupski, L. R. Martin, *J. Phys. Chem. B,* 2014, **118**, 12725–12733; [5] Nicolas Schaeffer, et al., *Green Chem.,* 2025 (DOI: 10.1039/D5GC00489F); [6] L. Wadsö, Cement Concrete Res., 2010, **40**, 1129-1137.

AdsorptionCAL – design and construction of a gas-adsorption microcalorimetry system

ORAL_O10.5 - Instrumentation and Methods

Alexandre C. P. M. Alves*, José C. S. Costa, and Luís M. N. B. F. Santos

CIQUP, Institute of Molecular Sciences (IMS), Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Porto, Portugal

*alexandrecostapalves@gmail.com

The study of harmful gases under controlled conditions is of great importance and has become a very hot topic in recent years. The use of MOFs for the adsorption/desorption of gases such as CO_2, SO_2 and CH_4 is very common because of the great results shown throughout the last years, which show a higher adsorption capability for these materials.[1] For the study of the energy involved in the adsorption/desorption process, a highly sensitive and controlled system is needed due to the following reasons: i) for the temperature and pressure stabilization; ii) for the signal detection of smaller energy amounts considered. For this purpose, a new system was designed for the simultaneous measurement of adsorption/desorption of CO_2, through a differential quartz crystal microbalance (QCM), vacuum microbalance (VMB) and a Calvet calorimeter (MS80). This presentation will focus on the description of the project and preliminary results obtained with the calorimeter, model Calvet LV 4C (MS80). The experimental setup is able to work at different experimental conditions, with temperatures from ambient to 200° C, very high pressures (up to 350 bar), and high vacuum. In this case, since we intend to study adsorption isotherms at lower pressures, we will focus on pressures up to 5 bar and high vacuum. **AdsorptionCAL** system will allow simultaneous or individual measurements and by combination of the calorimetric measurement, derive the entropic contribution of the adsorption/desorption processes.

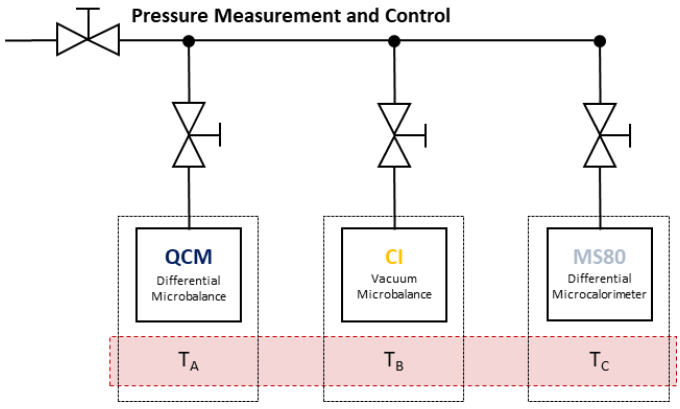


Figure 1: Schematic representation of the **AdsorptionCAL** system.

Acknowledgments
This work was supported by the Fundação para a Ciência e Tecnologia (FCT) (funded by national funds through the FCT/MCTES (PIDDAC)) to CIQUP, Faculty of Science, University of Porto (Project UIDB/00081/2020: DOI 10.54499/UIDP/00081/2020), IMS-Institute of Molecular Sciences (LA/P/0056/2020)) A.C.P.M.A. also thanks the FCT and the European Social Fund (ESF) for the award of a Ph.D. Research Grant (ref. 2022.11108.BD).

References

1. G. Férey, C. Serre, T. Devic, G. Maurin, H. Jobic, P. L. Llewellyn, G. De Weireld, A. Vimont, M. Daturi and J.-S. Chang, *Chem. Soc. Rev.* 2011, **40**, 550-562.

POSTER COMMUNICATIONS (P)

The specific heat measurement of R1132a

POSTER_P1.1 - Energy and Sustainability

S. Lee[1,*], D. Kim[1], S.H. Lee[1], W. Kang[1], S. Kwon[1], X. Xiao[2]

[1]*Thermometry and Fluid Flow Metrology Group, Korea Res. Inst. of Standards and Science. (KRISS), Daejeon 34113, Rep. of Korea*
[2]*Fluid Sci. & Res. Division, Dept. of Chemical Engineering, The University of Western Australia, Crawley, WA 6009, Australia*

[*]*lsjun@kriss.re.kr*

As global environmental regulations tighten, research activities aimed at identifying alternative refrigerants with low Global Warming Potential (GWP) have been intensifying. Among these, R1132a (1,1-difluoroethylene) has emerged as a promising refrigerant due to its low GWP, which can contribute to the design of efficient industrial cooling systems. However, apart from density, the physical properties of R1132a remain largely unexplored, highlighting the need for reliable experimental measurements to develop an accurate equation of state (EOS). Increased measurement data on R1132a could position it as a viable alternative refrigerant with low GWP and excellent thermodynamic properties. Additionally, R1132a can be used in mixed refrigerants, helping to reduce environmental impact while maintaining cooling performance. To measure the specific heat of R1132a, a sample preparation and injection device was constructed with a commercial calorimeter system (Setaram BT2.15) consisting of syringe pumps (Teledyne ISCO, 260x) and a mixer (Floxlab, BTSP-500-5). The system's temperature is precisely controlled between 203.15 K and 333.15 K, and the pressure is monitored and actively adjusted in real-time, ranging from 1 bar to 100 bar.

Using the measurement system, the specific heat of R1132a was measured, and the uncertainty in the measurements was found to be less than 5%. This experimental setup and the results obtained, including further discussions on the experimental procedures such as volume calibration and estimation of uncertainty budget in measurement, will be presented in this poster.

Figure 1: Measurement system for specific heat: sample preparation and injection part (left), and calorimetry part (right).

Acknowledgments
This work was supported by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government (MOTIE) (20212020800070, Development of next-generation alternative refrigerant and efficient heat pump system).

Enhanced thermodynamic performance of $LiFePO_4$ cathode with carbon coating layer formed by sulfur-modification

POSTER_P1.2 - Energy and Sustainability

Yong Joon Park* and Suhyun Kwak

Department of Advanced Materials Engineering, Graduate School Kyonggi University, 154-42, Gwanggyosan-Ro, Yeongtong-Gu, Suwon-Si, Gyeonggi-Do, 16227, Republic of Korea

**yjpark2006@kyonggi.ac.kr*

In recent years, market interest in $LiFePO_4$(LFP) cathodes has surged due to increased price competition in the electric vehicle (EV) market and heightened safety concerns. LFP cathodes are more cost-competitive than NCM cathodes because they primarily utilize low-cost iron (Fe) instead of cobalt (Co) and nickel (Ni). Additionally, LFPs offer excellent cyclic performance and high safety due to their structural stability. Despite these advantages, LFP's application is limited by its low lithium-ion diffusion coefficient and poor electronic conductivity, which hinder its rate capability. One effective method to enhance LFP's rate capability is to form a carbon coating layer on its surface. This reduces the lithium-ion diffusion length within a particle and facilitates electron transfer. While this carbon coating technique has achieved commercial success, efforts to develop an improved carbon coating layer continue. In this study, we modified the carbon coating layer using sulfur to enhance electronic conductivity and stabilize the carbon surface layer[1]. Two methods were explored, 1-step process: mixing sulfur powder with cellulose to form a carbon coating layer through a heating process. This method was expected to enhance the properties of the carbon formed, thereby improving the rate capability of LFP, 2-step process: applying an additional coating layer using sulfur vapor after forming the initial carbon layer. This aimed to create a new coating layer predominantly composed of sulfur components on top of the carbon coating, which was anticipated to enhance the stability of the carbon layer and protect the LFP from side reactions. Electrochemical measurements showed that the 1-step sulfur-modified LFP significantly improved the discharge capacity and rate capability compared to pristine LFP. Raman analyses indicated that sulfur mixed with a carbon source increases the graphitization of the carbon layer. Although the 2-step sulfur modification did not surpass the 1-step process in enhancing rate capability, it improved the storage characteristics and thermodynamic performance of LFP at high temperatures. The residual sulfur elements observed in TOF-SIMS analyses are believed to provide a protective effect on the surface. These findings confirm that sulfur modification of the carbon layer is an effective strategy to improve the properties of LFP cathodes, offering a promising approach to enhance the performance and stability of LFP-based lithium-ion batteries.

Acknowledgments
This work was supported by the Materials and Components Technology Development Program (grant No. 20024249 and RS-2024-00427225) funded By the Ministry of Trade, Industry and Energy (MOTIE, Republic of Korea)

References

1. S. Kwak,Y. J. Park, *Batteries* 2024, **10**, 348.

Low-loading iridium and nickel alloys supported on titanium nitride applied for electrochemical hydrogen evolution reaction

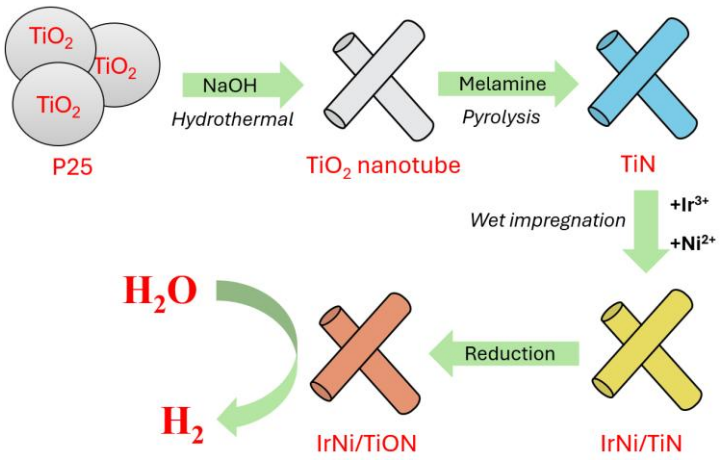
POSTER_P1.3 - Energy and Sustainability

Jinsoo Kim[1,*], Toan Minh Pham[1]

[1]*Kyung Hee University, Yongin-si, Korea*

[*]*jkim21@khu.ac.kr*

Iridium serves as the active electrocatalyst in driving the hydrogen evolution reaction (HER), an important process in water-splitting technology for generating green hydrogen. Importantly, the current research interest is focusing on the efficiency of Ir catalysts through the utilization of robust support materials and transition metal alloys. In this study, we synthesized highly stable titanium nitride (TiN) as the support material for a low-loading Ir-Ni alloy employed in HER. Varying the percentage of Ni was prepared to evaluate the effect of the alloy on Ir activity. Electrochemical tests conducted in 0.5M H_2SO_4 and 1.0M KOH revealed that Ir-Ni/TiN obtained improved activity with small overpotentials (η_{10}) of 8 mV and 22 mV, respectively. Furthermore, the employment of TiN has increased the long-term stability of the catalyst compared to the carbon support. Thus, this study presents an effective approach to enhancing the performance of Ir-based electrocatalysts in HER.



Scheme 1: Synthesis Procedure for IrNi/TiON

Acknowledgments
This work was supported by the National Research Foundation of Korea(NRF) grant funded by the Korea government(MSIT) (RS-2024-00345635).

Re-evaluating the role of purification adsorbents in ortho-para hydrogen conversion for liquefaction systems

POSTER_P1.4 - Energy and Sustainability

Guinevere M. Sellner[1,*], Michael L. Johns[1], Eric F. May[1], Paul L. Stanwix[1]

[1]*Fluid Science & Resources, School of Engineering, University of Western Australia, 6009 WA, Australia*

[*]*gwen.sellner@research.uwa.edu.au*

In the global transition toward clean energy alternatives, hydrogen has emerged as a promising energy carrier due to its high energy density and low environmental impact, particularly in its liquefied form. However, hydrogen liquefaction requires extreme cryogenic conditions, which pose engineering challenges, particularly in managing the slow and exothermic conversion between hydrogen's nuclear spin isomer states: *ortho*- and *para*-hydrogen. The associated heat release of the conversion, required for hydrogen to reach an equilibrium state, can cause excessive boil-off losses and reduce transport efficiency. To mitigate this, catalyst beds are integrated into the heat exchangers utilised in hydrogen liquefaction processes to ensure rapid and controlled *ortho–para* (*o-p*) conversion. Recent developments in hydrogen liquefaction technology have focused on high-performance catalysts, especially those based on hydrous ferric oxides (HFOs), to improve this process efficiency.[1] However, a key consideration often overlooked is that hydrogen may undergo significant pre-conversion before reaching these catalyst beds, particularly during cryogenic purification steps, such as adsorbent beds at liquid nitrogen temperature (77 K).[2]

In this study, we present new kinetic measurements of *o–p* hydrogen conversion on four adsorbents commonly employed in gas purification: activated carbon, molecular sieve carbon, NaX zeolite, and NaY zeolite. A custom-built experimental system was used to expose normal hydrogen streams to these materials at temperatures between 40–80 K, pressures up to 3 MPa, and flow rates up to 5 SLPM. *o-p* compositional data was measured using in situ Raman spectroscopy.[3] As in previous work,[1] the kinetics for the adsorbents were evaluated assuming first order reaction kinetic behaviour to enable direct comparison.

While the observed conversion rates are notably lower than those of commercial HFO-based catalysts such as Ionex®, our results show that these adsorbents, particularly zeolites, exhibit significant kinetic ability at the scale of a typical adsorbent bed, suggesting a non-negligible effect on total conversion in the liquefaction stream. Moreover, the data suggest that surface area may play a more critical role than previously theorized in governing conversion kinetics, offering insight into the mechanistic factors influencing *o–p* catalysis.[4] These findings highlight the importance of considering adsorbent-driven *o–p* conversion when designing liquefaction systems and may inform optimized placement and sizing of catalytic beds to avoid overengineering or underestimating upstream contributions.

Acknowledgments

The authors would like to acknowledge the support from Ehsan Sadeghi Pouya from The University of Western Australia for aiding us in sourcing the adsorbents and information on their properties.

References

1. F. Jiao, *et al.*, *React. Chem. Eng.* 2024, **9**, 2846-2862.
2. S. Z. S. Al Ghafri, *et al.*, *Energy Environ. Sci.* 2022, **15**, 2690-2731.
3. F. Luther, G.M. Sellner, M. Richter, P.L. Stanwix, *Int. J. Hydrogen Energy* 2025, **102**, 778-789.
4. E. Ilisca, *Prog. Surf. Sci.* 1992, **41**, 217-335.

Bio-based materials for selective and sustainable platinum group metal recovery

POSTER_P1.5 - Energy and Sustainability

Pedro J. S. Teixeira[1,2], Rita M. Carvalho[1,2,3], Amir Nobahar[3], Cláudia Silva[1,2], Helena Passos[1,2*]

[1]LSRE-LCM – Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[2]ALiCE – Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
[3]CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

[*]hpassos@fe.up.pt

The recovery of Platinum Group Metals (PGMs), classified by the EU Commission as critical raw materials (estimated concentration of only 0.01 ppm in the Earth's continental crust)[1], has become increasingly relevant due to their scarcity and high demand across various industrial sectors (automotive, electronics, medical, aerospace, energy technologies, etc.).[2] In particular, PGMs have a critical role in newer green technologies, and as these industries continue to flourish, such as the case with the hydrogen-based energy industry, a shortage of PGMs in the near future has become less of a possibility and more of a certainty. Moreover, their conventional mining processes are highly energy-intensive and generate toxic byproducts, so the need for enhancing their recovery efficiency is more important than ever.[3]
As for the conventional methods used for PGM recovery, these entail significant costs, are environmentally harmful, and require complex processes, driving research toward more sustainable alternatives. In the last decade, bio-derived materials have been shown as promising alternatives for metal recovery, showcasing high selectivity, sustainability and environmental benefits, with adsorption being achieved through various mechanisms (ion exchange, redox reactions, chelation, etc.).[4]
This study investigates the preparation of novel bio-based materials as adsorbents for the recovery of PGMs. These adsorbents were applied for the selective separation and recovery of PGMs from synthetic HCl-based multi-metallic solutions. Different key parameters, including pH, temperature, metal concentration, and contact time, were evaluated to optimize the adsorption process and maximize PGM recovery efficiency.

Acknowledgments
This work was supported by FCT – Fundação para a Ciência e a Tecnologia, I.P., within the scope of the project PlatILPlus (2022.04478.PTDC, DOI: 10.54499/2022.04478.PTDC). This work was further supported by national funds through FCT/MCTES (PIDDAC): LSRE-LCM, UIDB/50020/2020 (DOI: 10.54499/UIDB/50020/2020) and UIDP/50020/2020 (DOI: 10.54499/UIDP/50020/2020); ALiCE, LA/P/0045/2020 (DOI: 10.54499/LA/P/0045/2020); CICECO-Aveiro Institute of Materials, UIDB/50011/2020 (DOI: 10.54499/UIDB/50011/2020), UIDP/50011/2020 (DOI: 10.54499/UIDP/50011/2020), LA/P/0006/2020 (DOI: 10.54499/LA/P/0006/2020).

References

1. I. E. European Commission: Directorate-General for Internal Market, Smes, M. Grohol and C. Veeh, *Study on the critical raw materials for the EU 2023 – Final report*, Publications Office of the European Union, 2023.
2. S. Zhang, X. He, Y. Ding, Z. Shi and B. Wu, *Renewable and Sustainable Energy Reviews* 2024, **204**, 114821.
3. C. Saguru, S. Ndlovu and D. Moropeng, *Hydrometallurgy* 2018, **182**, 44-56.
4. S. Ndlovu and A. Kumar, in *Biological Metal Recovery from Wastewaters*, eds. S. Hedrich and O. Wiche, Springer Nature Switzerland, *Cham* 2024, DOI: 10.1007/10_2024_257, pp. 119-146.

Thermophysical properties of sustainable liquid fuels

POSTER_P1.6 - Energy and Sustainability

Lillian R. T Ladu[1,*] J.P Martin Trusler[1]

[1]*Department of Chemical Engineering, Imperial College London, London SW7 2AZ, UK*

[*]*lrl17@imperial.ac.uk*

The transport sector remains heavily reliant on fossil fuels[1], making the transition to sustainable liquid fuels critical for reducing carbon emissions—particularly in hard-to-electrify applications such as aviation or heavy-duty vehicles[2]. However, the adoption of alternative fuels is hindered by limited thermophysical property data, which are essential for engine design, optimization, and emissions simulations[3]. To overcome this, our study aims to establish a well-characterized five-component surrogate system, modelled with a multifluid Helmholtz framework, to predict thermophysical properties of complex fuels within acceptable uncertainties. This approach explores the potential to map unknown fuels onto this system by measuring select properties and using techniques such as gas chromatography to distil hundreds of components into a five-component recipe. Currently, this study has analysed seven gasoline samples and six surrogate mixtures, designed to mimic gasoline behaviour. Density and viscosity were measured at temperatures from (0 to 40)˚C and at pressures up to 70 MPa using a bespoke vibrating tube–vibrating wire apparatus. Specific heat capacity, thermal conductivity, and surface tension were measured at atmospheric pressure by means of flow calorimetry, transient hot-wire, and pendant drop methods, respectively. Additionally, vapor pressure was determined using a recirculating still across a boiling range of (20 to 100)˚C. Gasoline samples exhibited densities of between (620 and 860) kg·m-^{3} and viscosities of (4 to 6) mPa·s at a temperature of 20˚C and pressure of 0.1 MPa; the surrogates also fall within these ranges, confirming their suitability for model development. These results provide a robust dataset for developing and validating the proposed modelling approach. This supports broader net-zero goals by accelerating sustainable fuel adoption in the transport sector, bypassing costly, time-intensive experiments. While development of a comprehensive predictive model is still in progress, these data lay the groundwork for advancing sustainable fuel design revealing trends that could inform fuel blending and combustion efficiency. Future work will focus on refining the multifluid Helmholtz energy framework leveraging speed of sound and VLE data to tune binary interaction parameters and enhance model accuracy.

References

1. H. Ritchie, P. Rosado and M. Roser, *Fossil fuels*, *Our World in Data*.
2. P. Cazzola, F. Gerard, M. Gorner, M. Gibbs and K. Young, Research for TRAN Committee: Assessment of the potential of sustainable fuels in transport.
3. M. J. Assael, *Energy and Environment* 2001, 162-178.

Optimizing solubility of redox species to boost energy density in redox flow batteries

POSTER_P1.7 - Energy and Sustainability

Gabriel L. Camilo*, Murilo L. Alcântara, Catarina M. S. S. Neves, Ana M. Ferreira, Dinis O. Abranches, Mara G. Freire, João A. P. Coutinho

CICECO - Aveiro Institute of Materials, Chemistry Department, University of Aveiro, Aveiro, Portugal

gcamilo@ua.pt

Renewable energy sources like solar and wind suffer from intermittency, creating a need for Energy Storage Systems (ESS) that can store excess energy during peak production and release it when generation is low. While lithium-ion batteries have made significant advancements, their widespread adoption is limited by metal scarcity and high costs. Redox-Flow Batteries (RFBs) provide a more economical alternative, particularly for long-duration energy storage. These batteries utilize liquid-state redox species dissolved in electrolyte solutions, offering extended operational life and cost advantages. However, Vanadium-based RFBs, though commonly used, are expensive and prone to corrosion. Organic redox compounds offer a promising, cost-effective alternative due to their structural diversity and abundance.

Aqueous RFBs are advantageous for their non-flammable nature and superior ionic conductivity, but improving the solubility of redox-active species is crucial for enhancing energy density and preventing precipitate formation. Organic redox species often face solubility limitations that require complex synthesis processes. A novel, more sustainable approach involves the use of battery additives that enhance performance without interfering with battery reactions. These solubilizing additives improve solubility by bridging the aqueous solution and redox compounds, enhancing solubility without complex molecular modifications, while also acting as supporting electrolytes.

This study explores the effectiveness of additives in improving the solubility of redox-active compounds such as Hydroquinone, TEMPO, Potassium Ferrocyanide, Ferrocene, and Anthraquinone derivatives. Using experimental testing and Gaussian Process modeling, the research aims to identify the most effective additives to enhance energy density and long-term stability. By integrating experimental results with artificial intelligence-driven modeling, this approach supports the development of sustainable and scalable energy storage solutions for the renewable energy grid.

Acknowledgments
This work was developed under the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, funded by national funds through FCT/MCTES (PIDDAC). It also received funding from the European Innovation Council (EIC), grant agreement 101046742, supported by the EU's Horizon Europe research and innovation program. GLC acknowledges FCT for the PhD grant 2024.00343.BD.

Membrane approaches for efficient separation of platinum group metals from leachate streams

POSTER_P1.8 - Energy and Sustainability

Rita M. Carvalho[1,2,3], Filipe H. B. Sosa[1*], Helena Passos [2,3], João A.P. Coutinho[1]

[1]*CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal*
[2]*LSRE-LCM – Laboratory of Separation and Reaction Engineering – Laboratory of Catalysis and Materials, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal*
[3]*ALiCE – Associate Laboratory in Chemical Engineering, Faculty of Engineering, University of Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal*

[*]*filipesosa@ua.pt*

Platinum Group Metals (PGMs) are rare elements with distinct properties used in various applications.[1] As demand for the elements grows, there is an increasing interest in exploring methods to increase their market availability. One promising approach involves recovering PGMs from secondary sources, such as spent automotive catalytic converters, providing an alternative to conventional mining and helping to mitigate environmental impacts.[1,2] Hydrometallurgy is a widely used recycling approach, with aqua regia leaching being a traditional method. However, due to aqua regia significant environmental footprint, alternative oxidizing agents, such as aluminum salt solutions, are under development.[3] After leaching, purification processes, such as solvent extraction, ion exchange resins, and precipitation, are used to separate individual metals. Recent research suggests that membrane separation could serve as a promising alternative to reduce reagent consumption and environmental harm in hydrometallurgical processes. While membranes have long been used in water treatment, their application for metal separation and concentration is gaining attention.
In this context, different membrane characteristics (such as material and pore size) should be evaluated regarding flow rates and separation efficiency (rejection %) to identify membranes with optimal performance for metal separation.[4]
This study aims to develop a methodology for separating and purifying PGMs from aluminum-leaching solutions using membranes. Key objectives include assessing the performance of commercially available membranes in separating PGM compounds, optimizing separation conditions (temperature, pressure, and agitation) and determining the effectiveness of these membranes in separating target metals. By analyzing solutions with varying concentrations of salt and metals, the study seeks to understand how different membranes behave with specific target solutions and explore the separation kinetics in the leaching solutions. The ultimate goal of this research is to improve the efficiency and sustainability of PGM recycling processes.

Acknowledgments
This work was financially supported by national funds through FCT – Fundação para a Ciência e a Tecnologia, I.P., within the scope of the project PlatILPlus (2022.04478.PTDC, DOI: 10.54499/2022.04478.PTDC). This work was further supported by national funds through FCT/MCTES (PIDDAC): LSRE-LCM, UIDB/50020/2020 (DOI: 10.54499/UIDB/50020/2020) and UIDP/50020/2020 (DOI: 10.54499/UIDP/50020/2020); ALiCE, LA/P/0045/2020 (DOI: 10.54499/LA/P/0045/2020); CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020. F.H.B. Sosa acknowledges FCT for the researcher contract CEECIND/07209/2022

References

1. A. E. Hughes, N. Haque, S. A. Northey and S. Giddey, *Resources* 2021, **10**, 93.
2. EC-European Commission, Study on the Critical Raw Materials for the EU 2023 – Final Report, 2023.
3. F. Forte, S. Riaño and K. Binnemans, *Chemical Communications* 2020, **56**, 8230-8232.
4. J. Xia and A. Ghahreman, *Separation and Purification Technology* 2023, **311**, 123357.

Thermodynamic analysis of photocatalytic ammonia synthesis via quantum chemical calculations with process-level considerations

POSTER_P1.9 - Energy and Sustainability

Bruno Ramos[1,*], Gustavo V. Olivieri[1], Ricardo B. Torres[1]

[1]*Centre for Research and Innovation in Energy Transition for Sustainable Mobility (IGNIS), Centro Universitario FEI, São Bernardo do Campo, Brazil*

[*]*brunoramos@fei.edu.br*

The photocatalytic synthesis of ammonia under ambient conditions has emerged as a viable alternative to the Haber–Bosch process, particularly when driven by solar energy and earth-abundant materials. In this study, following experimental investigations[1], we evaluate the thermodynamic feasibility of nitrogen reduction to ammonia on hematite (α-Fe_2O_3) surfaces, coupling quantum chemical calculations with process-level simulations. Density Functional Theory (DFT) calculations were performed using the ORCA package on a finite Fe_2O_3 cluster model to simulate key steps in the reaction pathway, including N_2 adsorption, protonation sequences, NH_3 formation, and product desorption[2]. Thermodynamic parameters (ΔE, ΔH, ΔG) were obtained at ambient and elevated temperatures via frequency calculations, allowing assessment of the driving forces associated with key steps. The formation of surface-bound intermediates such as $^*NNH$ and $^*NH_2$ was examined, and the overall ΔG for ammonia evolution was computed. Preliminary results indicate that while the initial N_2 activation barrier remains high, subsequent hydrogenation steps are thermodynamically favourable. Calculated equilibrium constants were then incorporated into a simplified Aspen Plus model (Fig. 1) of a solar-driven photocatalytic reactor to evaluate ammonia yields and estimate solar-to-chemical conversion efficiency. This multiscale approach enables the identification of thermodynamic bottlenecks and operational windows for low-temperature ammonia production using semiconductor-based photocatalysts.

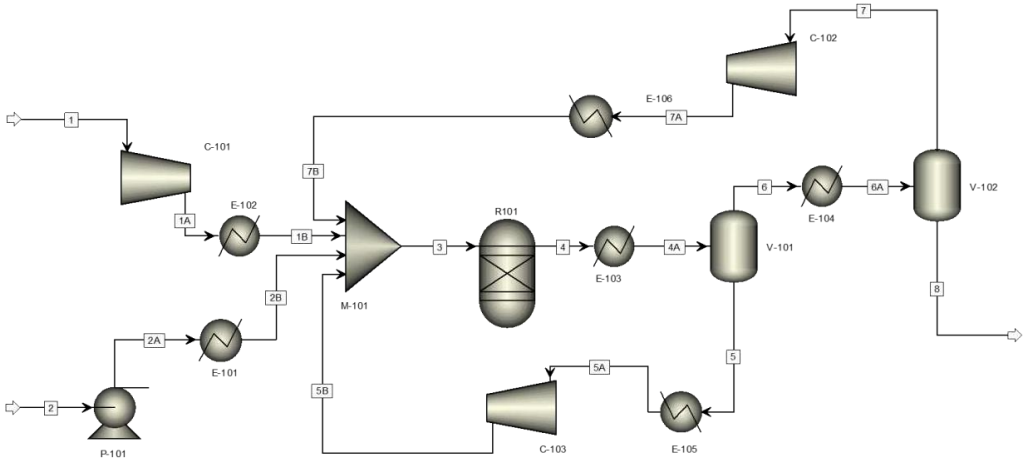


Figure: Solar-driven photocatalytic plant flowsheet

Acknowledgements
The authors acknowledge the support of the Sao Paulo Research Foundation (FAPESP), grant 23/14214-4, and the institutional support of Centro Universitario FEI.

References

1. C.A.P. Alves, P.H. Palharim, B. Pratto, A.L. da Silva, D. Gouvêa and B. Ramos, *J. Photochem. Photobiol. A: Chem.* 2025, **460**, 116159.
2. T. Žibert, B. Likozar and M. Huš, *ChemSusChem* 2024, **17**, e202301730.

Energetic study of α- and γ-pyrones

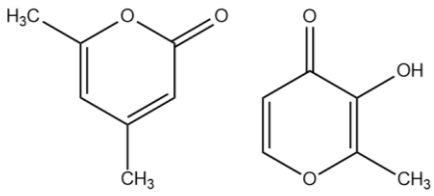
POSTER_P1.10 - Energy and Sustainability

Ana Margarida M. Pereira[1,*], Ana Luísa R. Silva[1], Maria D. M. C. Ribeiro da Silva[1]

[1]*Faculty of Sciences of University of Porto, Department of Chemistry and Biochemistry, Centro de Investigação em Química (CIQUP), Institute of Molecular Sciences (IMS), Rua do Campo Alegre, P-4169-007 Porto, Portugal*

[*]*margaridapereira@fc.up.pt*

Biomass is the most used source of renewable energy, reducing dependence on fossil fuels and benefiting the agricultural and industrial sectors by adding value to their waste. Another application is its use in the chemical industry for the conversion of biomass-derived carbohydrates to platform molecules, which can contribute to a stream of end products that can replace the ones used as petrochemicals.[1,2] Despite its economic impact, producing biofuels via biomass remains a challenge, since it cannot be immediately used due to its viscosity, chemical instability and the presence of oxygenated compounds.
Pyrones constitute a family of six-membered unsaturated cyclic compounds, with a prevailing structure in various naturally and synthetically occurring bioactive molecules. α- and γ-Pyrones have a large presence in nature and can serve as good platform molecules in the production of high-value biofuels and chemicals.[1,3]
The present work aims to contribute to a systematic experimental study on key platform bio-based molecules. The compounds studied are derivatives of pyrone, and are the following: 4,6-dimethyl-α-pyrone and 3-hydroxy-2-methyl-γ-pyrone (Maltol) (Figure 1). Our goal is to evaluate the thermal stability of these compounds by determining their thermal behaviour and the corresponding enthalpy of fusion, by using differential scanning calorimetry. Additionally, we present their energies of combustion, measured by static bomb calorimetry. The results obtained allow to derive the standard molar enthalpy of formation in the crystalline phase.



a) b)

Figure 1: Compounds studied: a) 4,6-dimethyl-α-pyrone, b) 3-hydroxy-2-methyl-γ-pyrone (Maltol).

Acknowledgements
This work was supported by the Fundacão para a Ciência e Tecnologia (FCT) (funded by national funds through the FCT/MCTES (PIDDAC)) to CIQUP, Faculty of Sciences, University of Porto (Project UID/00081, Centro de Investigação em Química da Universidade do Porto) and IMS-Institute of Molecular Sciences (LA/P/0056/2020)). A.L.R.S. thanks FCT/MCTES for her contract under Stimulus of Scientific Employment 2017 (CEECIND/01161/2017).
The team acknowledges further support from Exploratory Project of reference 2023.13829.PEX funded by FCT, Portugal.

References

1. M. Chia, T. Schwartz, B. Shanks, J. Dumesic, *Green Chemistry* 2012, **14**, 1850.
2. D. Mignogna, M. Szabó, P. Ceci, P. Avino, *Sustainability* 2024, **16**, 7036.
3. T. Schäberle, *Beilstein Journal of Organic Chemistry* 2016, **12**, 571.

Development of a corn cob biochar anode with LDH (Ni-Fe) for the degradation of nicosulfuron

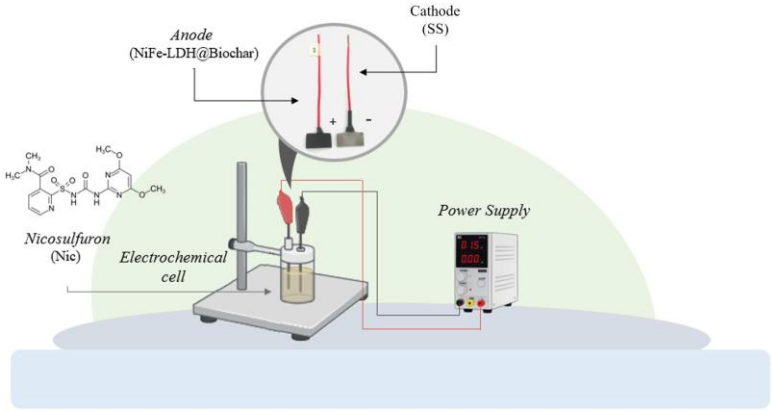
POSTER_P1.11 - Energy and Sustainability

Jesús Lino-Quimis[1], Mario Franco-Bravo[1], Yasiel Arteaga-Crespo[2], Nuria Boluda-Botella[3], María Dolores Saquete[3], Bryan Fernando Rivadeneira-Mendoza[1], Luis Angel Zambrano-Intriago[1,4], Joan Manuel Rodríguez-Díaz[1,5*]

[1] *Laboratorio de Análisis Químicos y Biotecnológicos, Instituto de Investigación, Universidad Técnica de Manabí, S/N, Avenida Urbina y Che Guevara, Portoviejo, 130104, Ecuador*
[2] *Universidad Estatal Amazónica. Puyo, Pastaza, Ecuador*
[3] *Instituto Universitario de Ingeniería de los Procesos Químicos, Universidad de Alicante, Alicante, E-03080, Spain*
[4] *Departamento de Ciencias Biológicas, Facultad de Ciencias de la Salud, Universidad Técnica de Manabí, Portoviejo 130105, Ecuador*
[5] *Departamento de Procesos Químicos, Alimentos y Biotecnología, Facultad de Ingenierías y Ciencias Aplicadas, Universidad Técnica de Manabí, Portoviejo, Ecuador*

**joan.rodríguez@utm.edu.ec*

The degradation of the pesticide Nicosulfuron, a potentially hazardous pollutant [1], was studied using an advanced electrochemical oxidation process with an electrode composed of nickel–iron layered double hydroxides supported on corn cob-derived biochar structure (NiFe-LDH@Biochar) as anode, and stainless steel as reference electrode as cathode, both with area of 2 cm^2(Scheme 1). The influence of various operating parameters, such as the concentration of the supporting electrolyte, pH of the solution, electrode area, electrical potential, distance between electrodes, electrical charge, concentration of Nicosulfuron as a contaminant pesticide, operating time, treatment volume and lifetime were investigated. The degradation occurred in the presence of K_2SO_4 (10 mM) as supporting electrolyte. In such a single 10 min operation, complete degradation of Nicosulfuron was achieved at pH = 4, potential of 1.5 V, current density of 0.100 mA cm^{-2}, and distance of 1 cm between electrodes. The degradation kinetics of Nicosulfuron followed a pseudo zero-order reaction, indicating a steady and efficient degradation over time. Finally, it was demonstrated that the electrode maintained a lifetime of 42 cycles without decreasing its degradation performance.



Scheme 1: Diagram of the experimental setup used in the electrochemical oxidation of Nicosulfuron

Acknowledgements
We acknowledge the Universidad Estatal Amazónica (SGD-DINV-PI-0015) for funding, and the University of Alicante for their contribution to material characterization

References

1. J. Zhong, S. Wu, W.-J. Chen, Y. Huang, Q. Lei, S. Mishra, P. Bhatt and S. Chen, *Chemosphere* 2023, **326**, 138390.

Structured design of a hydrochar-supported LDH/MOF composite for improved photocatalytic applications

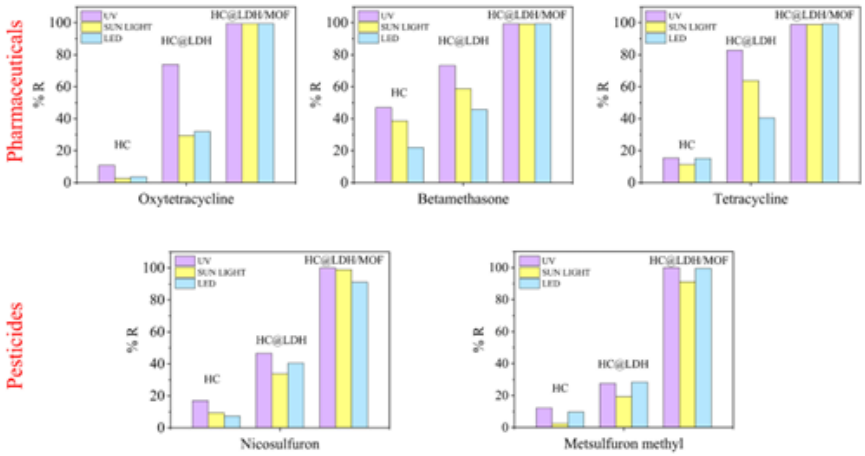
POSTER_P1.12 - Energy and Sustainability

Gilberto R. Jarre-Vera[1,2], Bryan F. Rivadeneira-Mendoza[2], Kevin J. Fernández-Andrade[3], María D. Saquete[1], Nuria Boluda-Botella[1], Joan M. Rodríguez-Díaz[2*]

[1] *Instituto Universitario de Ingeniería de los Procesos Químicos, Universidad de Alicante, Spain*
[2] *Departamento de Procesos Químicos, Alimentos y Biotecnología, Facultad de Ingenierías y Ciencias Aplicadas, Universidad Técnica de Manabí, Portoviejo, Ecuador*
[3] *Universidad del Bío-Bío, Chile*

**joan.rodriguez@utm.edu.ec*

This work reports the sequential synthesis and performance assessment of a new hierarchical hybrid materialHC@MgFe-LDH/MIL-53(Al) comprising Mg/Fe layered double hydroxide (LDH) nanoplatelets and MIL-53(Al) metal–organic framework (MOF) crystals grown in situ on hydrochar (HC) derived from corn-stover waste. The HC simultaneously serves as a lignocellulosic support and electronic modulator at the interface, promoting a homogeneous dispersion of LDH active sites and the subsequent nucleation of the MOF. Hydrochar was produced via hydrothermal carbonization (190 °C, 24 h) and preliminarily characterized by SEM/TEM, XRD, and XPS. MgFe-LDH was then deposited on HC by controlled co-precipitation (pH 9–10). The resulting HC@LDH composite was coated with MIL-53(Al) in a DMF–H_2O medium (130 °C, 24 h). XRD confirmed the step-wise architecture—cellulosic HC signals, amorphous LDH reflections, and orthorhombic MIL-53(Al) peaks—while EDX/XPS mapping identified HC C=O groups and LDH Mg^{2+} sites as preferential anchors for MOF growth. UV-Vis DRS revealed a semiconductor heterojunction with a 1.55 eV bandgap, markedly narrower than those of the precursors (LDH ≈ 2.0 eV; MOF > 3.5 eV). The combined texture (BET = 133 m^2 g^{-1}; total porosity ≈ 77 %) and H4 micro-/mesoporous architecture enabled excellent reactant accessibility. AOP tests demonstrated that pharmaceuticals (tetracycline, betamethasone and oxytetracycline) and pesticides (metsulfuron-methyl and nicosulfuron) were degraded by over 99% within 60 min under a commercial visible-LED source (λ ≈ 450 nm), simulated sunlight or UV-C irradiation. By contrast, HC@LDH achieved 70–90% removal, and pristine HC less than 25%. This high activity arises from (i) synergistic band-gap narrowing with extended visible-light absorption; (ii) efficient electron–hole separation across the LDH–MOF heterojunction; and (iii) the extensive active surface area and mass-transfer pathways provided by the HC layer.



Scheme 1: Degradation test results of several families of pollutants by photocatalysis, irradiated with different light sources and using the three materials (HC, HC@LDH, and HC@LDH/MOF).

Acknowledgements
We acknowledge the Universidad Técnica de Manabí (PYT3064-CONV2023-FCMFQ0020) for funding, and the University of Alicante for their contribution to material characterization.

Photocatalytic-assisted hydrogenation over Cu/Fe oxide derived from layered double hydroxides for nitro group reduction

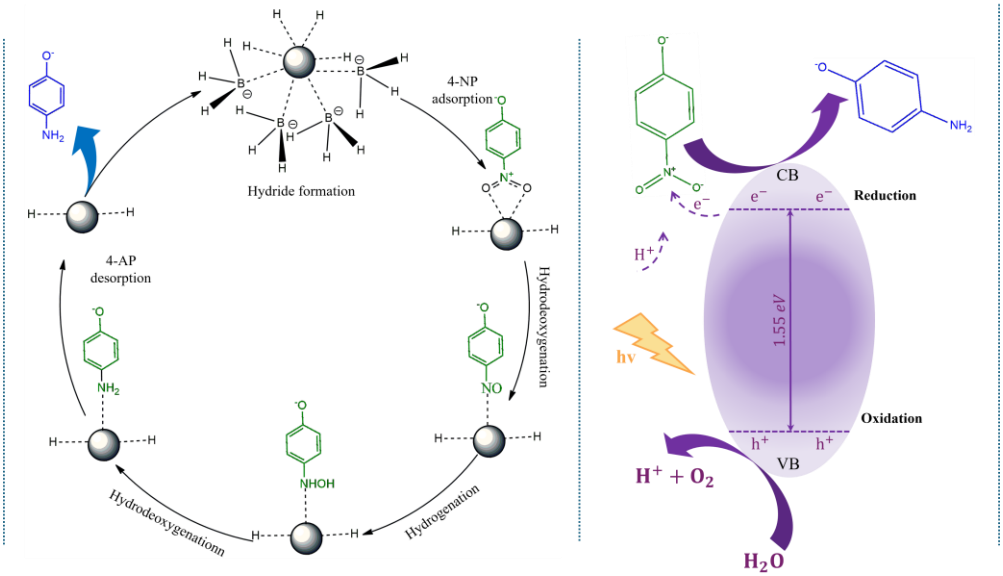
POSTER_P1.13 - Energy and Sustainability

Bryan Fernando Rivadeneira-Mendoza[1], Jesús Moreira[1], Clarissa Muñoz[1], Nuria Boluda-Botella[2], María Dolores Saquete[2], Joan Manuel Rodríguez-Díaz[1*]

[1] *Laboratorio de Análisis Químicos y Biotecnológicos, Instituto de Investigación, Universidad Técnica de Manabí, S/N, Avenida Urbina y Che Guevara, Portoviejo, 130104, Ecuador*
[2] *Instituto Universitario de Ingeniería de los Procesos Químicos, Universidad de Alicante, Alicante, E-03080, Spain*

**joan.rodriguez@utm.edu.ec*

The effective elimination of 4-nitrophenol can proceed through various pathways, among which the hydrogenation to 4-aminophenol stands out as the most economically attractive. 4-Aminophenol is a valuable compound widely used in the pharmaceutical, cosmetic, and other industries. This transformation typically requires robust catalysts, often based on noble metals. Moreover, the widespread and excessive use of sodium borohydride ($NaBH_4$) as a hydrogen donor remains a significant challenge. Here, we have developed thermally treated Cu/Fe lamellar oxides derived from layered double hydroxides (LDHs) in the presence of sacrificial biomass, serving as efficient photocatalysts for this reaction under LED light irradiation. Structural characterization by SEM and XRD confirms the successful and complete formation of Cu and Fe oxides. Additionally, optical properties analyzed by diffuse reflectance spectroscopy (DRS) and evaluated using the Tauc plot method reveal a band gap value ≈1.55 eV, which is ideal for visible light absorption. It has been demonstrated that 5 mg of the photocatalyst are sufficient to achieve >99% conversion of 4-nitrophenol within 30 minutes in 10 mL of solution, with a 4-nitrophenol to $NaBH_4$ molar ratio of approximately 0.15 (≈1:6.5). The results demonstrated that approximately 80% of the catalytic activity occurred in the absence of light, while values exceeding 99% were achieved under LED illumination. Reusability tests confirm the catalyst's stability, as no decrease in conversion efficiency was observed over eight consecutive cycles.



Scheme 1: Schematic representations of the 4-nitrophenol hydrogenation reaction under dark conditions and LED light irradiation.

Acknowledgements
We are grateful to the Universidad Técnica de Manabí for financing the authors' experimental development.

A thermochemical approach to catalytic hydrodeoxygenation of eugenol as a model for lignin valorization

POSTER_P1.14 - Energy and Sustainability

Aleksey A. Pimerzin[1,*], Aleksandr P. Glotov[1], Artemiy A. Samarov[2], Sergey V. Vostrikov[3], Sergey P. Verevkin[4]

[1]*Gubkin Russian State University of Oil and Gas, Russian Federation*
[2]*Saint Petersburg State University, Russian Federation*
[3]*Samara State Technical University, Russian Federation*
[4]*Institute of Technical Thermodynamics, University of Rostock, Germany*

[*]*al.pimerzin@gmail.com*

The catalytic hydrodeoxygenation (HDO) of lignin-derived phenolics is a promising pathway for the production of biosynthetic fuels. In this study, eugenol was used as a model compound for lignin, incorporating key reactive moieties (hydroxyl, methoxy, and allyl groups). A thermodynamic hybrid approach was developed, combining high-level quantum chemical (QC) methods (G4) with validated experimental data on combustion and vaporization to calculate Gibbs free energies (G°) for 18 HDO reactions.

Gas-phase enthalpies and entropies of formation were derived via QC calculations and corrected through empirical correlations. Liquid-phase reaction thermodynamics were obtained using experimentally determined vaporization data and entropy contributions. The results revealed that all 18 reactions are thermodynamically feasible ($\Delta rG^\circ < 0$), suggesting that product distribution is governed by kinetics rather than thermodynamic limitations.

Catalytic experiments over Ru supported on pristine and acid-etched halloysite nanotubes (HNT, HNT-t) confirmed the theoretical predictions. Ru/HNT with low acidity showed high selectivity (79%) to partially hydrogenated intermediates, while Ru/HNT-t promoted deeper HDO to fully deoxygenated cycloalkanes.

This work underscores the utility of integrated thermochemical modeling for guiding catalyst development and optimizing biofuel production processes.

Acknowledgements
The authors gratefully acknowledge financial support from DFG (Germany), RFBR (Russia), and technical assistance from the participating universities.

References

1. S. P. Verevkin et al., *Chem. Eng. J.* 2023, **464**, 142723.
2. Y. Yang et al., *ACS Catal.* 2020, **10**, 4511-4531.
3. T. Yoshikawa et al., *Energy Fuels* 2018, **32**, 2672-2683.

3-Hydroxy-4-pyridine chelators: Exploring membrane interactions for enhanced metal ion management

POSTER_P2.1 - Bio and Pharmaceutical Materials

Luísa M. P. F. Amaral[1,*], Maria Rangel[2]

[1]*REQUIMTE, LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, R. do Campo Alegre, 4169-007, Porto, Portugal*
[2]*REQUIMTE, LAQV, Instituto de Ciências Biomédicas de Abel Salazar, Universidade do Porto, Rua Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal*

**luisaamaral@fc.up.pt*

Chelation therapy is a vital intervention for controlling metal levels in the body. While a range of chelating agents exists, many have significant disadvantages, including adverse side effects. Therefore, it is crucial to develop more specific and advanced chelating agents to address disorders associated with metal ions. Applications of chelators in medicinal inorganic chemistry generally fall into two main areas: i) development of ligands to enhance the formation of metal-ion complexes in situ, facilitating the removal of excess metal ions; ii) formation of metal ion–ligand complexes to improve the absorption and biodistribution characteristics of the specific metal ions.
The class of 3-hydroxy-4-pyridinone (3,4HPO) chelators is well-recognized for their valuable applications in biomedical and pharmaceutical research due to their ability to chelate biologically relevant transition metal ions. These chelating properties make 3,4HPOs ideal building blocks for developing metal chelation agents. A key advantage of 3,4HPOs is the ability to modulate the hydrophilic/lipophilic balance of the ligands and their complexes through structural modifications on the heterocyclic ring, without compromising the stability of the metal complexes. This property is critical for designing molecules with optimized permeation characteristics across biological membranes, which is essential for understanding drug mechanisms and advancing the development of new bioactive compounds.
In this study, we present the synthesis and evaluation of a novel series of 3,4HPO chelators with varying lipophilicities. The interactions of these chelators with DMPC liposomes, used as model membranes, were systematically investigated. To probe the molecular interactions between the 3,4HPO ligands and DMPC liposomes, we employed Differential Scanning Calorimetry (DSC) and Electron Paramagnetic Resonance (EPR) spectroscopy. These biophysical techniques offer valuable insights into the permeation behavior of the chelators, shedding light on their potential as therapeutic agents.

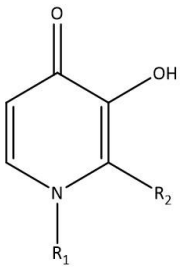


Figure 1: Structures of bidentate 3,4HPO chelators.

Acknowledgments This work received support from PT national funds (FCT/MCTES, Fundação para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) through the projects UIDB/50006/2020 and UIDP/50006/2020. L.M.P.F. Amaral thanks FCT/MCTES funding through the Individual Call to Scientific Employment Stimulus 2018 (CEECIND/03202/2018) DOI 10.54499/CEECIND/03202/2018/CP1545/CT0001.
Funding: This work received financial support from PT national funds (FCT/MCTES, Fundação para a Ciência e Tecnologia and Ministério da Ciência, Tecnologia e Ensino Superior) through the projects UIDB/50006/2020 and UIDP/50006/2020.

Thermodynamic study on the stability of some oral anticoagulant drugs

POSTER_P2.2 - Bio and Pharmaceutical Materials

Roxana D. Pasca[1], Attila Bende[2,*], Dan R. Rusu[1], Ioana D. Felecan[1]

[1] *Physical Chemistry Discipline, 2nd Department, Faculty of Pharmacy, Iuliu Haţieganu University of Medicine and Pharmacy, Victor Babeş street, no. 8, 400012, Cluj-Napoca, Romania*
[2] *Department of Isotopic and Molecular Technologies, National Institute for Research and Development of Isotopic and Molecular Technologies, Donath street, no. 67-103, 400293, Cluj-Napoca, Romania*

**attila.bende@itim-cj.ro*

Apixaban and rivaroxaban are two breakthrough oral anticoagulants used to lower the risk of deep vein thrombosis, pulmonary embolism and ischemic stroke in patients with non-valvular atrial fibrillation. They are frequently used in patients with polymedication and drug-drug interactions have been reported with classes of antibiotics, betablockers, immunosuppressants and antifungals.
Conformational stabilities of the apixaban and rivaroxaban anticoagulant drugs were studied alone and in interaction with some representatives of these classes of drugs, namely: antibiotics (clarithromycin), betablockers (diltiazem, verapamil) and antifungals (ketoconazole) considering ab initio molecular modeling methods. The Global Optimizer Algorithm implemented in the Orca program package was used for fully mapping the conformational topology of each drug molecule, while the DOCKER automated docking algorithm was considered for finding the drug-drug pair geometry configuration with the lowest interaction energy.

Deep eutectic systems for rifampicin delivery: Solubility and stability toward enhanced tuberculosis treatment

POSTER_P2.3 - Bio and Pharmaceutical Materials

Vanessa Vieira[1*], Abel A. R. Jr [1,2], Alessandra L. Viçosa [2], Mara G. Freire [1]

[1] *CICECO-Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal*
[2] *LabFE – Farmanguinhos, Avenida Comandante Guaranys, 447 - Jacarepaguá - Rio de Janeiro - RJ Cep: 22.775-903 - Brasil*

[*] *vanessa.vieira@ua.pt*

Tuberculosis, caused by *Mycobacterium tuberculosis*, remains a globally prevalent disease of significant epidemiological concern.[1] Treatment failure - particularly in cases of meningoencephalic tuberculosis among children under 10 years of age - is often associated with limitations of one of the key active pharmaceutical ingredients (APIs), rifampicin. These limitations include its poor water solubility, limited permeability across the blood-brain barrier, and low palatability - an especially critical factor in pediatric therapies.[2]
Deep eutectic solvents (DES) have demonstrated considerable promise in pharmaceutical development, particularly in enhancing the aqueous solubility of APIs. Previous studies have shown that DES can improve drug solubility by several orders of magnitude compared to water, as observed with various anti-inflammatory and antifungal agents, thereby improving biocompatibility and bioavailability.[2]
This study investigates the ability of various DES formulations to enhance the solubility and stability of rifampicin in solution. A series of DES, inspired by literature and composed of components with Generally Recognized As Safe (GRAS) status, was evaluated. Given rifampicin's pH sensitivity, systems with near-neutral pH were prioritized. Notably, DES composed of betaine and 1,3-propanediol, in different molar ratios, exhibited pH values closer to neutrality, demonstrating enhanced solubilization capacity for rifampicin when compared to both literature reports and experimental data in aqueous media across different pH levels.
Ongoing and future work will focus on assessing the stability, palatability, and pharmaceutical performance of these formulations. The goal is to support the suitability of these formulations for additive manufacturing (3D pharmaceutical printing), enabling the development of personalized therapies tailored to individual patient characteristics and therapeutic needs, with particular emphasis on the pediatric population.

Acknowledgements
This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 (DOI 10.54499/UIDB/50011/2020), UIDP/50011/2020 (DOI 10.54499/UIDP/50011/2020) & LA/P/0006/2020 (DOI 10.54499/LA/P/0006/2020), financed by national funds through the FCT/MEC (PIDDAC). LabFE – Farmanguinhos Experimental Pharmacotechnical Laboratory – Institute of Pharmaceutical Technology/FIOCRUZ e LQFEX – Chemical and Pharmaceutical Laboratory of the Brazilian Army.

References

1. World Health Organization, "Global Tuberculosis Report 2024", https://www.who.int/teams/global-tuberculosis-programme/tb-reports/global-tuberculosis-report-2024, accessed January 28, 2025.
2. B. D. Daniel, G. A. Grace, and M. Natrajan, *Indian J. Med. Res*. 2019, **150**, 117-130.
3. S. N. Pedro, C. S. R. Freire, A. J. D. Silvestre, and M. G. Freire, *Encyclopedia* 2021, **1**, 942-963.

Chalcone-containing catanionic vesicles for precise photoregulation of paclitaxel release kinetics

POSTER_P2.4 - Bio and Pharmaceutical Materials

Dmitriy Moreira[1], Filipa Santos[1], Nuno Basílio[2], Eduardo F. Marques[1,*]

[1] *CIQUP, IMS, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto 4169-007, Porto, Portugal*
[2] *LAQV-REQUIMTE, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516, Caparica, Portugal*

[*] *efmarque@fc.up.pt*

Controlled delivery of active principles through stimuli-sensitive/smart nanocarriers constitutes a pivotal strategy to mitigate the adverse effects of traditional drug therapy such as drug toxicity and prolonged treatments.[1] Among the various nanocarriers and stimuli that can be employed, catanionic vesicles and light responsiveness hold great potential. On one hand, catanionic vesicles offer advantages such as the spontaneous formation of stable vesicles with tunable size and charge.[1,2] On the other hand, light responsiveness, allows for a noninvasive yet precise spatiotemporal control over drug release.[2] In this work, we developed light-responsive, highly stable and spontaneously formed catanionic vesicles composed of a cationic 2-hydroxychalcone derivative (C_6NCh), as the photoresponsive unit (Figure 1a), and *N*-Lauroylsarcosine sodium salt (SLSar) (Figure 1b) for the encapsulation and light-modulable release of paclitaxel (PTX) (Figure 1c). The vesicles demonstrated the ability to undergo diverse morphological transitions upon light irradiation, including vesicle-to-micelle conversion and membrane perturbation. Encapsulation studies showed that the system achieves high PTX loading efficiencies (up to ~95 %) and capacities (up to ~9 %), release kinetics of PTX were shown to be tunable through light irradiation, allowing for both acceleration or retardation of release rates depending on mixture composition.

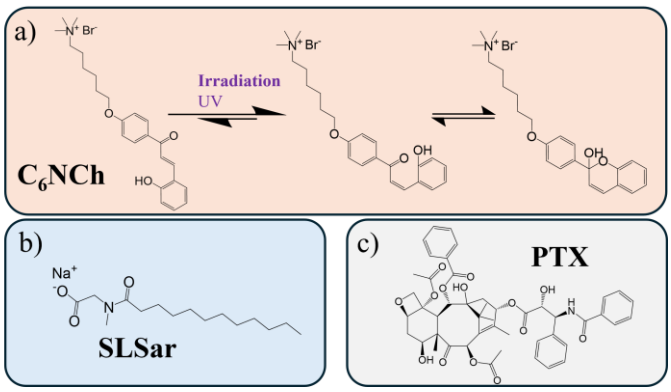


Figure 1: Molecular structures of the compounds employed in the formation of the nanocarriers: a) the cationic chalcone derivative and C_6NCh, in their trans form,; upon near-UV irradiation the molecule interconverts to a mixture of the *cis* isomer and an hemiketal; b) the anionic surfactant N-Lauroylsarcosine sodium salt, SLSar; c) the hydrophobic antineoplastic agent Paclitaxel, PTX.

Acknowledgements
We thank FCT, FEDER/COMPETE and P2020|COMPETE for financial support through projects POCI-01-0145-FEDER-032351 (PhotoSAN), 2022.05543.PTDC (Smart4Vir), UID/QUI/0081/2020, IMS (LA/P/0056/2020), and UID/QUI/50006/2019. Dmitriy Moreira also acknowledges financial support from FCT through the PhD grant 2021.06067.BD.

References

1. R. C. F. Gonçalves Lopes, O. F. Silvestre, A. R. Faria, M. L. C. do Vale, E. F. Marques and J. B. Nieder, *Nanoscale* 2019, **11**, 5932-5941.
2. D. Moreira, O. Regev, N. Basílio, E. F. Marques, *J. Colloid Interface Sci.* 2023, **650**, 2024-2034.

PROFHET project: Thermodynamic characterization of hydrofluoroethers

POSTER_P3.1 - Phase Equilibria and Fluid Properties

Vojtěch Štejfa[1,*], Štefan Kocian[1], Olga Prokopová[2], Pavel Vrbka[1], Andreas Jäger[3], Václav Vinš[2]

[1] *Department of Physical Chemistry, University of Chemistry and Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic*
[2] *Institute of Thermomechanics of the Czech Academy of Sciences, Dolejškova 5, 182 00 Prague 8, Czech Republic*
[3] *Institute of Power Engineering, Faculty of Mechanical Science and Engineering, Technische Universität Dresden, Helmholtzstraße 14, 01069 Dresden, Germany*

[*] *stejfav@vscht.cz*

Working fluids based on halogenated hydrocarbons are used in a wide variety of areas, including refrigeration and heat transfer applications, surface engineering, or as propellants in sprays. However, many of the substances are phased out step by step due to their negative environmental impact.[1] Chlorofluorocarbons (CFC) and hydrochlorofluorocarbons (HCFC) are already prohibited and per- and polyfluoroalkyl substances (PFAS) are under consideration due to their high global warming potential (GWP) and possible contamination of water and soil. As a consequence, the search for new alternative working fluids is a current topic in many technical areas. CO_2, ammonia, and small hydrocarbons meet some of the technical requirements in addition to being environmentally suitable. However, selection is always the result of a trade-off between safety, environmental considerations, physical and chemical properties.[2]
The PROFHET project aims to investigate the thermodynamic properties of hydrofluoroethers (HFEs) of the Novec fluid family. HFEs are chemically inert, non-flammable, allow direct contact with human skin, have low viscosity, and low atmospheric lifetime. In addition, they have low water solubility and no known health effects. With their high dielectric constant, HFEs can be used for electronics cooling, including immersion cooling of high-performance computers or military electronics. Other applications cover cleaning solvents in magnetic and electronic devices, a protective atmosphere for the thermal treatment of alloys, or working fluids in research, for example, as an admixture in water for the investigation of thermal turbulence.[3]
The goal of the project is to provide a description of a variety of thermophysical properties of selected HFEs, which would enable them to be considered as alternative working fluids in refrigeration and heat transfer applications. These cover the temperature-pressure-density relationship (vibrating tube densimeter),[4] vapour pressure (static method and ebulliometry), isobaric heat capacity (Tian-Calvet calorimetry), and speed of sound. New data will also be provided for viscosity and thermal conductivity. The description of HFEs with various approaches of molecular modelling also takes place: a) *ab initio* calculations of ideal-gas thermodynamic properties, b) COSMO-SAC predictions of pure fluid properties, such as vapour pressure, and c) molecular dynamics simulations of transport properties. All inputs will be used to develop accurate property models valid over wide pressure and temperature ranges consistent for both the liquid and vapour phases, starting with assessment of less accurate while more predictive EoSs such as cubic EoSs and physically sound SAFT-type models and finalizing with the development of multiparameter equations of state (EoS).

Acknowledgments
Financial support from the Czech Science Foundation (GACR No. 24-10191K) is acknowledged.

References

1. Paris Agreement, Paris, 2015, Chapter XXVII, 7.d, 4-18, https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX:22016A1019(01).
2. M. O. McLinden, C. J. Seeton and A. Pearson, *Science* 2020, **370**, 791-796.
3. Z. Wang, V. Mathai and C. Sun, *Nature Communications* 2019, **10**, 3333.
4. O. Prokopová, A. Blahut, J. Hajduch, K. Kučnirová, M. Čenský, A. Aminian, M. Richter and V. Vinš, *Int. J. Thermophys.* 2023, **44**, 139.

Sensitivity analysis of epoxidation reaction effects on partition coefficients based on the UNIFAC model

POSTER_P3.2 - Phase Equilibria and Fluid Properties

Maysa Nesti[1], Bruno Ramos[1], Ricardo B. Torres[1], Ronaldo G. dos Santos[1], Gustavo V. Olivieri[1,*]

[1]*Department of Chemical Engineering, Centro Universitário FEI, São Bernardo do Campo, Brazil*

[*]*gustavo.vo@fei.edu.br*

The epoxidation of soybean oil (SO) is a chemical reaction that produces the epoxidized soybean oil (ESO), a potential candidate for replacement of phthalates (petroleum-based compounds with carcinogenic potential) as plasticizers for polyvinyl chloride (PVC).[1] The industrial conduction of this reaction occurs in a liquid- liquid system. The epoxidation occurs in the organic phase, with the reaction of the double bonds of SO with performic acid (PFA) to generate the oxirane groups that characterize ESO and formic acid (FA). The PFA is generated *in situ* in the aqueous phase, based on the reaction of FA with hydrogen peroxide (HP) in solution with water (W). Therefore, the performance of the reaction system is highly dependent on mass transfer and liquid-liquid equilibrium (LLE) effects, specifically for the components that participate in the main reactions for both phases (PFA and FA). An experimental study from the literature focused on the determination of partition coefficients for FA based on a simplified system containing only SO+W.[2] However, the development of experimental studies to determine the partition coefficients of FA and PFA in more complex systems, considering other substances jointly in the reaction system (PFA, HP, and ESO), becomes more difficult because the measurements would need to be dynamic based on intrinsic reactions occurring, without a phase equilibrium condition being achieved. The literature also presents an estimated correlation for the partition coefficients for PFA based on its structure and considering only the temperature effects,[3] which were employed in the development of kinetic models for this reaction system. The present study aimed to contribute to the estimation of partition coefficients for FA and PFA in systems containing SO, ESO, W, and HP based on the predictive model for the excess Gibbs energy UNIFAC (Universal Quasi-Chemical Functional-group Activity Coefficients). The sensitivity analysis was conducted in the *software* Aspen Plus, considering the effects of the HP-to-W ratio, the ESO-to-SO ratio, the FA-to-(aqueous+organic) ratio, and the PFA-to- (aqueous+organic) ratio, based on typical ranges employed in the epoxidation reaction. The results indicated that the partition coefficients for both FA and PFA are considerably influenced by the composition of the reaction system, being associated with the reaction stage. The partition coefficients of FA and PFA may vary up to 48.8% and 47.0%, respectively, considering the data evaluated in the same temperature conditions. This study can be applied to complement the epoxidation kinetic models considering a thermodynamic model.

Acknowledgments
We kindly thank Centro Universitário FEI for the infrastructure to develop this project and the funding for the Scientific Initiation scholarship.

References

1. S. G. Tan, W. S. Chow, *Polym.-Plas. Techn. Eng.* 2010, **49**, 1581-1590.
2. G. V. Olivieri, T. Cogliano, R. B. Torres, T. Salmi, R. Tesser, V. Russo, M. Di Serio and R. Giudici, *Ind. Eng. Chem. Res.* 2023, **62**, 13825-13836.
3. E. Santacesaria, R. Tesser, M. Di Serio, R. Turco, V. Russo, D. Verde, *Chem. Eng. J.* 2011, **173**, 198–209.

Strategies to increase the solubility of organic redox active materials using thermodynamic principles

POSTER_P3.3 - Phase Equilibria and Fluid Properties

Murilo L. Alcantara[1,*], Dinis O. Abranches[1], Catarina M. S. S. Neves[1], Mara G. Freire[1], Rubén Rubio-Presa[1], Edgar Ventosa[2], João A. P. Coutinho[1]

[1]*Universidade de Aveiro, CICECO – Aveiro Institute of Materials, Portugal*
[2] *ICCRAM – International Research Center in Critical Raw Materials, University of Burgos, Pza. Misael Bañuelos s/n, E-09001 Burgos, Spain.*

[*]*murilo.la@ua.pt*

The solubility of redox-active organic molecules (ROMs) is a critical parameter for increasing energy density and minimizing precipitation in redox flow batteries.[1,2] However, many ROMs exhibit poor solubility due to high melting points and unfavorable intermolecular interactions. This study presents thermodynamic strategies to enhance ROM solubility by modifying molecular structures to lower melting properties and activity coefficients, thereby improving solute-solvent interactions.
A systematic approach using COSMO-RS, previously validated, modeling was employed to evaluate the impact of molecular asymmetry, functional group rearrangement, and the introduction of co-solvents and additives. The results reveal that increasing molecular asymmetry via alkylation or functionalization significantly reduces melting enthalpy, leading to higher solubility. Additionally, co-solvents and specific ion additives can effectively reduce activity coefficients, further enhancing solubility.
The findings suggest that thermodynamic-guided molecular design can substantially improve the solubility of ROMs, enabling the development of higher-energy-density organic batteries. This approach provides a clear framework for the rational selection of ROM structures and solvent systems, offering practical solutions for next-generation redox flow battery technologies.

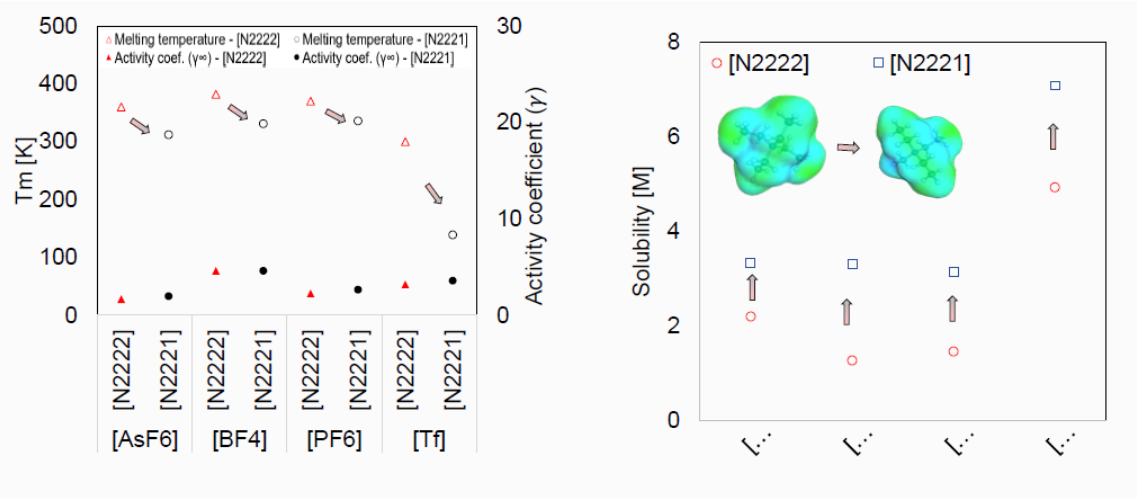


Figure 1: Asymmetry induction by alkylation influencing melting temperature and solubility of solutes.

Acknowledgments
This work was developed within the scope of the project CICECO - Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MCTES (PIDDAC). Additionally, we acknowledge financial support from the European Innovation Council (EIC) MeBattery project under grant agreement 101046742.

References

1. P. Navalpotro, J. Palma, V. Muñoz-Perales, A. Martínez-Bejarano, M. V. Martín-Arroyo, D. P. Taylor, A. Platek-Mielczarek, P. G. Rivano, F. Paratore, E. D. Re and R. Marcilla, *APL Energy* 2025, **3**, 012001.
2. J. P. Wojeicchowski, C. M. S. S. Neves, P. Navalpotro, R. Rubio-Presa, E. Ventosa, R. Marcilla and J. A. P. Coutinho, *J Energy Storage* 2023, **72**, 108584.

Measurement of density and speed of sound in biodiesel-nitrogen mixtures as surrogates for biodiesel-air systems in injection conditions

POSTER_P3.4 - Phase Equilibria and Fluid Properties

Alanderson Arthu Araújo Alves[1,2], Jean-Patrick Bazile[2], Hosiberto Batista de Sant'Ana[1], Filipe Xavier Feitosa[1], Jean-Luc Daridon[*2]

[1]*Grupo de Pesquisa em Termofluidodinâmica Aplicada, Chemical Engineering Department, Universidade Federal do Ceará – UFC, 60455-760, Fortaleza, CE, Brazil*
[2]*Universite de Pau et des Pays de l'Adour, E2S UPPA, CNRS, LFCR, Pau 64000, France*

[*]*jean-luc.daridon@univ-pau.fr*

Biodiesel is a renewable, biodegradable, and environmentally friendly alternative to conventional fossil fuels. Derived from vegetable oils or animal fats, biodiesel has gained prominence as a sustainable energy source that reduces greenhouse gas emissions and enhances energy security. To utilize biodiesel efficiently, it is essential to thoroughly understand its thermophysical properties under conditions relevant to fuel injection systems. Key parameters such as density and speed of sound are crucial for predicting spray dynamics, atomization behavior, and combustion characteristics in engines.

Density directly influences the volumetric flow rate during injection, affecting spray penetration and air-fuel mixing. Meanwhile, the speed of sound significantly impacts compressibility and pressure wave dynamics within injection systems. The properties of biodiesel can change in the presence of surrounding air during injection under high-pressure conditions in diesel engines. Therefore, thermophysical data on such mixtures are vital for evaluating the behavior of biodiesel-air interactions in the engine combustion chamber. While several studies have investigated the thermophysical properties of pure biodiesel and its blends with diesel, there is limited data on biodiesel mixtures with air, which are essential for simulating biodiesel-air systems in injection processes. This study aims to address this gap by providing experimental data on the density and speed of sound in these systems.

However, mixing biodiesel with air under high-pressure, high-temperature conditions poses potential risks of combustion reactions within the experimental setup, making it particularly challenging to conduct experiments using conventional high-pressure devices. Consequently, nitrogen (N2) was selected as an inert substitute for air, and the thermophysical properties were measured in biodiesel-nitrogen mixtures, which serve as surrogates for biodiesel-air systems under injection conditions.

The speed of sound was measured using the pulse-echo technique across an extended range of pressure and temperature in various mixtures formed with two different methyl biodiesels and nitrogen at different concentrations. The biodiesels were sourced from coton and palm oil feedstocks. Additionally, density measurements were conducted under the same conditions for the same mixtures using a U-shaped vibrating tube density meter. By combining the speed of sound and density datasets, the isentropic compressibility and acoustic impedance were calculated. Ultimately, the obtained data were compared to correlation and predictive models to evaluate their predictive capabilities.

Vapor-liquid equilibrium, density, and speed of sound measurements for butan-1-ol or butan-2-ol + oct-1-ene between 313.2-353.2 K

POSTER_P3.5 - Phase Equilibria and Fluid Properties

Kuveneshan Moodley*

Thermodynamics Research Unit, School of Engineering, University of KwaZulu-Natal, Howard College Campus, Durban, South Africa

*moodleyk6@ukzn.ac.za

This study focuses on the thermodynamic properties of mixtures containing butan-1-ol/butan-2-ol with oct-1-ene. The vapor-liquid equilibrium (VLE) behaviors of these systems were measured using the circulation method over a range of temperatures from (313.2 K, 333.2, and 353.2 K) and sub-atmospheric conditions. The pure component vapor pressures correlated well with the literature data. The VLE data was found to be significantly non-ideal. The combined (γ-Φ) method was employed to correlate the VLE data, with the NRTL and UNIQUAC activity coefficient models utilized in combination with the virial equation of state to account for the non-ideality of the liquid phase and the vapor phase, respectively. The measured data was found to be thermodynamically consistent by the Area, Point and Infinite Dilution tests using criteria of D < 10%, Δy <0.01 and I¬i <30 respectively. Prediction of excess enthalpy using simultaneously regressed model parameters for all isotherms provided a reasonable correlation with literature data, confirming the conformity of the VLE results presented.

The densities and speeds of sound of the mixtures were measured in the same temperature range and at atmospheric pressures using an Anton Paar DSA device. Pure component properties correlated well with literature data, along with some mixture properties that were previously measured. Derived property data such as excess volumes were calculated and modelled using standard Redlich-Kister polynomials.

This data has practical implications for the hydrocarbon process industries, where alcohols can be used as an additive, blend stock, or inhibitor.

Solubility of CO_2 in the mixed DBN/ethylene glycol, along with physical properties of unloaded and CO_2-loaded DBN with ethylene glycol

POSTER_P3.6 - Phase Equilibria and Fluid Properties

Behnaz Asadzadeh*, Mohammed Saad, Petri Uusi-Kyyny, Ville Alopaeus

Aalto University, School of Chemical Engineering, Department of Chemical and Metallurgical Engineering, P.O. Box 11000, FI-00076 Aalto, Finland

**Behnaz.Assadzadeh@aalto.fi.*

Excessive CO_2 emissions cause major environmental challenges, such as global warming, extreme weather, and rising sea levels.[1] Chemical absorption methods are the most widely used for removing acid gases from gaseous streams. Solvent-based methods are the most developed CO_2 capture and storage technology due to their widespread commercial application in natural gas purification. To design absorption and desorption processes, experimental data such as CO_2 solubility, kinetic constants, and physical properties such as density and viscosity must be known.[2] A comprehensive understanding of different properties (solubility, density, viscosity) is needed to design and optimize CO_2 capture processes. This also helps to understand the underlying molecular-level phenomena better, as they indirectly affect each of those properties in different ways. Superbases as potential absorbents for CO_2 separation have received a lot of interest. To better understand the mixed behavior of organic solvents and superbase (amidine-alcohol), the solubility values of CO_2 in the mixed 1,5-Diazabicyclo [4.3.0] non-5-ene (DBN)/ ethylene glycol (EG), along with density data of unloaded and CO_2-loaded (DBN) in (EG), were measured. The density of the CO_2-loaded system was determined at three different loading amounts (α = mol CO_2/mol DBN), ranging from 0 to 0.691 for DBN/ EG and temperatures ranging from 293.15 K to 373.15 K. The measured densities of unloaded and loaded systems were correlated using various models[3], and the findings revealed a good agreement between experimental data and calculated models. Furthermore, the viscosities of unloaded mixtures were measured at the same compositions. The viscosity data were correlated using the logarithmic approach. The results were consistent with the experimental results.

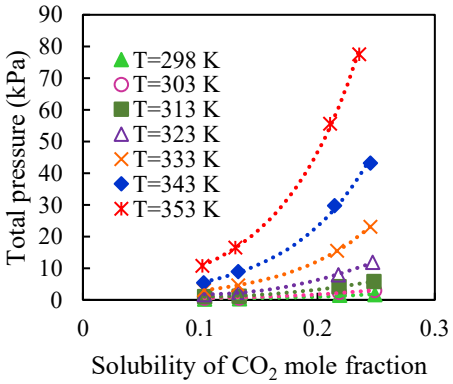


Figure 1: Solubility of CO_2 in DBN/EG mixture at (X_{DBN}=0.50; X_{EG}=0.50) composition.

Acknowledgments
This work was supported by Business Finland, project number 211921. Many thanks to the partners involved in the Veturi CO_2 Capture project for their invaluable feedback and guidance throughout.

References

1. L. Wang, S. Liu, R. Wang, Q. Li, S. Zhang, *Environ Sci Technol* 2019, **53**, 12873-12881.
2. S. Mokraoui, A. Valtz, C. Coquelet, D. Richon, *Thermochim Acta* 2006, **440**, 122-128.
3. D. D. D. Pinto, J. G. M. S.Monteiro, B. Johnsen, H. F. Svendsen, H. Knuutila, *International Journal of Greenhouse Gas Control* 2014, **25**, 173-185.

Refining inconsistent data with stochastic machine learning: The salt effect on the solubility of amino acids

POSTER_P3.7 - Phase Equilibria and Fluid Properties

Christopher A. Piske[1,2], Priscilla G. Leite[2], Mónia A. R. Martins[1], Olga Ferreira[1], João A. P. Coutinho[3], Dinis O. Abranches[3], Simão P. Pinho[1,*]

[1]CIMO-Centro de Investigação de Montanha, LA SusTEC, Instituto Politécnico de Bragança, Campus de Santa Apolónia, Bragança, Portugal
[2]UTFPR – Universidade Tecnológica Federal do Paraná, 84016-210 Ponta Grossa, Brazil
[3]CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Aveiro, Portugal

*spinho@ipb.pt

Aqueous solutions containing electrolytes serve as the natural environment for many biomolecules, playing a crucial role in regulating their structure and physicochemical behavior, which in turn governs various biochemical processes. Understanding the solubility of amino acids, peptides, and proteins in the presence of salts is critical from a biological standpoint, particularly in food and pharmaceutical applications, but also for the development of different extraction and separation processes. Although data on the solubility of amino acids in aqueous electrolyte solutions are available, many inconsistencies can be found, and significant gaps remain, especially for aromatic amino acids and those containing multiple amino or carboxyl groups.
For the most studied amino acids glycine and alanine, a satisfactory number of data points are available for the effect of ions on the solubility of amino acids in water, matching also a large diversity of anions (F^-, Cl^-, Br^-, I^-, NO_3^-, SCN^-, CH_3COO^-, and SO_4^{2-}) and cations (Na^+, K^+, NH_4^+, Ba^{2+}, Ca^{2+} and Mg^{2+}). Unfortunately, too many datasets present big inconsistencies[1-3], as shown in Figure 1, that must be checked and tested.

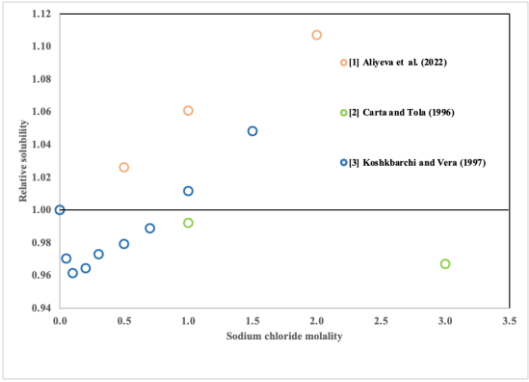


Figure 1: The effect of NaCl on the solubility of glycine in water at 298.2 K.

In this regard, the main purpose of this work is to use stochastic machine learning to assess the experimental uncertainty of the experimental solubility data, opening new pathways to check the reliability and consistency of solubility data. Gaussian processes are applied to that purpose, and machine learning algorithms are developed to analyze the experimental solubility data and predict outcomes for untested conditions.

Acknowledgements
This work was supported by national funds through FCT/MCTES (PIDDAC): CIMO, UIDB/00690/2020 (DOI: 10.54499/UIDB/00690/2020) and UIDP/00690/2020 (DOI: 10.54499/UIDP/00690/2020); and SusTEC, LA/P/0007/2020 (DOI: 10.54499/LA/P/0007/2020), CICECO, UIDB/50011/2020 (DOI 10.54499/UIDB/50011/2020), UIDP/50011/2020 (DOI 10.54499/UIDP/50011/2020) & LA/P/0006/2020 (DOI 10.54499/LA/P/0006/2020.

References

1. M. Aliyeva, P. Brandão, J. R. B. Gomes, J. A. P. Coutinho, O. Ferreira, S. P. Pinho, *Ind. Eng. Chem. Res.* 2022, **61**, 5620.
2. R. Carta, G. Tola, *J. Chem. Eng. Data* 1996, **41**, 414.
3. M. K. Koshkbarchi, J. H. Vera, *Ind. Eng. Chem. Res.* 1997, **36**, 2445.

Improving calculations of vapor-liquid equilibria for hydrogen mixtures using the Peng-Robinson equation of state with quantum-corrections

POSTER_P3.8 - Phase Equilibria and Fluid Properties

Thomas J. Hughes*

Department of Civil and Environmental Engineering, Monash University, Clayton, Victoria, Australia

*Tom.Hughes@monash.edu

Accurate calculations of vapor-liquid equilibrium (VLE) for binary mixtures involving hydrogen and common gases such as nitrogen, methane, carbon dioxide and carbon monoxide are critical for various industrial applications. These include hydrogen liquefaction, carbon capture and storage, synthesis gas production and fuel cell technologies. The phase behaviour of hydrogen in these mixtures significantly influences separation processes, energy efficiency and equipment design, particularly at cryogenic temperatures and high pressures.

Cubic equations of state (EOS), such as the Peng-Robinson (PR) model, offer a practical and computationally efficient approach to modelling VLE and are commonly employed in engineering process simulators used to design processes. These EOS balance accuracy and simplicity, capturing key thermodynamic behaviours with relatively few parameters. Their simplicity makes them advantageous over more complex models, such as molecular-based equations of state, particularly when experimental data are limited. However, there are significant limitations arise when using cubic equations of state to predict the VLE of mixtures containing quantum fluids like H_2.[1]

In this work, the quantum-corrected PR EOS developed by Aasen et al.[2] for mixtures of quantum fluids like H_2 + He is extended to H_2 mixtures with the non-quantum fluids nitrogen, methane, carbon dioxide, and carbon monoxide. The methodology applies a temperature-dependent quantum correction for the covolume parameter mapped from excluded volumes predicted by quantum-corrected Mie potentials for H_2. The quantum correction significantly improves VLE calculations for these industrially relevant mixtures, as illustrated for the N_2 + H_2 binary in Figure 1 where this approach is compared to the default PR EOS. These findings suggest that applying similar quantum corrections for other quantum fluids (e.g., He) in mixtures with non-quantum fluids could enhance phase equilibrium predictions across a broader range of industrially relevant systems, particularly at cryogenic temperatures and/or high pressures.

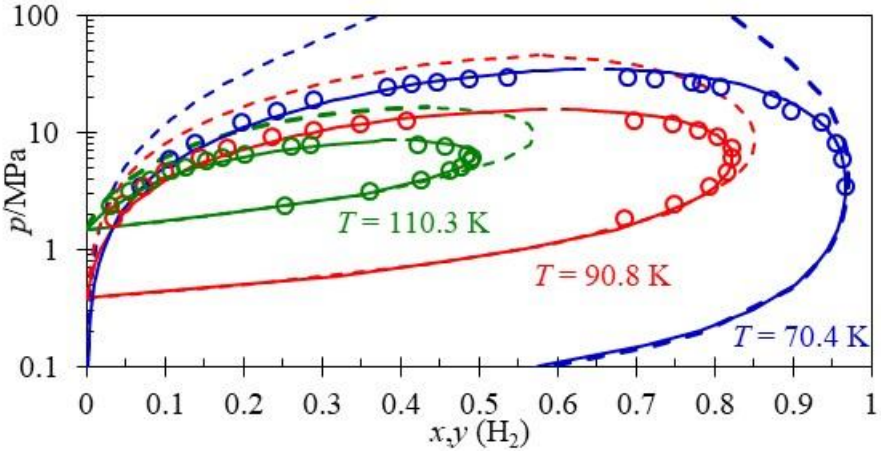


Figure 1: Vapour-liquid equilibrium of N_2 + H_2. Points are data of Streett and Calado,[3] dashed lines are default simulator PR EOS, solid likes PR EOS using the approach of Aasen et al.[2] for hydrogen.

References

1. D. Rowland, T. J. Hughes and E. F. May, *J. Chem. Eng. Data* 2017, **62**, 2799-2811.
2. A. Aasen, M. Hammer, S. Lasala, J.-N. Jaubert and Ø. Wilhelmsen, *Fluid Phase Equilibria* 2020, **524**, 112790.
3. W. B. Streett and J. C. G. Calado, *The Journal of Chemical Thermodynamics* 1978, **10**, 1089-1100.

Supramolecular structures in systems containing halide organic salts: solid – liquid phase equilibria in systems with α,ω-alkanediols

POSTER_P3.9 - Phase Equilibria and Fluid Properties

Mikołaj Więckowski[1,*], Marek Królikowski[1], Kamil Paduszyński[1]

[1]*Chair of Physical Chemistry - Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland*

[*]*mikolaj.wieckowski@pw.edu.pl*

The formation of supramolecular compounds (co-crystals) containing *N*-alkylisoquinolinium bromides and α,ω-alkanediols was discovered during research into the preparation of eutectic phase change materials (ePCMs).[1] These discoveries have been followed up by subsequent studies, of which, in this work, we present analogous systems composed of *N*-alkylquinolinium bromides and α,ω-alkanediols.
This research has been initiated by the synthesis of a series of ionic liquids (ILs), namely *N*-alkylquinolinium bromides with different lengths of aliphatic substituents: [Quin-C_n][Br] for n = 4, 8, 10, 12. The chemical identity of the synthesized salts was then confirmed by nuclear magnetic resonance (NMR) studies. The thermal analysis of the obtained bromides was then carried out, from which the melting point and enthalpy were determined, and the thermal stability of the obtained ILs was also verified. The subsequent section presents the results of solid-liquid phase equilibrium (SLE) studies in binary systems containing the aforementioned ILs and α,ω-alkanediols: 1,6-hexanediol, 1,8-octanediol, 1,10-decanediol and 1,12-dodecanediol. In the case of IL with the shortest aliphatic chain, no change in monotonicity is observed on any liquidus - all pairs of compounds (IL and α,ω-diol) form simple eutectic systems in the temperature range studied. In contrast to the systems with [i-Quin-C_8][Br],[1] the [Quin-C_8][Br] isomer tends to aggregate with all tested α,ω-diols. Comparison of the C_{12}-substituted isomers confirms that the geometry of the cation significantly affects the stoichiometry of the formed intermolecular compounds. Furthermore, this work contains a characterization of binary systems, including a description of thermochemical properties.
According to studies conducted with other ILs, it can be concluded that self-organization in binary systems with α,ω-diols applies to both chlorides and bromides, while for bromides the phenomenon is more evident (Figure 1). The most important structural element determining the possibility of a sustained interaction between IL and α,ω-diol is the matching of the lengths of the lipophilic fragments of both molecules.

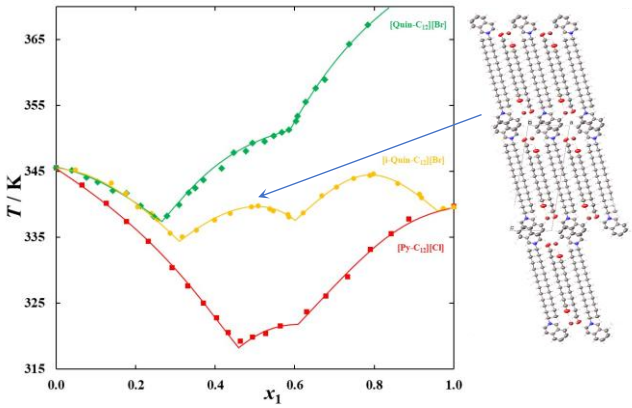


Figure 1: SLE phase diagrams for systems with 1,10-decanediol and: ■– [Py-C_{12}][Cl],[2] ●– [i-Quin-C_{12}][Br],[1] ♦– [Quin-C_{12}][Br], along with crystal structure of ([i-QuinC_{12}][Br])$_1$(1,10-decanediol)$_1$.

Acknowledgments
Studies were funded by POSTDOC PW-V project granted by Warsaw University of Technology under the program Excellence Initiative: Research University (ID-UB). Agreement number: CPR-IDUB/367/Z01/Z10/2023

References

1. M. Więckowski, P. Guńka, N. Świtalska and M. Królikowski, *J. Mol. Liq.* 2024, **398**, 1-11.
2. M. Więckowski, M. Królikowski, M. Żywólko, Ł. Scheller and M. Dzida, *J. Mol. Liq.* 2023, **379**, 121660.

Green eutectic formulations for antimalarial drug delivery

POSTER_P3.10 - Phase Equilibria and Fluid Properties

Nathalie L. Araújo[1], Olga Ferreira[1], João A. P. Coutinho[2], Simão P. Pinho[1], and Mónia A. R. Martins[1,*]

[1]CIMO, LA SusTEC, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal
[2]Department of Chemistry, CICECO – Aveiro Institute of Materials, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal

**moniamartins@ipb.pt*

Malaria, a life-threatening disease transmitted by infected mosquitoes, remains a major health issue, particularly in sub-Saharan Africa, where it claims hundreds of thousands of lives each year. One of the primary treatments for malaria involves artemisinin-based combination therapies, which have proven highly effective in managing the disease. However, these therapies face a significant challenge due to the low water solubility of the most common active pharmaceutical ingredients (APIs) used, such as artemisinin, pyrimethamine, and quinine. This limitation reduces their absorption by the body, diminishing their therapeutic efficacy.
The objective of this work is to explore green excipients to enhance the solubility and bioavailability of common drugs used in the malaria treatment through the formation of eutectic mixtures. First, predictive tools like COSMO-RS and the Hansen Solubility Parameters are used to model interactions between these molecules and a range of natural solvents. Then, alternative approaches are explored, combining drug extraction from natural sources with the formation of eutectics using natural green excipients, allowing direct application without complex purification steps. The formation of eutectics (Figure 1), particularly with terpenes and their mixtures, shows promise in improving the solubility of the studied compounds. The approaches investigated align with the principles of green chemistry, promoting more environmentally friendly solutions for the pharmaceutical industry.

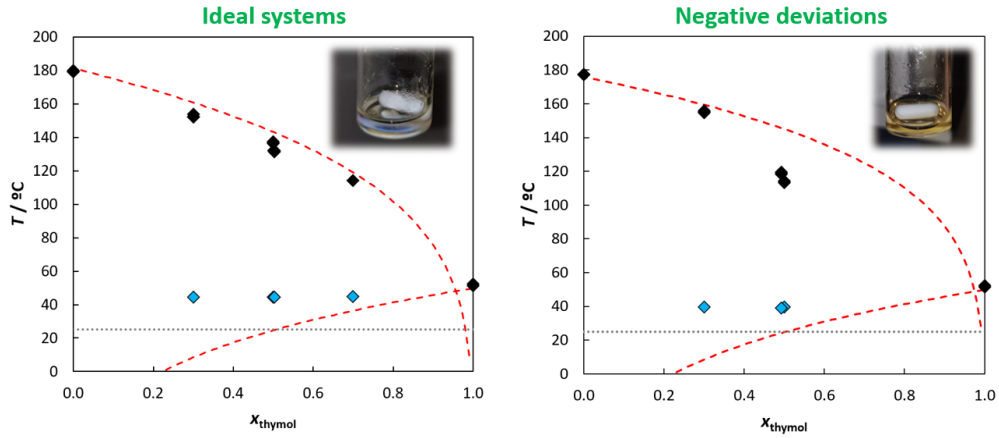


Figure 1: Solid–liquid phase diagrams of mixtures composed of terpenes and antimalarial drugs: ♦, melting temperatures; ♦, eutectic temperatures; ---, ideal solubility lines; and ····, T = 298.15 K.

Acknowledgments
This work was supported by national funds through FCT/MCTES (PIDDAC): CIMO, UIDB/00690/2020 (DOI: 10.54499/UIDB/00690/2020) and UIDP/00690/2020 (DOI: 10.54499/UIDP/00690/2020); and SusTEC, LA/P/0007/2020 (DOI: 10.54499/LA/P/0007/2020). This work was also developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 (DOI 10.54499/UIDB/50011/2020), UIDP/50011/2020 (DOI 10.54499/ UIDP/50011/2020) & LA/P/0006/2020 (DOI 10.54499/LA/P/0006/ 2020), financed by national funds through the FCT/MCTES (PIDDAC).

Solubility of nitrous oxide and carbon dioxide in an aqueous mixture of 2-(Dimethylamino)ethanol + N-Methyl-1,3-propanediamine

POSTER_P3.11 - Phase Equilibria and Fluid Properties

Juan D. Arroyave[1], Alejandro Moreau[1], M. Carmen Martín[1], J.P Martin Trusler[2], Xavier Paredes[1,*]

[1]*TermoCal Research Group, Research Institute on Bioeconomy, University of Valladolid, Valladolid (Spain)*
[2]*Department of Chemical Engineering, Imperial College London, London (UK)*

[*]*xavier.paredes@uva.es*

Aqueous Monoethanolamine (MEA) scrubbing, while a mature post-combustion CO_2 capture technology, suffers from significant operational drawbacks including corrosivity, high maintenance demands, poor thermal stability, a substantial regeneration energy penalty (~4 GJ/t-CO_2), and reactivity with contaminants like NO_x and SO_2. Consequently, recent research has focused on alternative chemical and physical solvents to mitigate these limitations. Blended amine systems, such as those containing 2-(Dimethylamino)ethanol (DMAE) and N-Methyl-1,3-propanediamine (MAPA), have emerged as promising candidates due to their potential for improved CO_2 absorption capacity, high cyclic capacity and moderate environmental impact[1]. Reactivity of a tertiary amine as DMAE with CO_2 in aqueous media could be further improved by mixing with an alkyl amine with multiple amino groups. For example, MAPA, a diamine, is known to enhance CO_2 reactivity by nearly 15 times compared to MEA[2]. However, limited Vapor-Liquid Equilibrium (VLE) data exists for these kinds of blends. For this reason, this study aims to expand the thermodynamic understanding of the aqueous DMAE (30 wt%) + MAPA (10 wt%) system by investigating its VLE with CO_2 and N_2O at temperatures of 313.15, 333.15, 363.15, and 393.15 K. The selection of this composition was guided by two key factors: limiting solvent viscosity to below 10 mPa·s and minimizing absorption heat by ensuring the MAPA concentration remains lower than that of the tertiary amine.

The physical solubility of CO_2 in this system was determined using the N_2O/CO_2 analogy. Physical solubility measurements of N_2O were conducted using a monobloc equilibrium cell with a sapphire window, covering bubble pressures from 1 to 5 MPa[3]. The expanded relative uncertainty of the N_2O solubility, expressed in molality, was estimated to be 0.8% (k = 2) and Henry constant was derived using a Krichevsky-Ilinskaya (KI) analysis. Accurate volumetric data, essential for mass balance calculations, were obtained by measuring the density of the aqueous amine solution with an automated system based on a vibrating tube densimeter (Anton Paar DMA 512P) over a temperature range of (273.15 to 393.15) K and pressures up to 70 MPa, with an expanded relative uncertainty of 0.1% (k = 2)[4]. The densimeter was calibrated with water and under vacuum. Density data were correlated using a modified Tammann-Tait equation. For chemical solubility measurements (CO_2-loading, expressed as mol-CO_2/mol-amine), a static-isochoric Van Ness-type apparatus was employed. This apparatus has a maximum working pressure of 10 MPa and operating temperature range of (313.15 to 393.15) K, with an expanded relative uncertainty of (0.5 to 4) % (k = 2). Finally, the speciation profile, pH, and heat of CO_2 absorption were predicted using modified Kent-Eisenberg, empirical soft, and Deshmukh-Mather models.

Acknowledgments
Juan D. Arroyave has been funded by the call for predoctoral contracts UVa 2021. This work was funded by the Ministry of Science and Innovation and the European Union (project PID2021-125749OB-I00).

References

1. P. Brúder, K. G. Lauritsen, T. Mejdell and H. F. Svendsen, *Chem Eng Sci* 2012, **75**, 28-37.
2. I. M. Bernhardsen, A. A. Trollebø, C. Perinu and H. K. Knuutila, *J. Chem. Thermodyn.* 2019, **138**, 211-228.
3. Q. Chen and J. P. M. Trusler, *Chem Eng Sci* 2024, **293**, 120038.
4. J. J. Segovia, O. Fandiño, E. R. López, L. Lugo, M. C. Martín and J. Fernández, *J. Chem. Thermodyn.* 2009, **41**, 632-638.

Density measurements of hydrogen + propane and hydrogen + butane mixtures for decarbonizing the gas grid

POSTER_P3.12 - Phase Equilibria and Fluid Properties

Xavier Paredes, Alejandro Moreau*, Fredy Vélez, Iván M. Zerón, José J. Segovia

TERMOCAL Research Group, Research Institute on Bioeconomy, University of Valladolid, Valladolid, Spain

**alejandro.moreau@uva.es*

The European Union promotes different actions such as making a cleaner energy system using renewable energy and increasing energy efficiency, to tackle climate change and environmental degradation and the final purpose of decarbonizing energy systems.
In the case of the gas grid, decarbonization strategies include, for example, the use of hydrogen-enriched natural gas or pure hydrogen as well as the introduction of biomethane along with carbon capture and storage. Our research group has been involved in different European research projects with the purpose of contributing to fulfil some gas industry needs such as thermodynamic and thermophysical properties of new energy gases, due to the lack of these accurate data and the requirement of these data to improve the reference equations of state for them.
Our objective is to provide accurate density data of mixtures of hydrogen and hydrocarbons present in gas natural. In this contribution, density data of (hydrogen +butane) and (hydrogen + propane) mixtures are reported in the gaseous region.
The density of these mixtures was determined by means of a single sinker densimeter with magnetic suspension coupling. The technique provides density data in the in the range (10 to 2000) kg/m^3, with a relative expanded uncertainty better than 0.05 %. The technique operates based on the Archimedes' principle and the magnetic suspension coupling system enables to determine the buoyancy force on a sinker immersed in the medium whose density is going to measure.
Densities for (hydrogen + propane) mixtures at compositions $x_{C_3H_8}$ = 0.15; 0.20 and 0.30 were measured in the temperature and pressure ranges from 253.15 K to 333.15 K and from 2 bar to 35 bar, respectively. On the other hand, (hydrogen + butane) mixtures at compositions $x_{C_4H_{10}}$ = 0.02; 0.05 and 0.10 were measured in the temperature and pressure ranges from 253.15 K to 333.15 K and from 2 bar to 120 bar, respectively.
Finally, the experimental data were compared with the GERG 2008 equation of state[1] which is recommended for calculating properties for natural gas and currently serves as the ISO standard (ISO 20765-2)[2]. It estimates the thermophysical properties in the entire fluid region for natural gases and related mixtures of up to 21 components. However, it has only been validated using limited test conditions for hydrogen enriched natural gas and new accurate data are required.

Acknowledgments
This work was funded by EURAMET, EMPIR project number: 20IND10 Decarb.

References

1. O. Kunz and W. Wagner, *J. Chem. Eng. Data* 2012, **57**, 3032–3091.
2. ISO 20765-2. *Natural gas — Calculation of thermodynamic properties — Part 2: Single-phase properties (gas, liquid, and dense fluid) for extended ranges of application*, 2015.

Effect of lithium salts on the phase equilibrium of the water + 1-propanol binary system at 40°C

POSTER_P3.13 - Phase Equilibria and Fluid Properties

María Dolores Saquete*, Nuria Boluda-Botella, Alicia Font, Aida Tovar, Vicente Gomis

University of Alicante. PO Box 99 E-03690, Alicante (Spain)

md.saquete@ua.es

Demand for lithium-ion batteries reached annual growth rates of 24% between 2015 and 2018[1], mainly due to transportation applications, and is projected to increase by 16% after 2025, with lithium carbonate demand exceeding 800,000 tonnes in 2025 and two million tonnes in 2028[2]. Lithium is extracted from continental brines[3] and from pegmatite mining[4]. Due to the continued increase in demand and its rising cost, other minority sources such as marine brines are beginning to attract interest in countries, with extensive coastal areas such as Alicante, which has several salt companies.

This study aims to contribute to the sub-product recovery processes development that enable large-scale lithium purification and production. To achieve this, it is essential to fully define the thermodynamic equilibrium of mixtures of water+ alcohol+ lithium salt, with a predominance of brine ions, such as chloride, sulfate, carbonate, and nitrate. The final salt purification processes require a washing step with an organic solvent in which they are poorly soluble. To increase the sustainability of the process, a short-chain alcohol of renewable origin (1-propanol), fully miscible with water, will be included in the equilibrium. Temperature increases the solubility of salts, which can favor the appearance of a region of insolubility in the water-1-propanol binary in these saline equilibria. In this work, the water-1-propanol equilibrium systems with the salts LiCl, Li_2SO_4, $LiNO_3$ and Li_2CO_3 have been determined at 40°C.

The ternary systems water + 1-propanol + $LiNO_3$ or Li_2CO_3 did not split into two liquid phases. The ternary systems water + 1-propanol + LiCl or Li_2SO_4 showed the appearance of an insolubility region.

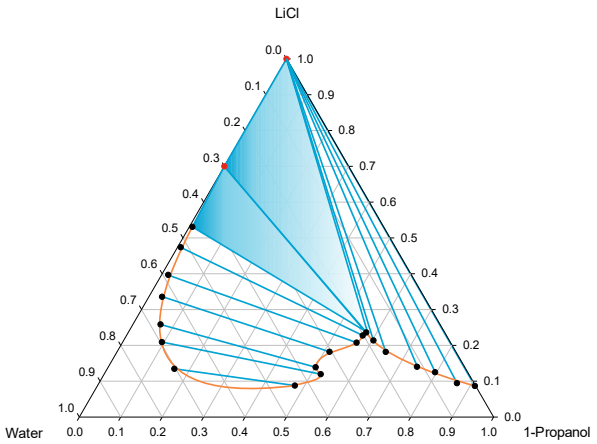


Figure 1: The ternary systems water + 1-propanol + LiCl at 40°C

Acknowledgments

The authors wish to thank the Spanish Ministry of Science, Innovation and Universities (PID2021-126990NB-I00) and regional government Generalitat Valenciana (CIAICO/2021) for the financial support to the projects.

References

1. A. Yáñez-Fernández, M. J. Inestrosa-Izurieta, J. I. Urzúa, *Desalination* 2011, **517**, 115269.
2. https://www.millenniallithium.com/corporate/about-us/
3. F. Meng, J. McNeice, S. S. Zadeh, A. Ghahreman, *Null* 2021, **42**, 123-141.
4. P.W. Gruber, P. A. Medina, G. A. Keoleian, S. E. Kesler, M. P. Everson, T. J. Wallington, *Journal of Industrial Ecology* 2011, **15**, 760-775.

Molecular dynamics approach to solubility of amino acids in aqueous salt solutions

POSTER_P3.14 - Phase Equilibria and Fluid Properties

Zuzana Součková[1,*], Magdalena Bendová[1] Jan Heyda[1], Simão P. Pinho[2]

[1]*UCT Prague, Faculty of Chemical Engineering, Department of Physical Chemistry*

[2] *Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal*

[*]*souckovu@vscht.cz*

The solubility of biomolecules in aqueous electrolyte solutions plays a crucial role in both nature, biochemistry, biotechnology and in fundamental research. Salts (electrolytes) significantly influence the physico-chemical properties of solutes, particularly affecting their chemical potential, i.e., they affect their solubility. These effects are salt-specific, following the Hofmeister series of ions:[1]

$SO_4^{2-} > F^- > Cl^- > NO_3^- > I^- > SCN^-$, $NH_4^+ > Cs^+ > K^+ > Na^+ > Ca^{2+} > Mg^{2+}$.

On one end of the series are strongly hydrated, high charge density anions (e.g., SO_4^{2-}), which decrease solubility of the biomolecule, promoting a salting-out effect. On the other end are weakly hydrated anions of low charge density (e.g., SCN^-), which increase the biomolecule's solubility.

Despite extensive and long-standing research into salt-specific effects in ion–biomolecule interactions, a detailed and quantitative understanding of these effects remains incomplete. This lack of a well-supported microscopic picture presents a critical challenge in fields such as biochemistry, pharmaceuticals, and medicine. Molecular dynamics simulations combined with statistical thermodynamic approaches (such as the Kirkwood-Buff theory) offer valuable insights into these complex interactions and the quantitative determination of thermodynamic effects.[2,3]

Understanding the ion-specific salting-out effect on biomolecules in aqueous solutions often relies on amino acid and dipeptides as model compounds.[4] In this study, we performed molecular dynamics simulations of N-acetyl glycine and the dipeptide diglycine in aqueous solutions containing a variety of salts: Na_2SO_4, K_2SO_4, $CaSO_4$, $MgSO_4$, and $(NH_4)_2SO_4$. For each system, we analysed the hydration structures and salt distributions around the biomolecules and determined the extent of the preferential ion binding. Salting-out constants were calculated and compared with available experimental data. Additionally, we compared data from systems with salts containing the same cation but different anions (NaCl, KCl, $CaCl_2$, $MgCl_2$, and NH_4Cl) to further explore ion-specific effects. Such a comparison provides a better understanding of how SO_4^{2-} and Cl^- anions interact with biomolecules and reveals the way in which different cations influence these interactions in aqueous solutions.

Acknowledgments

This work is supported by the project "The Energy Conversion and Storage", funded as project No. CZ.02.01.01/00/22_008/0004617 by Programme Johannes Amos Commenius, call Excellent Research and Specific university research – grant No. A1_FCHI_2025_001.

References

1. H. I. Okur; J. Hladílková; K. B. Rembert; Y. Cho; J. Heyda; J. Dzubiella; P. S. Cremer; P. Jungwirth, *The Journal of Physical Chemistry B* 2017, **121**, 1997.
2. K. B. Rembert; J. Paterová; J. Heyda; C. Hilty; P. Jungwirth; P. S. Cremer, *Journal of the American Chemical Society* 2012, **134**, 10039.
3. L. I. N. Tomé; S. P. Pinho; M. Jorge; J. R. B. Gomes; J. A. P. Coutinho. *The Journal of Physical Chemistry B* 2013, **117**, 6116.
4. G. Pérez-Sánchez; Y. S. Santos; O. Ferreira; J. A. P. Coutinho; J. R. B. Gomes; S. P. Pinho, *Journal of Molecular Liquids* 2020, **310**, 113044.

The influence of carbon chain length on hydrotropic effect using carbamazepine as a model compound

POSTER_P3.15 - Phase Equilibria and Fluid Properties

Isabella W. Cordova[1,2,3], Dinis O. Abranches[1], Olga Ferreira[2,3], Simão P. Pinho[2,3], João A. P. Coutinho[1*]

[1]CICECO – Aveiro Institute of Materials, University of Aveiro, 3810-193, Aveiro, Portugal
[2]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, 5300-253, Portugal
[3]Laboratório para a Sustentabilidade e Tecnologia em Regiões de Montanha, Instituto Politécnico de Bragança, 5300-253, Portugal

*jcoutinho@ua.pt

The low solubility of drug and drug-like compounds in aqueous solutions remains a major challenge in pharmaceutical applications, affecting purification, formulation, and bioavailability[1]. Hydrotropes can help increase the aqueous solubility, being a promising alternative to traditional organic solvents. This study investigates the hydrotropic effect of eleven sodium salts with different carbon chain lengths. The selected model solute was carbamazepine due to its non-dissociative behavior in aqueous solutions, presenting a pH-independent solubility in water, eliminating the influence of pH variations on the assessment of hydrotropic effects. The Conductor-like Screening Model for Realistic Solvents (COSMO-RS), a quantum chemistry-based equilibrium thermodynamics model, was used to assess the apolarity of each hydrotrope. The Setschenow constant was calculated to evaluate hydrotropic mechanisms in the dilute region, where hydrotrope self-association is negligible.

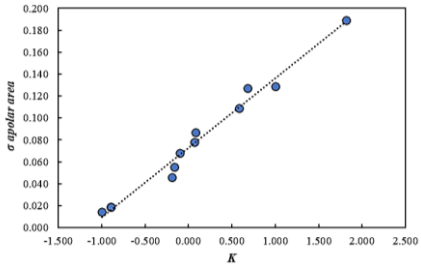


Figure 1: Linear correlation between σ apolar areas obtained with COSMO-RS and Setschenow constants for several sodium salts.

The solubility curves indicate a salting-out effect for shorter carbon chains (with zero or one carbon), while longer chains exhibit hydrotropic behavior. From Figure 1, the Setschenow and COSMO-RS sigma-profile analysis revealed that apolarity-driven interactions govern the hydrotropic effect as postulated by the cooperative hydrotropy model[2,3], suggesting a common underlying mechanism for salting-in and salting-out effects. Further analysis using the Shimizu model and NMR analysis can provide more insights into these hydrotropic systems.

Acknowledgments
The authors are grateful to the Foundation for Science and Technology (FCT, Portugal) for financial support through national funds FCT/MCTES (PIDDAC) to CIMO (UIDB/00690/2020 and UIDP/00690/2020) and SusTEC (LA/P/0007/2020) and CICECO-Aveiro Institute of Materials, UIDB/50011/ 2020 & UIDP/50011/2020. I. W. Cordova is grateful to FCT for her contract 2022.12407.BD.

References

1. S. Soltanpour and A. Jouyban, *J Solution Chem* 2011, **40**, 2032-2045.
2. B. P. Soares, D. O. Abranches, T. E. Sintra, A. Leal-Duaso, J. I. García, E. Pires, S. Shimizu, S. P. Pinho and J. A. P. Coutinho, *ACS Sustain Chem Eng* 2020, **8**, 5742-5749.
3. P. Bauduin, A. Renoncourt, A. Kopf, D. Touraud and W. Kunz, *Langmuir* 2005, **21**, 6769-6775.

Thermophysical properties, dissociation and partitioning of chiral imidazolium-based chloride salts in water-octanol systems

POSTER_P3.16 - Phase Equilibria and Fluid Properties

Magdalena Bendová*[1,2], Jan Heyda[1], Joanna Feder-Kubis[3], Martin Melčák[1], Jakub Polák[1,]

[1]University of Chemistry and Technology, Prague, Technická 5, CZ-166 28 Prague 6
[2]Institute of Chemical Process Fundamentals of the CAS, v.v.i., Rozvojová 135/1, CZ-165 02 Prague 6,
[3]Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, PL-50-370 Wrocław

*bendovam@vscht.cz

Although aqueous solutions of organic and inorganic compounds—ionic liquids included—are among the most extensively studied systems in physical chemistry, our understanding of solute–solvent interactions at the molecular level, particularly between ionic liquid ions and water, remains incomplete. These systems are not only of fundamental interest but also of growing practical relevance, as the properties of ionic liquids can be tuned both structurally and through the addition of appropriate molecular solvents such as water or alcohols.

In our previous work,[1] we investigated the volumetric and transport properties of aqueous solutions of several members of a homologous series of 1-alkyl-3-[(1R,2S,5R)-(–)-menthoxy-methyl]imidazolium chlorides. Combining experimental measurements with molecular dynamics (MD) simulations, we aimed to elucidate the solvation and dissociation behavior of these chiral organic salts. Experimental data—including volumetric, osmometric, thermal, and transport measurements—provide valuable insight into the solution chemistry of these systems. MD simulations complement this by offering molecular-level perspectives and enabling validation of bulk properties against experimental observations.

In this contribution, we extend this approach to the study of water-saturated octanol solutions of two representative salt from the series, 1-alkyl-3-[(1R,2S,5R)-(–)-menthoxymethyl]imidazolium chlorides (alkyl=butyl, nonyl). Using both experimental methods and MD simulations, we explore their volumetric and transport properties and octanol-water partitioning. Beyond their fundamental significance in co-solvent systems, these results enhance our understanding of octanol–water partitioning and support environmental fate assessments of such chiral ionic liquids.

Acknowledgments
This work is supported by the project "The Energy Conversion and Storage", funded as project No. CZ.02.01.01/00/22_008/0004617 by Programme Johannes Amos Commenius, call Excellent Research.
MEYS e-INFRA CZ (ID:90140) and National Science Centre, Poland (Grant No. UMO-2020/37/B/NZ9/04201) are greatly acknowledged.

References

1. M Bendová, J Heyda, Z Wagner, J Feder-Kubis, J Polák, T Tankam, and A Sýkorová, *J. Mol. Liq.* 2023, **378**, 121591.

Moisture-induced phase transitions in reciprocal quaternary salt mixtures

POSTER_P3.17 - Phase Equilibria and Fluid Properties

Shaoheng Wang[1*], Sebastiaan Godts[2], Amelie Stahlbuhk[1], Michael Steiger[1]

[1]*Department of Chemistry, University of Hamburg, Hamburg, Germany*
[2]*Royal Institute for Culture Heritage (KIK-IRRA), Brussels, Belgium*

[*]*shaoheng.wang@uni-hamburg.de*

The interaction between salt mixtures and water vapor is commonly observed in both natural environments and industrial applications, including atmospheric aerosol particles, thermal heat storage materials, and the production of food and pharmaceuticals.[1-3] Moisture-induced phase transitions are of significant interest, as they play a crucial role in these applications and can markedly affect the stability of materials. Various techniques have been employed to investigate the phase behavior of salt mixtures upon exposure to water vapor.[4,5] Studies have shown that the formation of double salts and mutual deliquescence can occur in the salt mixtures before the individual components reach their deliquescence point.[2,4] In reciprocal quaternary salt system, solid-solid transformation from metastable pair to thermodynamically stable pair, such as $NaCl + (NH_4)2SO_4 \rightarrow Na_2SO_4 + NH_4Cl$, may also proceed via interaction with water vapor.[5]

In this study, water vapor sorption, Raman spectroscopy, and environment scanning electron microscope (ESEM) were combined to investigate moisture-induced phase transitions in two reciprocal salt systems $Na^+–Cl^–K^+–NO_3^-//H_2O$ and $Na^+–Cl^–NH_4^+–SO_4^{2-}//H_2O$. The results reveal that the mutual deliquescence relative humidity (MDRH) of ternary salt mixtures are lower than that of the corresponding pure salts. Furthermore, we propose that the solid-solid transformation from metastable pair to thermodynamically stable pair, e.g. $KCl + NaNO_3 \rightarrow NaCl + KNO_3$ initiate at low humidity though the formation of a water film at the grains interface, as demonstrated by Figure 1. These finding highlight the critical role of interfacial water films in facilitating complex phase transition in salt mixture, with implications for both environmental process and material stability.

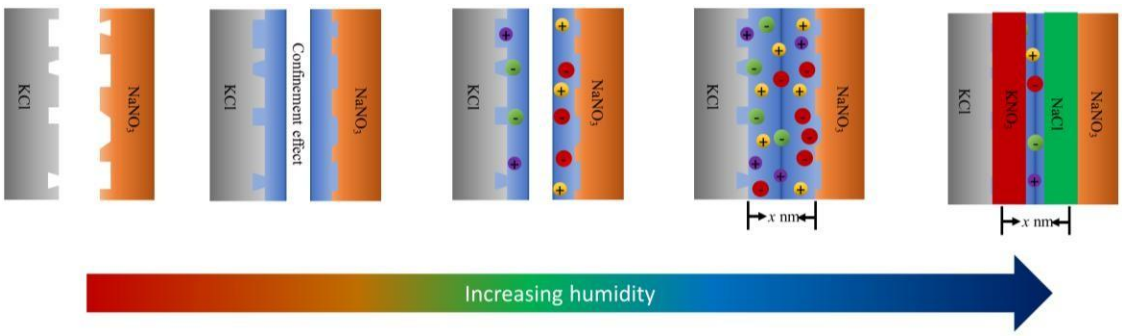


Figure 1: Mechanism of the phase transition from metastable pair $KCl + NaNO_3$ to stable pair $NaCl + KNO_3$

References

1. B.J. Finalyson-Pitts. *Chem. Rev.* 2003, **103**, 4801-4822
2. R Hamze et al. *J. Energy Storage* 2024, **86**, 11404-11418
3. L.J. Mauer and L.S. Taylor. *Annu. Rev. Food. Sci. Technol*. 2010, **1**, 41-63
4. AK Salameh et al. *Pharm. Res.* 2005, **22**, 318-324
5. J Rissler et al. *Environ. Sci. Technol.* 2023 **57**, 2706-2714

Solvent selection methods in aromatic extraction processes towards optimal and sustainable design choices

POSTER_P3.18 - Phase Equilibria and Fluid Properties

Nivaar Brijmohan[1*], Kuveneshan Moodley[1], Caleb Narasigadu[2]

[1]*University of KwaZulu-Natal (UKZN)*
[2]*North-West University (NWU)*

[*]*brijmohann@ukzn.ac.za*

A novel process decision-making framework was developed that simultaneously considers all aspects of process systems engineering, applied to solvent extraction processes. Computer-Based Molecular Design (CAMD) of solvents using group contribution methods and Artificial Neural Network (ANN) Quantitative Structure Property Relationship (QSPR) models were amalgamated with Health, Safety, and Environmental (HSE) impacts using a rating-based risk assessment method. The ANN developed was found to serve as an effective supplement to group contribution methods in screening potential solvents. This QSPR model uses 31 descriptors as input with absolute average deviations of 0.23 and 0.19 for each pair of binary interaction parameters. Validation of CAMD results were done by conducting experimentally measured liquid-liquid equilibrium (LLE) compositions for the systems *n*-heptane + toluene + (butane-1,4-diol or glycerol) as well as *n*-nonane + o-xylene + (butane-1,4-diol or glycerol). The influence of 2-methyl-2,4-pentanediol on solvent capacity was determined by LLE experimental data for the quaternary system *n*-heptane + toluene + (butane-1,4-diol or glycerol) + 2-methyl-2,4-pentanediol. All ternary systems studied were found to exhibit type 2 LLE behavior and were correlated with the NRTL and UNIQUAC models. Economic comparisons were conducted for the proposed co-solvent mixtures against that of conventional solvents used for this application. Indicators such as energy consumption, capital costs, operating costs and total annual costs were used to make an assessment with process simulations performed in ASPEN Plus V10. The results indicated that the co-solvent mixtures may offer benefits in reducing total annual cost. The energy intensity of the process varied between 1000 – 1400 kJ/kg. Capital costs ranged between 5.8 – 6.2 million dollars, and total annual costs between 2.4 – 2.6 million dollars. The outcome of the work was a platform based on systematic methods where solvent extraction processes are optimized by simultaneously considering interlinking steps of molecular design to the economics of large-scale processes in the context of sustainable development.

Influence of pressure and temperature on the physical properties of crude oil emulsions

POSTER_P3.19 - Phase Equilibria and Fluid Properties

Ana C.S. da Cunha[1,2,*], Juliana O. Bahú[1], Suelen G. Trindade[1], Sérgio A. M. V. Boas[1], Carlos E. Perles[1], Vanessa C. B. Guersoni[1], and Marcelo S. de Castro[1,2]

[1]Centro de Estudos de Energia e Petróleo (CEPETRO), Universidade Estadual de Campinas (UNICAMP), Campinas, Brazil
[2]Faculdade de engenharia mecânica, Universidade Estadual de Campinas (UNICAMP), Campinas, Brazil

[*]a289343@dac.unicamp.br

The oil and gas industry has developed significant technical and scientific advancements, achieving the level of maturity observed today. In the field of flow assurance, this progress has also been consolidated, particularly regarding water/oil (W/O) emulsions, characterized by an unstable thermodynamic system with two immiscible liquids.[1] These systems can reduce production efficiency and the lifespan of pipelines, causing operational and economic concerns for the sector.[2] However, few studies have explored the impact of pressure and temperature variations on emulsions during flow from the reservoir to the surface.[3] This research investigates how high pressures and temperatures affect emulsions' physical properties (density and viscosity). Therefore, the importance of this research lies in analyzing the behavior of emulsions under conditions similar to those found in oil fields, along the lifting path from the reservoir to the surface unit. Initially, density measurements were conducted on crude (dead) and recombined (live) oil samples under different pressure and temperature conditions. Hydrated and dehydrated dead crude oil samples were analyzed using a high-pressure densimeter (Anton Paar, mPDS 5) at 1 and 250 bar, with a 5 - 115°C temperature range. Subsequently, oils were recombined with methane gas (5 m^3/m^3 of GOR) in a recombination cell (Sanchez Technologies, RC 1500/1000) and subjected to further density analyses at pressures from 40 to 250 bar and temperatures in the range of 50 - 82 °C, with varying water-cut in the emulsions. The results for dead crude oil showed a reduction in density with increasing temperature and an increase in density with increasing pressure, indicating a compressibility of crude oil under high pressures. This research provides valuable insights for establishing correlations between pressure, temperature, and the physical properties of petroleum emulsions, contributing to optimizing flow assurance and enhanced oil production efficiency.

Acknowledgements
We gratefully acknowledge the support of EPIC – Energy Production Innovation Center, hosted by the University of Campinas (UNICAMP) and sponsored by FAPESP – São Paulo Research Foundation (2017/15736-3), scholarship A.C.S. da C. (2024/00038-2), J.O.B. (2022/09052-2), and S.G.T (2024/13886-1). We acknowledge the support and funding from Equinor Brazil and the support of ANP (Brazil's National Oil, Natural Gas and Biofuels Agency) through the R&D levy regulation - Project reference number 24177-8. Acknowledgements are extended to the Center for Energy and Petroleum Studies (CEPETRO), School of Mechanical Engineering (FEM), and (other Institutes of UNICAMP or other University).

References

1. F. Leal-Calderon, V. Schmitt and J. Bibette, *Emulsion Science: Basic Principles*, Springer Science & Business Media, New York, 2007.
2. X. Hao, E. Yogarajah, M. Shimokawara, Y. Kato, R. Kitamura and N. Hiroyoshi, *Energy Fuels* 2024, **38**, 979-994.
3. M. Mohammadpour, M. R. Malayeri, Y. Kazemzadeh and M. Riazi, *Scientific Reports* 2023, DOI: 10.10'38/s41598-023-42886-5.

Solubility of olive oil phenolic compounds in green solvents

POSTER_P3.20 - Phase Equilibria and Fluid Properties

Mariana Vale[1], Aline Zambom[1,2], Felipe Krüger[1], Mónia A. R. Martins[1], João A. P. Coutinho[2], Simão P. Pinho[1], António M. Peres[1], Olga Ferreira[1,*]

[1]*CIMO, LA SusTEC, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal*
[2]*CICECO, Aveiro Institute of Materials, Complexo de Laboratórios Tecnológicos, Universidade de Aveiro, Campus Universitário de Santiago, Aveiro, Portugal*

**oferreira@ipb.pt*

The production of olive oil generates various by-products that are rich in phenyl alcohols, secoiridoids, phenolic acids and aldehydes, flavonoids, and other bioactive compounds. Due to their diverse biological activities, these compounds have promising potential as functional additives in the food, pharmaceutical, and cosmetics industries.[1] However, data on their solubility in water and common volatile organic solvents, as well as partitioning behavior—critical for optimizing extraction, purification, and formulation processes—remains very limited.[2]

In this study, the solubility of tyrosol (a phenyl alcohol) was experimentally determined in ten pure solvents and five aqueous binary solvent mixtures, using acetone, ethanol, 2-propanol, 1,3-butanediol, and 1,3-propanediol as co-solvents. Measurements were performed at 298 K using the analytical isothermal shake-flask method. Additionally, the COnductor-like Screening MOdel for Real Solvents (COSMO-RS)[3] using the default conformer distribution was employed to predict the solubility of tyrosol, hydroxytyrosol, and oleuropein in a wide range of pure organic solvents varying in polarity and functional groups, as well as in aqueous binary solvent mixtures. For tyrosol, the influence of solvent conformers and their apolar, hydrogen-bond donor, and acceptor characteristics on COSMO-RS predictions was analyzed, as illustrated in Figure 1 for water–ethanol mixtures. Overall, the model effectively captures general solubility trends, though with reduced quantitative accuracy in polar aprotic solvents, indicating its utility for preliminary solvent selection.

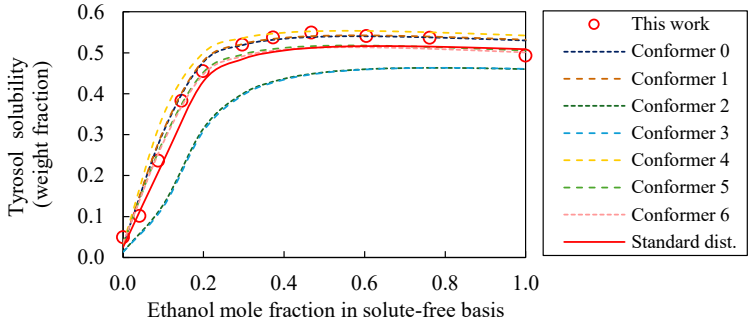


Figure 1: Solubility of tyrosol (in weight fraction) in binary mixtures of water and ethanol, at 298 K: experimental data (○, this work) and COSMO-RS predictions for different conformers of Tyrosol (C0 – C6).

Acknowledgements
National funds supported this work through FCT/MCTES (PIDDAC): CIMO, UIDB/00690/2020 (DOI: 10.54499/UIDB/00690/2020) and UIDP/00690/2020 (DOI: 10.54499/UIDP/00690/2020); SusTEC, LA/P/0007/2020 (DOI: 10.54499/LA/P/0007/2020); CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 and LA/P/0006/2020. National funding by FCT through the individual research grant (UI/BD/154740/2023) of A. Zambom.

References

1. J. Madureira, F. M. A. Margaça, C. Santos-Buelga, I. C. F. R. Ferreira, S. C. Verde and L. Barros, *Compr Rev Food Sci Food Saf* 2022, **21**, 453-476.
2. A. Sánchez-Monedero, R. Santiago, I. Díaz, M. Rodríguez, E. J. González and M. González-Miquel, *J Mol Liq* 2024, **408**, 125368.
3. F. Eckert and A. Klamt, *AIChE Journal* 2002, **48**, 369-385.

Vapor-liquid equilibrium behavior for ethanol and linoleic acid system

POSTER_P3.21 - Phase Equilibria and Fluid Properties

Fedra A.S.V.M. Ferreira[1], Humberto N.M. Oliveira[1], Osvaldo Chiavone-Filho[1,*]

[1]*Universidade Federal do Rio Grande do Norte - UFRN, DEQ, Natal–RN-Brasil*

[*]*osvaldo.chiavone@ufrn.br*

The knowledge of reliable vapor-liquid equilibrium (VLE) data is essential for process design and operation of units of separation. Mixtures with species that have high volatility and molar mass differences present experimental issues for complete VLE data determination. Previous work demonstrated that infinite dilution activity coefficients for organic solutes in fatty acids measurements can provide a description of the nonidealities of these mixtures.[1] Systems composed of fatty acids or vegetable oils in ethanol are of interest in several process types. However, VLE behavior for the system ethanol + linoleic acid has not been described in the literature. In this work, a vapor pressure-temperature curve for linoleic acid is presented with the aid of the Fischer recirculation ebulliometer and literature.[2] An atmosphere without oxygen was carefully used to avoid decomposition. To reduce the experimental effort for measuring VLE data of the mixture, it was just performed analyses at the diluted linoleic acid with the Othmer type vapor recirculation ebulliometer. Density measurements were applied for the determination of the concentration of both liquid and condensed vapor equilibrium phases. Infinite diluted ethanol data in oleic acid were retrieved from the literature from 303 to 323 K.[1] It is shown that using the two diluted sides of VLE experimental data, together with accurate vapor pressure correlations for both ethanol and linoleic acid, temperature or pressure-concentration diagrams are properly described. The gamma-phi approach was used with the UNIQUAC and virial equations, respectively. Comparisons were also provided with the UNIFAC group contribution method. Furthermore, results with the system ethanol and oleic acid were also obtained with the same approach and compared, in this case for validation purposes, with available pressure-composition of the liquid phase experimental data[3], with quantitative agreement.

Keywords: recirculation ebulliometer; phase equilibria; activity coefficient; biomass processing.

References

1. P. C. Belting, J. Rarey, J. Gmehling, R. Ceriani, O. Chiavone-Filho, A. J. A. Meirelles, *J. Chem. Thermodyn.* 2013, **60**, 142-149.
2. L. B. Barbeiro, R. M. M. Falleiro, A. J. A. Meirelles, *J. Chem. Thermodyn.* 2021, **159**, 1-10.
3. G. H. Eduljee, A. P. Boyes, *J. Chem. Eng. Data* 1981, **26**, 55-57.

Effects of solvent addition and crosslinking on the melting behavior of poly(dimethylsiloxane)

POSTER_P4.1 - Organic Materials and Polymers

Ibuki Tanizawa*, Hal Suzuki

Department of Chemistry, Kindai University, Higashiosaka, Osaka 577-8502, Japan

**ib.tanizawa@gmail.com*

The melting behavior of semicrystalline polymers depends on their thermal history and degree of strain. This is because these factors influence the size of crystallites, which significantly affects their thermodynamic stability. In our previous study, we investigated the melting behavior of poly(dimethylsiloxane) (PDMS) rubber under strain and found that the melting temperature increased by approximately 4 K when stretched to an elongation ratio of 2.56.[1] In this study, to further explore the thermodynamic properties of polymer melting, we investigated the effects of solvent addition and crosslinking on PDMS.

Vinyl-terminated PDMS (M_w = 43,000) was purchased from Gelest and used without further purification as an uncrosslinked polymer sample. The PDMS elastomer was synthesized by crosslinking the vinyl terminal groups with tetrakis(dimethylsilyloxy)silane. Both uncrosslinked and crosslinked samples were swollen in 2-methylpentane (2MP), and their melting behavior was investigated using differential scanning calorimetry (DSC). The degree of swelling was evaluated based on the volume fraction of 2MP (φ).

For uncrosslinked PDMS without solvent (φ = 0.000), two consecutive endothermic peaks appeared at 226 and 238 K, corresponding to the melting of metastable and stable crystals, respectively. Upon adding the 2MP solvent, the size and temperature of the low-temperature peak increased discontinuously at $\varphi \geq 0.008$, while the size of the high-temperature peak decreased. At $\varphi \geq 0.056$, the two peaks merged into a single peak. Interestingly, at φ = 0.030, 0.046, and 0.051, the DSC curves appeared similar to that of φ = 0.000. These results indicate that there are at least three crystalline phases, two of which are metastable. The probability of observing these three crystalline phases depends of φ. For the crosslinked PDMS elastomer (φ = 0.000), a single melting peak was observed at 233 K, which decreased monotonically with increasing φ. The melting temperatures were close to the low-temperature peak of uncrosslinked PDMS observed at $\varphi \geq 0.008$, suggesting that the effect of crosslinking resembles that of solvent addition.

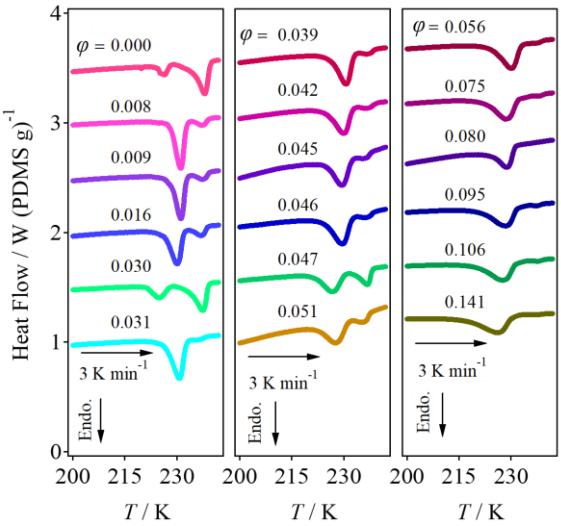


Figure 1: DSC heating curves of uncrosslinked PDMS

Reference

1. M. Umeda, T. Wakabayashi, T. Kamiyama, H. Suzuki, *Polymer* 2022, **254**, 125105.

Thermochemical characterization of sulfur-containing furan derivatives: Experimental and theoretical Study

POSTER_P4.2 - Organic Materials and Polymers

Luísa M. P.F. Amaral[1,*], Manuel A. V. Ribeiro da Silva [2]

[1]*REQUIMTE, LAQV, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 4169-007, Porto, Portugal*
[2]*Research Centre in Chemistry (CIQUP), Institute of Molecular Sciences (IMS), Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre, P-4169-007 Porto, Portugal*

**luisaamaral@fc.up.pt*

This study investigates the thermochemical properties of three sulfur-containing furan derivatives, 2-furanmethanethiol, furfuryl methyl sulfide, and methyl 2-methyl-3-furyl disulfide, using both experimental and theoretical approaches. The standard molar enthalpies of combustion were measured by combustion calorimetry, while enthalpies of vaporization were determined using Calvet microcalorimetry. This experimental data enabled the calculation of standard molar enthalpies of formation in the gas phase at T = 298.15 K. Complementary high-level chemical calculations (G3) provided additional insights, and the comparison between experimental and theoretical values showed excellent agreement, validating both experimental and computational methods. The findings significantly contribute to the thermochemical understanding of sulfur-containing furan derivatives, enhancing existing databases and supporting the development of predictive models for furan-based systems. The results have implications for applications in food, flavor, and fragrance industries, where these compounds are integral to aroma profiles. This research is part of a project to systematically investigate the energetics of furan derivatives.[1-5]

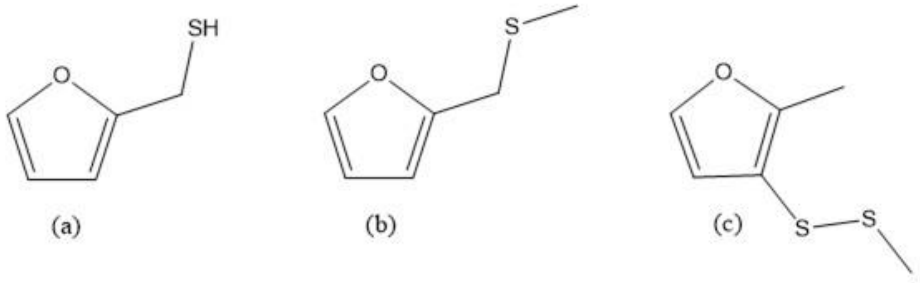


Figure 1: Structural formula of (**a**) 2-furanmethanethiol; (**b**) furfuryl methyl sulfide; (**c**) methyl 2-methyl-3-furyl disulfide.

Acknowledgments L.M.P.F. Amaral thanks FCT/MCTES funding through the Individual Call to Scientific Employment Stimulus 2018 (CEECIND/03202/2018) DOI 10.54499/CEECIND/03202/2018/CP1545/CT0001.

1. M.A.V. Ribeiro da Silva, L.M.P.F. Amaral, *J. Chem Thermodyn*. **2009**, 41, 26-29.
2. M.A.V. Ribeiro da Silva, L.M.P.F. Amaral, *J. Chem. Thermodyn.* **2009**, 41, 349-354.
3. M.A.V. Ribeiro da Silva, L.M.P.F. Amaral, *J. Therm. Anal. Calorim*. **2010**, 100, 375-380.
4. M.A.V. Ribeiro da Silva, L.M.P.F. Amaral, *J. Chem. Thermodyn.* **2011**, 43, 1-8.
5. L.M.P.F.; Amaral, A.R.R.P. Almeida, M.A.V. Ribeiro da Silva, *Molecules* **2024**, *29*, 2729.

Design of magnetic responsive cryogels based on hydroxypropyl cellulose derivatives for multi-functional sensors

POSTER_P4.3 - Organic Materials and Polymers

R.I. Baron[1,*], G. Biliuta[1], S. Coseri[1]

[1]Petru Poni" Institute of Macromolecular Chemistry, Department of Polyaddition and Photochemistry, 41A Grigore Ghica Voda Alley, 700487 Iasi, Romania

*baron.raluca@icmpp.ro

Hydrogels based on polysaccharides synthesized through green methods epitomize these principles and offer a promising avenue for sustainable biomaterials. The fine-tuning of the structure and functional patterns of polysaccharide-based hydrogels has opened up a broad range of their applications in medicine,[1] electronics,[2] food packaging,[1] and environmental remediation.[3] Fabricating composite cryogels with anti-freezing properties while meeting specific mechanical requirements poses significant challenges for certain applications. Nevertheless, their unique properties make them attractive for a wide range of uses. For successful real-world implementation, these cryogels must overcome hurdles such as scalable production, structural integrity, stability, mass transfer limitations, biocompatibility, and cost efficiency. In this context, we introduce a novel method to design composite cryogels with anti-freezing properties, ecological friendliness, magnetic responsiveness, and enhanced mechanical properties. To achieve the proposed requirements we used glycerol as a partial water replacement solvent and incorporated magnetic nanoparticles (FeNP) into hydroxypropyl cellulose (HPC)/polyvinyl alcohol (PVA) polymeric matrices. The obtained composite cryogels were thoroughly characterized using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), thermal analysis (TG/DSC), scanning electron microscopy (SEM), rheological and uniaxial compression measurements, and conductivity tests. This study introduces several innovative aspects: (i) employing an eco-friendly, highly specific oxidation method as a powerful, scalable approach for polysaccharide modification; (ii) developing new composites with anti-freezing and never-drying properties, using biodegradable and biocompatible raw materials without toxic chemical cross-linking agents; and (iii) eliminating the need for complex solvent mixtures or crosslinker agents. By prioritizing sustainability, this work offers new pathways for creating new materials from renewable sources.

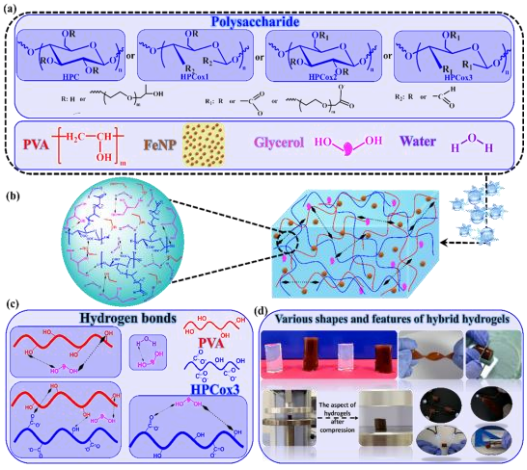


Figure 1. Schematic illustration of the preparation of composite cryogels, and their various shapes and features.

Acknowledgments

This work was supported by a grant of the Ministry of Research, Innovation and Digitization, CNCS-UEFISCDI, project number PN-IV-P1-PCE-2023-0558, within PNCDI IV.

References

1. C.A. Ghiorghita et al., *Carbohydr. Polym.* 2024, **334**, 122033.
2. H. Zhang et al., *J. Polym. Sci.* 2023, **61**, 7.
3. E.S. Dragan et al., *React. Funct. Polym.* 2020, **146**, 104372.

Fabrication and characterization of a novel polysaccharide-based composite nanofiber with improved physical properties

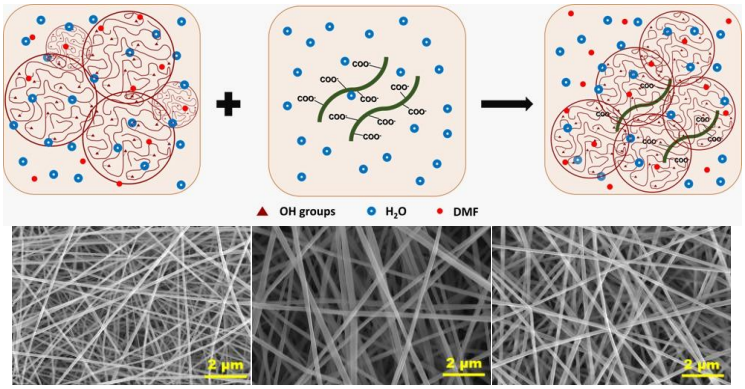
POSTER_P4.4 - Organic Materials and Polymers

G. Biliuta[1,*], R.I. Baron, S. Coseri[1], A.L. Chibac-Scutaru[1]

[1]*Petru Poni" Institute of Macromolecular Chemistry, Department of Polyaddition and Photochemistry, 41A Grigore Ghica Voda Alley, 700487 Iasi, Romania*

[*]*biliuta.gabriela@icmpp.ro*

Electrospinning is a simple, versatile, and promising technique for fabricating continuous, ultrafine, smooth, continuous, and bead-free fibers of micro- and nanoscale diameter from polymer solutions. The polymers used in electrospinning include synthetic and natural polymers. Compared with synthetic polymers, natural polymers, such as polysaccharides, have the advantages of non-toxicity, biodegradability, and excellent biocompatibility. Therefore, we fabricated homogeneous pullulan nanofibers that are strengthened by the addition of cellulose nanofibrils (CNF). Pullulan exhibits favorable physicochemical properties, including high hydrophilicity, enzymatic degradability, structural flexibility, and chemical reactivity.[1,2] Biomaterials produced from pullulan exhibit considerable promise as materials for wound dressings, as they have been demonstrated to stimulate skin regeneration and wound healing.[3,4] Cellulose nanofibrils (CNF) are excellent supporting materials for biopolymers because of their characteristic biocompatibility, biodegradability, renewability, and universality.[5] Pullulan/CNF cellulose nanofibers with varying amounts of CNF were prepared via the electrospinning process (Scheme 1). The rheological properties of the pullulan and pullulan/CNF solutions were investigated. Furthermore, the characterization of the nanofibers was carried out by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and thermogravimetric analysis (TGA).



Scheme 1: Schematic representation of entangled pullulan solution, CNF dispersion and the pullulan/CNF composite used for electrospinning and SEM images of nanofibrous samples with different concentrations of CNF.

Acknowledgments
This work was supported by a grant of the Ministry of Education and Research, CNCS – UEFISCDI, project number PN-IV-P1-PCE-2023-1020 (6PCE/08.01.2025), within PNCDI IV.

References

1. A. Spatareanu et al., *Carbohydr. Polym*. 2014, **111**, 63.
2. S. Coseri et al., *Eur. Polym. J*. 2016, **85**, 82.
3. O. Burduniuc et al., *Materials* 2021, **14** , 7041.
4. M. Bercea et al., *Carbohydr. Polym*. 2019, **206**, 210.
5. G. Biliuta et al., *Wood Sci. Technol*. 2023, **57**, 1443.

Thermodynamic properties of phenanthroline derivatives for thin film applications in organic optoelectronic devices

POSTER_P4.5 - Organic Materials and Polymers

Artur F. M. Farinha[1,*], Rodrigo M. A. Silva[1], Luís M. N. B. F. Santos[1], and José C. S. Costa[1]

[1] *CIQUP/Institute of Molecular Sciences (IMS), Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre s/n, 4169–007 Porto, Portugal*

[*] *up201506214@fc.up.pt*

Organic semiconductors (OSCs) have gained notable importance as thin film layers for organic optoelectronic devices. Phenanthroline and its derivatives are well-known OSCs that have been widely used in perovskite solar cells.[1-3] For effective application, these thin films must exhibit favorable thermodynamic behavior and structural and chemical stability within the operational temperature range of a solar cells. However, comprehensive thermodynamic investigations of this family of compounds are still lacking.
In this work, we employed a range of techniques to characterize phenanthroline (PHEN), neocuproine (DMPHEN), bathophenanthroline (BPHEN), and bathocuproine (BCP) (Figure 1). The Knudsen effusion method, combined with a quartz crystal microbalance, was used to measure the temperature dependence of vapor pressure, enabling the determination of molar enthalpies and entropies of sublimation. Thermogravimetric analysis (TGA) was employed to evaluate the temperature range over which these compounds remain chemically stable. Melting and glass transition temperatures, along with the enthalpies and entropies of fusion, were obtained using differential scanning calorimetry (DSC). Heat capacities were measured via both microDSC and drop calorimetry methods. Moreover, UV-Vis spectroscopy was used to investigate the optical properties of these compounds. The effect of the addition of methyl and/or phenyl groups on the thermodynamic and optical behavior of the four studied compounds was evaluated.

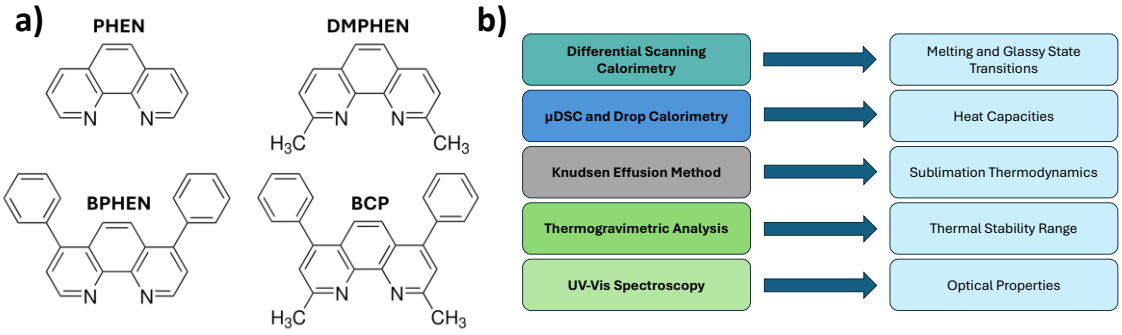


Figure 1: a) Molecular structures of phenanthroline (PHEN), neocuproine (DMPHEN), bathophenanthroline (BPHEN), and bathocuproine (BCP). b) Overview of techniques used for thermal or optical characterization, and the properties evaluated.

Acknowledgements
This work was supported by the Fundação para a Ciência e Tecnologia (FCT) (funded by national funds through the FCT/MCTES (PIDDAC)) to CIQUP, Faculty of Science, University of Porto (Project UIDB/00081/2020: DOI 10.54499/UIDP/00081/2020), and IMS-Institute of Molecular Sciences (LA/P/0056/2020)). RMAS is grateful to FCT for the award of his PhD grant (U1/BD/153093/2022). A.F.M. Farinha also thanks the FCT and the European Social Fund (ESF) for the award of a Ph.D. Research Grant (ref. 2022.11342.BD: DOI 10.54499/2022.11342.BD).

References

1. C. Chen, S. Zhang, S. Wu, W. Zhang, H. Zhu, Z. Xiong, Y. Zhang, W. Chen, *RSC advances* 2017, **7**, 35819-35826.
2. L. L. Jiang, S. Cong, Y. H. Lou, Y. H., Q. H. Yi, J. T. Zhu, J, H. Ma, G. F. Zou, *Journal of Materials Chemistry A* 2016, **4**, 217-222.
3. J. Troughton, M, Neophytou, N. Gasparini, A. Seitkhan, F. H. Isikgor, X. Song, Y. H. Lin, T. Liu, H. Faber, E. Yengel, J. Kosco, M. F. Oszajca, B. Hartmeier, M. Rossier, N. A. Lüchinger, L. Tsetseris, H. J. Snaith, S. D. Wolf, T. D. Anthopoulos, I. McCulloch, D. Baran, *Energy & Environmental Science* 2020, **13**, 268-276.

Alkyl substituent effects on the energetic properties of some 2-amino-5-R-1,3,4-thiadiazoles

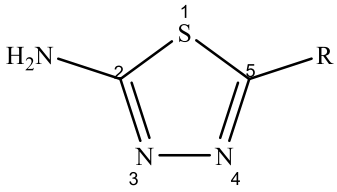
POSTER_P4.6 - Organic Materials and Polymers

Ana Luísa R. Silva*, Ana C. M. O. Lima, Maria D. M. C. Ribeiro da Silva

[1]*Faculty of Sciences of University of Porto, Department of Chemistry and Biochemistry, Centro de Investigação em Química (CIQUP), Institute of Molecular Sciences (IMS), Rua do Campo Alegre, P-4169-007 Porto, Portugal*

**analuisa.rs@fc.up.pt*

Thiadiazoles are pentacyclic compounds with one sulphur and two nitrogen as heteroatoms. In the case of 1,3,4-thiadiazoles, the thermodynamic properties of these compounds are not well-known, which complicates the selection of precise values for using in the development of novel prediction schemes for these properties. This study emerges within the goals of our Research Group that has being involved in a systematic experimental and computational study of different classes of five-membered heterocycles, namely oxazoles[1], thiazoles[2], triazoles[3] and thiadiazoles[4]. The present work reports a structural and thermochemical investigation on four 2-amino-5-alkyl-1,3,4-thiadiazole derivatives (Figure 1).



R= methyl; ethyl, isopropyl and tert-butyl

Figure 1: Molecular structure of the compounds studied.

The enthalpies of combustion and sublimation of the compounds were determined, respectively, by rotating bomb calorimetry and mass-loss effusion method. The standard molar enthalpies of formation of the methyl-, ethyl- and tert-butyl-substituted compounds in the gaseous phase were derived from the experimental results and from computational studies. The isopropyl-substituted thiadiazole was studied exclusively through a computational approach. Furthermore, it was evaluated the relative thermodynamic stability of each compound in the crystalline and gaseous phases. The analysis of the enthalpic increments enabled the establishment of the relation energy versus structure of the thiadiazoles studied.

Acknowledgements

This work was supported by the Fundacão para a Ciência e Tecnologia (FCT) (funded by national funds through the FCT/MCTES (PIDDAC)) to CIQUP, Faculty of Sciences, University of Porto (Project UID/00081, Centro de Investigação em Química da Universidade do Porto) and IMS-Institute of Molecular Sciences (LA/P/0056/2020)). A.L.R.S. thanks FCT/MCTES for her contract under Stimulus of Scientific Employment 2017 (CEECIND/01161/2017).
The team acknowledges further support from Exploratory Project of reference 2023.13829.PEX funded by FCT, Portugal.

References

1. A. L. R. Silva, V. M. F. Morais, M. D. M. C. Ribeiro da Silva, *J. Chem. Thermodyn*. 2018, **127**, 45
2. A. L. R. Silva, M. J. S. Monte, V. M. F. Morais, M. D. M. C. Ribeiro da Silva, *J. Chem. Thermodyn.* 2014, **74**, 66.
3. A. L. R. Silva, A. C. M. O. Lima, M. D. M. C. Ribeiro da Silva, *J. Chem. Thermodyn*. 2023, **186**, 107140
4. A. C. M. O. Lima, A. L. R. Silva, J. M. Gonçalves, M. D. M. C. Ribeiro da Silva, *J. Therm. Anal. Calorim*. 2024.

Phase behavior of phenylnaphthalenes and phenylanthracenes: Influence of the central acene core and substituent position

POSTER_P4.7 - Organic Materials and Polymers

Filipe V. Ribeiro, José C. S. Costa, Luís M. N. B. F. Santos, and Carlos F. R. A. C. Lima*

CIQUP, Institute of Molecular Sciences (IMS), Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, rua do Campo Alegre s/n 4169-007 Porto, Portugal

**carlos.lima@fc.up.pt*

In this study, we investigate the one-component phase equilibria of several phenylnaphthalenes and phenylanthracenes bearing one or two phenyl substituents. Differential scanning calorimetry (DSC) was employed to determine fusion temperatures, standard molar enthalpies and entropies of fusion, and to assess the presence of polymorphism and associated solid-solid transitions. Knudsen effusion methods were used to measure equilibrium vapour pressures as a function of temperature, from which standard molar enthalpies and entropies of sublimation were derived. Heat capacities of the solid compounds were measured by drop calorimetry, while those of the gas-phase molecules were obtained through computational methods.
The structural simplicity of these compounds enables the establishment of reliable structure-property relationships concerning phase behaviour and allows identification of the molecular features that govern phase stability and equilibrium. Together with literature data on related phenylbenzenes, the results were thoroughly analysed to evaluate the influence of the central acene core, as well as the number and position of phenyl substituents, on phase equilibria. Where available, thermodynamic data were complemented by structural information obtained via X-ray crystallography.

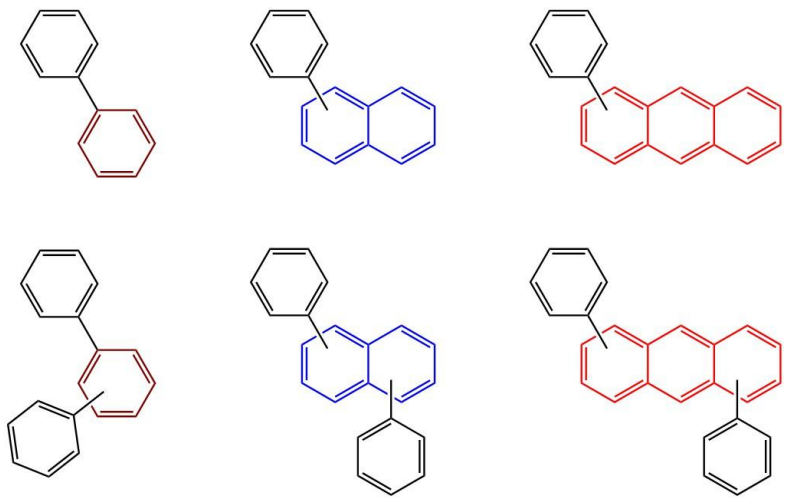


Figure 1: Schematic representation of the phenylacenes studied herein, illustrating the effects of (i) increasing the size of the central acene core, and (ii) the number and position of the phenyl substituents.

Acknowledgements
The authors thank the Portuguese Foundation for Science and Technology (FCT) for financial support to CIQUP, Faculty of Science, University of Porto (UIDB/00081/2020, DOI: 10.54499/UIDP/00081/2020) and IMS, Institute of Molecular Sciences (LA/P/0056/2020).

References

1. C. F. R. A. C. Lima, M. A. A. Rocha, B. Schröder, L. R. Gomes, J. N. Low and L. M. N. B. F. Santos, *J. Phys. Chem. B* 2012, **116**, 3557.

Influence of cation structure with allyl group and different anions on the glass transition and heat deflection temperatures of fiber reinforced epoxy composites

POSTER_P4.8 - Organic Materials and Polymers

Marcin Smiglak,[1,*] Dawid Zielinski,[1] Andrea Szpecht[1]

[1]*Poznan Science and Technology Park, Adam Mickiewicz University Foundation, ul. Rubiez 46, 61-612 Poznan, Poland.*

**marcin.smiglak@ppnt.poznan.pl*

Ionic liquids (ILs) are a unique class of molten salts known for their exceptional chemical and thermal stability, making them valuable in a wide range of scientific and technological applications.[1] Their highly tunable structures allow for the customization of properties through various combinations of cations and anions. Originally explored as green alternatives to traditional solvents, ILs have evolved into multifunctional materials with potential in fields such as energy, materials science, and pharmaceuticals.[2] Recently, they have gained attention as multifunctional agents in advanced materials.[3] Despite their versatility and broad application potential, challenges remain in their synthesis, environmental impact, and large-scale implementation, highlighting the need for further research and standardization.

Among them, allyl-functionalized ionic liquids (AILs) have emerged as promising curing agents for epoxy resin systems, offering improved curing efficiency and enhanced thermal and mechanical properties of the resulting composites. Their structural versatility allows for better control over polymerization processes and material performance. Studies show that incorporating AILs can lead to stronger, more thermally stable composites, making them valuable components in the development of advanced epoxy-based materials.

This study investigates the synthesis, curing behavior, and performance of epoxy-based composites using allyl-functionalized ionic liquids as hardeners in combination with two different reinforcement fabrics, flax and carbon. The curing behavior was studied in detail, emphasizing the influence of the IL anion type on polymerization dynamics. ILs containing the trifluoromethanesulfonate ([OTf]) anion exhibited a single, sharp polymerization peak with high enthalpy values, indicating rapid and efficient curing. In contrast, ILs with the dicyanamide ([DCA]) anion showed lower enthalpy and broader curing profiles, suggesting a slower and less energy-efficient process. Despite these differences, the polymerization occurred within similar temperature ranges, highlighting distinct reaction pathways governed by IL composition.

Thermal and mechanical tests were conducted on the resulting composites. Notably, flax fiber composites cured with [AMIM][DCA] displayed dual glass transition temperatures, suggesting complex, phase-separated structures. Carbon fiber composites consistently demonstrated excellent thermal stability. Dynamic mechanical analysis revealed that 1-Allyl-3-methylimidazolium dicyanamide [AMIM][DCA] and 1-Allyl-3-methylimidazolium trifluoromethanesulfonate [AMIM][OTf] imparted superior stiffness and thermal resistance. Furthermore, carbon fiber composites showed enhanced damping properties compared to flax fiber systems. The results highlight the potential of [AMIM]-based ILs as effective curing agents for high-performance epoxy composites.

Acknowledgements

This research was supported by the National Science Centre (Poland), project SONATA BIS (No. 2017/26/E/ST8/01059) entitled "Multifunctional composite systems based on epoxy resins with ionic liquids as crosslinking initiators".

References

1. S. K. Singh, A. W. Savoy, *Journal of Molecular Liquids* 2020, **297**, 112038.
2. Z. Lei, C. Dai, J. Hallett, M. Shiflett, *Chem. Rev.* 2024, **124**, 7533-7535.
3. Y. Pei, Y. Zhang, J. Ma, M. Fan, S. Zhang, J. Wang, *Materials Today Nano* 2022, **17**, 100159.

Formation thermodynamics of TiN interlayer and its effect on the reliability of active metal brazed Cu/AlN substrate for power module packaging

POSTER_P5.1 - Inorganic Materials and Metals

Min-Su Kim[1,*], Min-Ki Kim[2], Tae-Ik Lee[1], Dongjin Kim[1]

[1] *Advanced Packaging Integration Center, Korea Institute of Industrial Technology, Republic of Korea*
[2] *Flexible Manufacturing R&D Department, Korea Institute of Industrial Technology, Republic of Korea*

[*] *mskim927@kitech.re.kr*

Direct bond copper (DBC) ceramic substrates are commonly used in power electronics due to their high thermal conductivity, dielectric strength, and low thermal expansion. A fabrication process of DBC substrate utilizes the Cu_2O reaction to bond Cu to ceramics. The DBC substrates exhibit good thermal properties and low cost; however, they are prone to delamination under extreme thermal cycling conditions, particularly in automotive, aerospace, and defense applications[1]. To ensure good mechanical stability of the ceramic/Cu substrate, it is necessary to improve the interfacial bonding strength. An active metal brazing technique can improve interfacial bonding strength between metals and ceramics[2]. Here, we fabricated a robust Cu/AlN substrate with a Ti active layer by magnetron sputtering. In a Ti/AlN diffusion couple, Ti can react with AlN to form TiN because Ti has a stronger affinity for nitrogen compared to Al. Due to the negative formation energy of TiN (approximately -45 kJ/mol), the formation of it is thermodynamically favorable, indicating that TiN will form spontaneously (Figure 1). The Cu/AlN substrate with Ti active layer is very stable under temperature cycling with temperature fluctuation from – 40 to 150 ˚C up to 2000 cycles. An active metal brazed Cu/AlN substrate incorporating a Ti interlayer presents a promising solution for the packaging of wide bandgap power semiconductors.

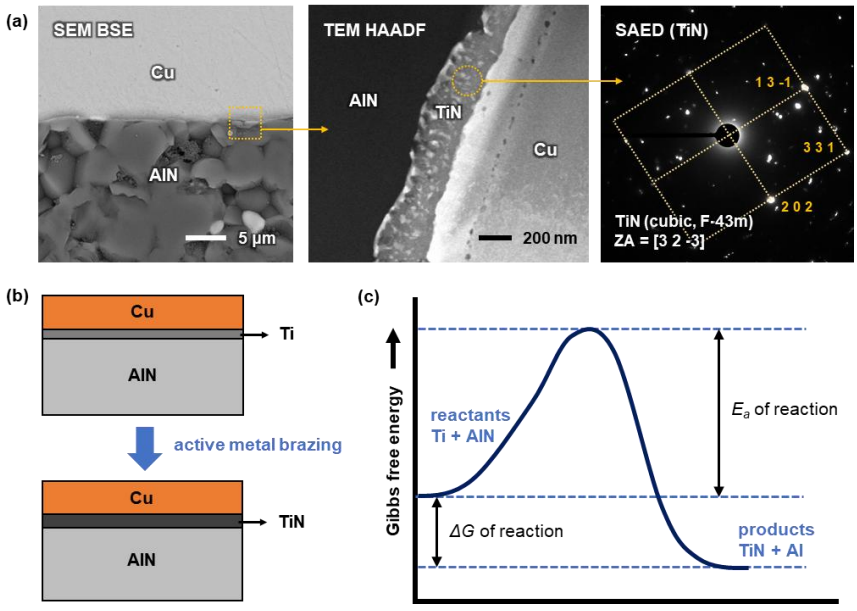


Figure 1: (a) SEM and TEM images of the interface of active metal brazed Cu/AlN substrate (b) schematic diagram of TiN interlayer formation by active metal brazing processing and (c) thermodynamics of Ti +AlN → TiN + Al reaction.

References

1. H. Tatsumi, S. Moon, M. Takahashi, T. Kozawa, E. Tsushima and H. Nishikawa, *Mater. Des.* 2024, **238**, 112637.
2. D. Sivaprahasam, T. Sujitha, U. Gowtham, B. Jayachandran and R. Gopalan, *Ceram. Int.* 2021, **47**, 16133.

Aero-TiO_2 materials for evaluation of near-ultraviolet photodetector

POSTER_P5.2 - Inorganic Materials and Metals

Cornelia Bandas[1*], Mircea Nicolaescu[1], Corina Orha[1], Mina-Ionela Morariu[1], Tatiana Galatonova[2], Simon Busuioc[2], Tudor Braniste[2], Carmen Lazau[1]

[1]*Condensed Matter Department, National Institute for Research and Development in Electrochemistry and Condensed Matter, Timisoara, Romania*
[2]*National Centre for Materials Study and Testing, Technical University of Moldova, Chisinau, Republic of Moldova*

[*]*cornelia.bandas@gmail.com*

In recent years, a new class of extremely highly porous and ultralightweight aeromaterials has emerged, with applications varying from energy conversion and storage to catalysis and sensor. The development of TiO_2 aero-nanomaterials, called aero-TiO_2, is expected to be a prospective direction of investigations. Titanium dioxide appears in numerous crystallographic variations, of which anatase and rutile phases are the most stable under ambient conditions. Between them, the anatase phase exhibits stronger photocatalytic activity than the rutile phase. Based on literature data, titania nanoparticles have been used in a wide range of applications, such as photocatalysts[1], dye-sensitized solar cells[2], gas sensors[3], and nanomedicine[4], due to their nontoxicity, cost effectiveness, and high stability. Interest in the field of UV radiation detection and monitoring has increased in the last year's due to climate change, and photodetectors have become of greater interest to researchers. In the field of photodetectors, one of the most promising materials has proven to be TiO_2 and ZnO oxide semiconductors, due to their optoelectrical properties during UV excitation. The metal oxide junction was a promising method in order to increase the sensibility of the sensor.

The aim of this paper is the development of aero-TiO_2 sensors for evaluation of UV photodetectors. The fabrication of aeromaterials was carried out on a sacrificial network of ZnO microtetrapods by deposition using atomic layer deposition (ALD) of TiO_2 thin films. This process is followed by citric acid etching of the sacrificial tetrapods. Before testing measurements, the properties of as-synthesized materials were evaluated using UV-Vis spectroscopy, Scanning Electron Microscopy (SEM), and X-ray diffraction (XRD) analysis. The development of photodetectors based on aero-TiO_2 was achieved by spin-coating (WS- 400-6NPPB Spin Coater) deposition, repeated three times for 10 sec with a speed rotation of 1500rot. Electrical measurements of the obtained photodetectors were performed using the Keithley 2450 SourceMeter SMU Instruments. *I⁄V* measurements were performed to test the functionality in dark and UV illumination.

Acknowledgements
This research was funded by a grant from the Ministry of Research, Innovation and Digitization, project number PN-IV-P8-8.3-ROMD-2023-0227 within PNCDI IV, and partially by the project code PN 23 27 01 02 INOMAT, 23-27 29N/2023.

References

1. O. Crap, C. L. Huisman, A. Reller, *Solid State Chem.* 2004, **32**, 133-177.
2. M. R. Mohammadi, D. J. Fary, M. C. Cordero-Cabrera, *Sens. Actuators B-Chem.* 2007, **124**, 74-83.
3. Y. Q. Wang, H. M. Zhang, R. H. Wang, *Colloids Surf. B Biointerfaces* 2008, **65**, 190-196.
4. M. M. Haghi, M. B. Hekmatafshar, S. S. Janipour, S. S. Gholizadeh, M. Kazem, F. Sayyadifar, M. Ghaedi, *Int. J. Adv. Biotechnol. Res.* 2012, **3**, 621-624.

Relationship between heat storage properties and crystallite size of lambda-type trititanium pentoxide

POSTER_P5.3 - Inorganic Materials and Metals

Riku Seiki,[1] Tomoko Kubota,[1] Akito Fujisawa,[1] Akhmad Fadel Fadilla,[1] Shin-ichi Ohkoshi,[2] Hiroko Tokoro[1*]

[1]*Department of Material Science, Faculty of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8577, Japan*
[2]*Department of Chemistry, School of Science, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan*

**tokoro@ims.tsukuba.ac.jp*

The lambda-type trititanium pentoxide (λ-Ti_3O_5) was reported as a pressure-responsive heat-storage material to preserve thermal energy in the long-term.[1,2] In this study, we developed a synthesis method for λ-Ti_3O_5 simply by preparing a precursor using titanium chloride ($TiCl_4$) as a starting material and evaluated the heat-storage properties.[3]

A mixed solution of H_2O, $TiCl_4$, and NH_3 was prepared in a round bottle flask. The solution was stirred at 50 ℃ for 20 hours in an oil bath. The precipitation was extracted from the solution by centrifugation, washed with ethanol, and heated at 60 ℃ for 24 hours. Then the obtained precursor was sintered under a hydrogen flow of 0.5 $dm^3\ min^{-1}$ at 1100 ℃ for 5 hours to synthesize a black powder sample.

XRF measurement indicated that the composition formula was $Ti_{3.00(5)}O_{5.00(5)}$ (Calculated: Ti 64.22, O 35.78 wt%; Found: Ti 64.53, O 35.47 wt%). SEM image showed that the particle size is 299 ± 54 nm. XRD pattern with Rietveld analysis indicated that the obtained sample was a single phase of λ-Ti_3O_5 (monoclinic, *C*2/*m*; *a* = 9.8332(2) Å, *b* = 3.78568(7) Å, *c* = 9.9688(2) Å, *β* = 91.259(2) °) and the crystallite size was estimated 57 ± 3 nm. The pressure threshold (P_{th}) for converting 50 % of λ-Ti_3O_5 to β-Ti_3O_5 was approximately 300 MPa. The transition enthalpy (ΔH_{trans}) for converting pressure-induced β-Ti_3O_5 to λ-Ti_3O_5 was 144 $kJ\ L^{-1}$ at 462 K. The examination of the relationship between the crystallite size and these two heat-storage properties (the P_{th} and the ΔH_{trans}) demonstrated that a reduction in crystallite size and an increase in ratio of surface atoms intensify the influence of surface energy on the Gibbs free energy and consequently it decreased the ΔH_{trans}. Additionally, thermodynamics analyses showed that the reduction in ΔH_{trans} makes the energy barrier between λ-Ti_3O_5 and β- Ti_3O_5 less like to dissipate, consequently it increased the P_{th}. Understanding these relationships is essential for developing more effective heat storage materials.

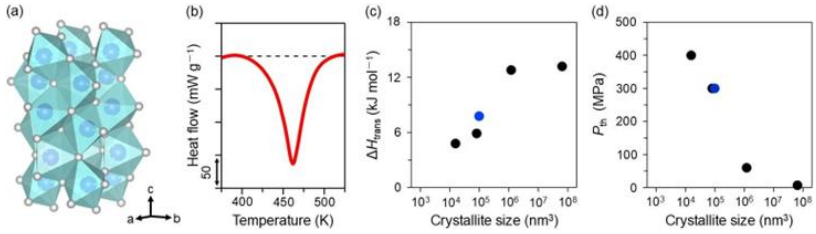


Figure 1: (a) Crystal structure of λ-Ti_3O_5, (b) DSC measurement for pressure-produced β-Ti_3O_5 by heating, (c) ΔH_{trans} versus crystallite size plot, and (d) P_{th} versus crystallite size plot. Black circles indicate previously reported data whereas blue circles indicate the present study.

References

1. S. Ohkoshi, Y. Tsunobuchi, T. Matsuda, K. Hashimoto, A. Namai, F. Hakoe, H. Tokoro, *Nature Chem.* 2010, **2**, 539-545.
2. H. Tokoro, M. Yoshikiyo, K. Imoto, A. Namai, T. Nasu, K. Nakagawa, N. Ozaki, F. Hakoe, K. Tanaka, K. Chiba, R. Makiura, K. Ptassides, S. Ohkoshi, *Nature Commun.*, 2015, **6**, 7037.
3. T. Kubota, R. Seiki, A. Fujisawa, A.F. Fadilla, F. Jia, S. Ohkoshi, H. Tokoro., *Materials Advances*, 2024, **5**, 3832-3837.

Zeolites made from fly-ash wastes as Fenton catalysts for the degradation of methylene blue dye from aqueous media

POSTER_P5.4 - Inorganic Materials and Metals

Nelson Nunes[1,2*], Gabriel Barros[1,3], Nuno Horta[1,2], Sofia Martins[2], Ana S. Mestre[1,3], Hugo F. Silva[1,2], Ana P. Carvalho[2,3], Angela Martins[1,2]

[1]*Centro de Química Estrutural, Faculdade de Ciências, Institute of Molecular Sciences, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal*
[2]*Departamento Engenharia Química, Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa, R. Conselheiro Emidio Navarro, 1959-007 Lisboa, Portugal;*
[3]*Departamento de Química e Bioquímica, Faculdade de Ciências Universidade de Lisboa, Ed. C8, Campo Grande, 1749-016 Lisboa, Portugal*

**nelson.nunes@isel.pt*

Worldwide, large amounts of coal fly ash (FA) are being daily discharged as a by-product from coal power plants, and only less than 20 % have some type of valorization. The rich composition in Si and Al makes this waste a suitable material for the synthesis of zeolites.[1] Also, the presence of small amounts of other metals such as Fe, essential for Fenton reactions, is advantageous since it reduces additional preparation steps for metal incorporation in the catalyst. In this study, FA from a Portuguese powerplant, with about 4 wt.% of Fe was used to produce Fe/ZSM-5_FA or Fe/Y_FA zeolites through hydrothermal treatment. The materials were characterized by powder X-ray diffraction and low temperature N_2 adsorption isotherms, allowing to confirm that the structural and textural properties of the obtained materials correspond to the targeted zeolite structures. The catalysts were tested in the degradation of methylene blue (MB) dye through Fenton reaction, in the presence of H_2O_2, at 40 ºC. MB dye (Figure 1) belongs to the phenothiazine family and was chosen as a representative model molecule for studying the degradation behavior of FA based zeolites. For comparison, Fe impregnated commercial (C) zeolites, Fe/ZSM-5_C and Fe/Y_C were tested as well as the pristine FA.

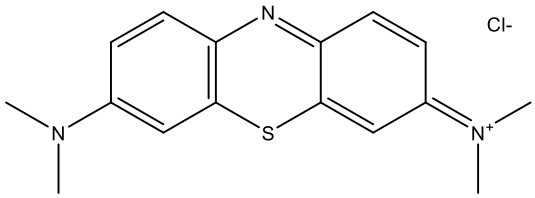


Figure 1: Methylene blue (MB) structure.

Preliminary results show that some degradation of MB occurs in the presence of FA due to the presence of Fe in its composition. However, a substantial increase in MB degradation is observed in the case of Fe/ZSM-5_FA, showing also an identical behavior when compared with the commercial ZSM-5 impregnated with Fe, Fe/ZSM-5_C. These results reveal the good potential of FA to produce effective Fenton catalysts that can be further studied in the degradation of other pollutants.

Acknowledgements
This research was funded by the Fundação para a Ciência e a Tecnologia (FCT) through projects UIDB/00100/2020 (https://doi.org/10.54499/UIDB/00100/2020) and UIDP/00100/2020 (https://doi.org/10.54499/UIDP/00100/2020) and IMS Associated Laboratory project LA/P/0056/2020 (https://doi.org/10.54499/LA/P/0056/2020). The work was also funded by Instituto Politécnico de Lisboa (IPL) through project IPL/2024/Ash2ZeoCat ISEL.

References

1. Y.-R. Lee, J.T. Soe, S. Zhang, J.-W. Ahn, M. B. Park, W.-S. Ahn, *Chem. Eng. J.* 2017, **317**, 821-843.

On the distribution of ruthenium in nanostructured WO_3 synthesized by the Pechini method

POSTER_P5.5 - Inorganic Materials and Metals

André Saliba[1], André Avancini Bernardes[1], Priscila Hasse Palharim[2], Andre Luiz da Silva[1], Douglas Gouvêa[1], Bruno Ramos[1,3*]

[1]*Laboratory of Ceramic Processes (LPC), Department of Metallurgical and Materials Engineering, Escola Politécnica, Universidade de São Paulo, São Paulo, Brazil*
[2] *Photoactive Nanomaterials Group, Centre for Natural & Human Sciences, Universidade Federal do ABC, Santo André, Brazil*
[3]*Centre for Research and Innovation in Energy Transition for Sustainable Mobility (IGNIS), Centro Universitario FEI, São Bernardo do Campo, Brazil*

**brunoramos@fei.edu.br*

Ruthenium-doped tungsten trioxide (Ru:WO_3) is a promising candidate for photocatalytic green ammonia synthesis due to its visible-light activity and potential to enhance charge carrier separation. In this study, nanostructured Ru:WO_3 powders were synthesized via the Pechini method. The main objective is to determine the spatial distribution of Ru in the material - whether it is incorporated into the bulk crystal lattice, segregated at grain boundaries, or enriched at the surface. Structural and compositional analyses were performed using X-ray diffraction with Rietveld refinement, X-ray photoelectron spectroscopy (XPS), and UV Diffusive Reflectance Spectroscopy (DRS). To quantify the surface-accessible Ru fraction, we applied selective alkaline lixiviation[1], and estimated the surface excess by normalising the extracted dopant content with specific surface areas obtained by the BET method. Preliminary results suggest that Ru is only partially incorporated into the WO_3 lattice, with a considerable fraction segregating to interfacial regions. This segregation is consistent with the thermodynamic tendency of dopants to reduce the system's free energy by concentrating at high-energy sites. The location of Ru is expected to significantly influence the material's photocatalytic performance. Ongoing photocatalytic tests under simulated solar irradiation and N_2 atmosphere[2] aim to correlate Ru distribution with ammonia synthesis efficiency.

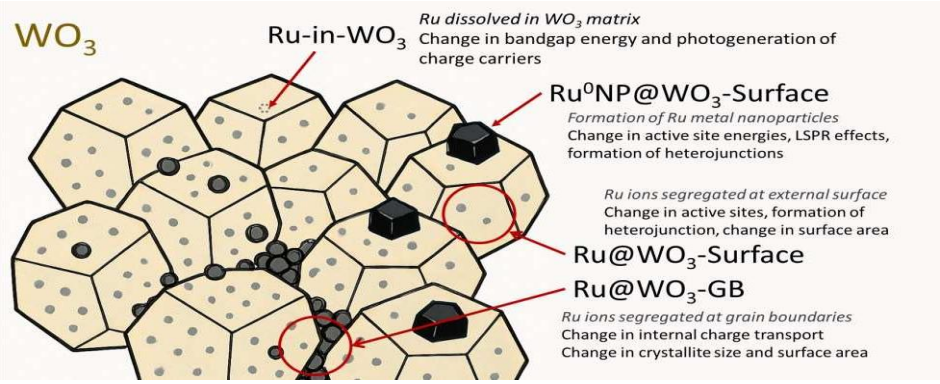


Figure: Illustration of Ru distribution in a WO_3 matrix and its probable effects

Acknowledgements
The authors acknowledge the support of the Sao Paulo Research Foundation (FAPESP), grant 23/14214-4.

References

1. G.M. Fortes, A.L. da Silva, B. Ramos, J. Bettini, F.C. Fonseca, R.V. Gonçalves, O.R. Junior and D. Gouvea. *ACS Appl. Nanomat.* 2025, **8**, 2481.
2. C.A.P. Alves, P.H. Palharim, B. Pratto, A.L. da Silva, D. Gouvêa and B. Ramos, *J. Photochem. Photobiol. A: Chem.* **2025**, 460, 116159.

Predicting CO_2 solubility in hydrophobic deep eutectic solvents using SAFT-VR Mie - Impact of repulsive exponent

POSTER_P6.1 - Ionic Fluids and Deep Eutectic Solvents

Cleiton S. Beraldo[1,*], Xiaodong Liang[2], Luis A. Follegatti-Romero[1]

[1] *Department of Chemical Engineering (PQI), University of São Paulo (USP), São Paulo–SP, Brazil*
[2] *Center for Energy Resources Engineering (CERE), Department of Chemical and Biochemical Engineering, Technical University of Denmark, DK–2800 Kgs. Lyngby, Denmark*

**cleitonberaldo@usp.br*

In this study, the solubility of CO_2 in hydrophobic deep eutectic solvents (DESs) is predicted using the SAFT-VR Mie equation of state, as implemented in *Clapeyron.jl*[1]. The segment parameters of the SAFT model (number *m*, diameter σ, and energy ε) are fitted to experimental pure-component density data for five capric acid-based DESs, treating them as self-associating species following the 1A association scheme. This fitting is conducted within the pseudo-pure component framework, wherein each DES is modeled as a single compound. The CO_2–DES phase equilibria are then predicted based on the pure-component parameters of CO_2 and the DESs. The Hudson–McCoubrey combining rule is employed to estimate the unlike interaction parameters between CO_2 and DES. The results demonstrate that accurate predictions of CO_2–DES phase equilibria are achieved when the SAFT-VR Mie repulsive exponent (λ_r) is set to 16, as opposed to the conventional value of 12. This adjustment is illustrated in Figure 1 for one of the evaluated DES systems. By increasing the repulsive exponent in the SAFT-VR Mie model for DES mixtures, the representation of short-range interactions is enhanced, free-volume estimation is improved, and the balance between attractive and repulsive forces is refined. As a result, this modification significantly improves the model's accuracy in predicting CO_2 solubility in hydrophobic DESs.

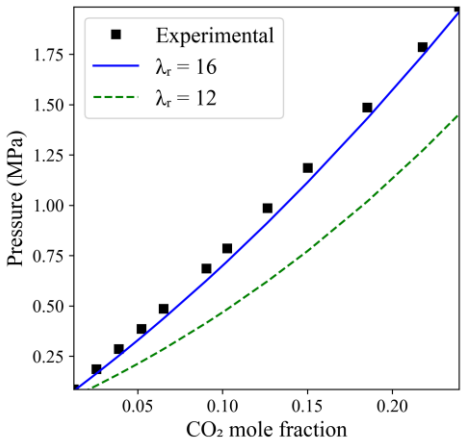


Figure 1: CO_2–DES phase equilibria of [TBA][Cl]:CA (1:2) at 298.15 K. Symbols represent experimental data[2], while the lines are the SAFT calculations.

Acknowledgments
This study was financed in part by the São Paulo Research Foundation (FAPESP), Brazil – Process Number 2024/10537-6. Luis A. Follegatti-Romero wishes to express his sincere gratitude for the support received from FAPESP under grant 2019/22085-4, as well as from Petronas (Petroliam Nasional Berhad) for Project No. ANP 23708-1. Xiaodong Liang wants to thank the support from the Independent Research Fund Denmark (Case number: 3105-00024B).

References

1. P. J. Walker, H. W. Yew and A. Riedemann, *Ind. Eng. Chem. Res.* 2022, **61**, 7130-7153.
2. L. F. Zubeir, D. J. G. P. Van Osch, M. A. A. Rocha, F. Banat and M. C. Kroon, *J. Chem. Eng. Data* 2018, **63**, 913-919.

Melting properties of thermally unstable quaternary ammonium salts using fast-scanning calorimetry

POSTER_P6.2 - Ionic Fluids and Deep Eutectic Solvents

Gabriel Teixeira[1,*], Nathanaël Guigo[2], Olga Ferreira[3,4], João A. P. Coutinho[1]

[1] *CICECO, Aveiro Institute of Materials, Complexo de Laboratórios Tecnológicos, University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal*
[2] *Université Nice Sophia Antipolis, Laboratoire de Physique de la Matière Condensée, Equipe Fluides et Matériaux Complexes CNRSUMR 7336, Parc Valrose, 06108 Nice Cedex 2, France*
[3] *Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal*
[4] *Laboratório para a Sustentabilidade e Tecnologia em Regiões de Montanha, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5300-253 Bragança, Portugal*

**gabriel.teixeira@ua.pt*

Accurate knowledge of melting properties is crucial for both interpreting and designing solid-liquid equilibria diagrams, as these provide fundamental insights into the thermodynamic behavior of mixtures and pure compounds. However, for many common deep eutectic solvent (DES) precursors – including choline chloride and related quaternary ammonium salts – traditional characterization methods such as differential scanning calorimetry (DSC) are inadequate due to thermal degradation during measurement.[1,2]
This study presents a comprehensive investigation of the melting properties of tetraalkylammonium chloride and bromide salts (N_{1111}, N_{2222}, N_{3333}, and N_{4444}) using Fast-Scanning Calorimetry (FSC), with conventional DSC and thermogravimetric analysis (TGA) serving as complementary techniques. The high heating rates achievable by FSC (up to 5000 $K{\cdot}s^{-1}$) enable precise measurement of phase transitions in these thermally labile compounds.[3] To ensure accurate quantification, two independent methods for sample mass determination were developed: (1) comparative analysis of specific heat capacities measured by FSC and literature data, and (2) validation through solid-solid transition enthalpy measurements. The methodology was rigorously validated using reference compounds with well-established melting properties prior to application to the target ammonium salts.
The reliability of our melting temperature and enthalpy measurements was further confirmed through systematic re-evaluation of nineteen published solid-liquid phase diagrams for binary mixtures containing these quaternary ammonium salts with either: (i) other ammonium salts of differing chain lengths (N_{XXXX}/N_{YYYY}), (ii) fatty acids (palmitic acid and capric acid), or (iii) urea. This extensive thermodynamic consistency check demonstrates that our FSC-derived data provides significantly improved agreement with phase equilibrium behavior compared to previous estimates. The results establish FSC as an essential tool for characterizing thermally unstable compounds and advance our fundamental understanding of ammonium salt thermodynamics, with direct implications for DES development and phase diagram prediction.

Acknowledgements
This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 and LA/P/0006/2020, and CIMO-Mountain Research Center, UIDB/00690/2020 and LA/P/0007/2020, financed by national funds through the Portuguese Foundation for Science and Technology/MCTES. Fruitful collaboration with Mettler-Toledo on Flash DSC 1 is gratefully acknowledged. Gabriel Teixeira thanks FCT for his Ph.D. grant (UI/BD/151114/2021).

References

1. A. Xenopoulos, J. Cheng, M. Yasuniwa and B. Wunderlich, Molecular Crystals and Liquid Crystals Science and Technology. Section A. *Molecular Crystals and Liquid Crystals* 1992, **214**, 63-79.
2. A. van den Bruinhorst, J. Avila, M. Rosenthal, A. Pellegrino, M. Burghammer and M. Costa Gomes, *Nat Commun* 2023, **14**, 6684.
3. N. Bosq, N. Guigo, E. Zhuravlev and N. Sbirrazzuoli, *J Phys Chem B* 2013, **117**, 3407-3415.

Physicochemical properties of selected isoquinoline-, piperidine- and pyridine-based ionic liquids

POSTER_P6.3 - Ionic Fluids and Deep Eutectic Solvents

Antoni Maciejewski[1,*], Kamil Paduszyński[1],

[1]*Chair of Physical Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland*

**antoni.maciejewski.stud@pw.edu.pl*

Ionic Liquids (ILs) are a specific class of salts composed, typically, of an organic cation and an anion. Their defining characteristic is that ILs remain in the liquid state at relatively low temperatures. They have a wide range of applications, including their use as "green solvents", i.e., environmentally friendly alternatives to conventional solvents.

Due to the essential role of the melting point value in the consideration of ILs, the aim of this work was to further investigate its variability as ion structure modifications are introduced. Accordingly, a series of selected isoquinolinium, *N*-methyl-piperidinium, and pyridinium based bromides were synthesized and their temperature and enthalpy of fusion were investigated. From prepared salts (denoted as [i-Quin,C_n][Br], [Pip-C_1,C_n][Br] and [Py-C_n][Br] for n = 2-10, 12, 14, 16, 18) those which can serve as ILs have been selected. Another key objective of this research was to combine the experimentally measured data with literature values[1] to develop a quantitative structure–property relationship (QSPR) model for predicting the enthalpy and temperature of fusion.

This study is part of a broader investigation focused on the formation of supramolecular structures of ILs in binary systems containing α,ω-alkanediols or water. The salts were synthesized via quaternization of the nitrogen atoms, and the final product was further purified by recrystallization. To confirm the identity of the synthesized compounds, nuclear magnetic resonance (NMR) spectroscopy was performed. The water content in each salt was assessed using coulometric Karl-Fischer titration and the thermal properties of the salts were analyzed using differential scanning calorimetry (DSC). Sample preparation for all tests was carried out under anhydrous conditions - in a nitrogen-filled dry box. Prior to measurements, the calorimeter was calibrated using the 99.9999 mol % purity indium sample, 99.999 mol % purity mercury and high-mass-purity *n*-heptane, phenyl salicylate, biphenyl, benzoic acid, cyclohexane, *n*-octadecane, naphthalene, and water.

Acknowledgments

Studies were funded by POSTDOC PW-V project granted by Warsaw University of Technology under the program Excellence Initiative: Research University (ID-UB). Agreement number: CPR-IDUB/367/Z01/Z10/2023.

References

1. A. Kazakov, J. W. Magee, R. D. Chirico, E. Paulechka, V. Diky, C. D. Muzny, K. Kroenlein and M. Frenkel, 'NIST Standard Reference Database 147: NIST Ionic Liquids Database - (ILThermo)', Version 2.0, National Institute of Standards and Technology, Gaithersburg MD, 20899, http://ilthermo.boulder.nist.gov.

Experimental and computational study on interactions in the ternary aqueous systems containing saccharides and 1-ethyl-3-methylimidazolium dicyanamide

POSTER_P6.4 - Ionic Fluids and Deep Eutectic Solvents

Gabriela M. Melo[1], Ronaldo G. dos Santos[1], Bruno Ramos[1], Gustavo V. Olivieri[1], Nelson H. Morgon[2], Ricardo B. Torres[1,*]

[1]*Department of Chemical Engineering, Centro Universitário FEI, São Bernardo do Campo, Brazil*
[2]*Department of Physical Chemistry, Institute of Chemistry, Campinas State University (UNICAMP), Campinas, São Paulo, Brazil*

[*]*belchior@fei.edu.br*

Ionic liquids (ILs) consist of a high variety of salts with melting points below 100 °C. ILs present applications as solvents or electrolytes in several processes, alternatively greener than traditional solvents, due to the reduced vapor pressure, low toxicity, and high electrical conductivity of the ILs.[1] Thermodynamic properties of ternary systems containing ILs and saccharides in aqueous solutions suggest valuable results about the interactions between the substances. Particularly, the quantification of apparent molal volumes can show if the IL may affect the taste quality of the saccharides.[2,3] The present study aimed to obtain new data of density of the ternary systems {water + saccharides (D(+)-glucose, D(+)-xylose, or sucrose) + the IL 1-ethyl-3-methylimidazolium dicyanamide ([Emim][DCA])}, at different temperatures, and different molalities of the IL and the saccharides. The experiments were conducted at p = 93,2 kPa and temperatures range T = (283.15 - 303.15) K. The experimental data enabled the determination of the apparent molal volumes of the saccharides, the transfer volume of saccharides from water to the ionic solution, and the apparent specific volumes (ASV), with interpretation supported by the cosphere overlap model. The Density Functional Theory (DFT) was also applied as a computational study to support the experimental results, focusing on intermolecular interactions. Both experimental and computational analyses resulted in thermodynamically favorable interactions between sucrose and the cation of the IL (hydrophilic-ionic interactions), while D(+)-glucose and D(+)-xylose led to weaker interactions with the IL (possible hydrophobic-ionic, hydrophobic-hydrophobic, and hydrophilic-hydrophobic solute-cosolute interactions). The ASV results also indicate that the presence of the IL does not affect the taste quality of the saccharide, since those values remain in typical ranges of the pure saccharide.

Acknowledgements
We kindly thank Centro Universitário FEI for the financial support to carry out the research.

References

1. K. N. Marsh, J. A. Boxall and R. Lichtenthaler, *Fluid Phase Equilibria* 2004, **219**, 93-98.
2. V. Singh and V. Kasaudhan, *Food Chemistry* 2024, **446**, 138864.
3. M. T. Zafarani-Moattar, H. Shekaari and E. M. H. Agha, *Food Chemistry* 2019, **295**, 662-670.

Ionic liquid incorporation in polymeric membranes for indoor air quality

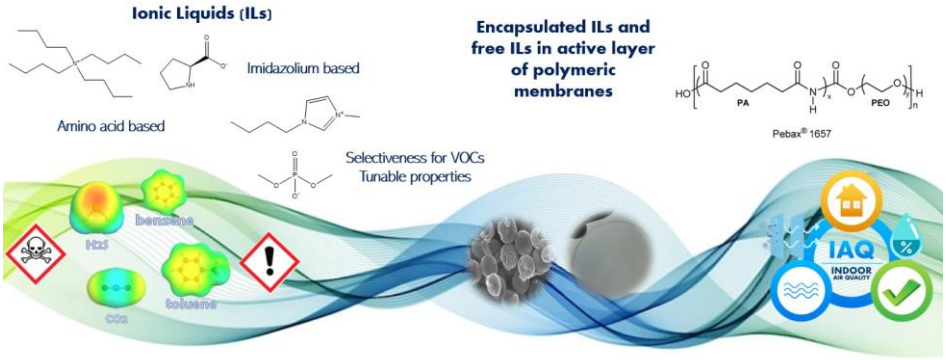
POSTER_P6.5 - Ionic Fluids and Deep Eutectic Solvents

Isabella M. G. de Souza[1,*], and Pedro J. Carvalho[1]

[1]*CICECO – Aveiro Institute of Materials, Chemistry Department, University of Aveiro, 3810-193 Aveiro, Portugal*

[*]*isabellamgsouza@ua.pt*

Roughly 2.4 billion people are exposed to dangerous household air pollution.[1] Different gases are responsible for indoor air pollution, including volatile organic compounds (VOCs), inorganic gases, and emerging contaminants. One of the most common indoor contaminants is carbon dioxide (CO_2), which can be associated with reduced professional performance and health problems such as respiratory and heart diseases.[2] The implementation of compact indoor CO_2 capture technologies is of great importance. Nevertheless, technologies for direct air capture are still scarce or non-existent to be used commercially. Ionic liquids (ILs) are a class of solvents with interesting properties such as low volatility, low vapor pressure, non-flammability, low corrosiveness, and high selectivity for CO_2 that can support the development of sustainable processes. Nonetheless, ILs generally present high viscosity, which leads to poor mass transfer and kinetics. To address this problem, our group has already proposed the incorporation of ionic liquids in sub-micron carbon capsules (ENILs) to achieve virtually instantaneous kinetics to absorb CO_2, improve mechanical stability, increase mass transfer rates, and lower the energy regeneration demand at mild conditions.[3] However, incorporating ENILS in conventional separation processes, such as fixed bed reactors, still faces important drawbacks, like high pressure drop due to the size of ENILs (< 900 nm). Aiming to overcome this limitation, incorporating the ENILs and/or ILs in polymeric membrane matrices is a promising approach. This work proposes to evaluate these approaches of incorporating ILs in polymeric membranes based on gas permeation measurements by the time lag method, thermal characterization, and spectroscopy techniques. The aim of the work is to develop a membrane separation unit for indoor air separation, as shown in Scheme 1.



Scheme 1: Development of a membrane separation unit for indoor air quality.

Acknowledgements
This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 (DOI 10.54499/UIDB/50011/2020), UIDP/50011/2020 (DOI 10.54499/UIDP/50011/2020) & LA/P/0006/2020 (DOI 10.54499/LA/P/0006/2020), financed by national funds through the FCT/MCTES (PIDDAC). We would also like to thank ARKEMA for providing PEBAX® 1657.

References

1. W. H. O. (WHO), 2022, preprint, https://www.who.int/publications/m/item/who-air-quality-database-2022.
2. L. R. López, P. Dessì, A. Cabrera-Codony, L. Rocha-Melogno, B. Kraakman, V. Naddeo, M. D. Balaguer and S. Puig, *Elsevier B.V.*, 2023, preprint, DOI: 10.1016/j.scitotenv.2022.159088.
3. L. P. Silva, C. Moya, M. Sousa, R. Santiago, T. E. Sintra, A. R. F. Carreira, J. Palomar, J. A. P. Coutinho and P. J. Carvalho, *Eur J Inorg Chem* 2020, **2020**, 3158-3166.

Bis(alkylsulfonyl)imide-based ionic liquids: Study of their thermodynamic properties

POSTER_P6.6 - Ionic Fluids and Deep Eutectic Solvents

Rodrigo M. A. Silva[1,*], Ana I. M. C. Lobo Ferreira[1], Patrícia M. Reis[2], Ana B. Pereiro[2], Luís P. N. Rebelo[2], Luís M. N. B. F. Santos[1]

[1]*Centro de Investigação em Química (CIQUP), Institute of Molecular Sciences (IMS), Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua Campo Alegre s/n, 4169-007 Porto, Portugal*
[2]*LAQV, REQUIMTE, Department of Chemistry, NOVA School of Science and Technology, NOVA University Lisbon, 2829-516 Caparica, Portugal*

[*]*rodrigo.m.a.silva98@gmail.com*

Previous studies revealed that the replacement of the terminal trifluoromethyl groups in the bis(trifluoromethylsulfonyl)imide anion by methyl groups dramatically influences the conformational flexibility of the anion, and consequently the transport properties of the ionic liquid (IL).[1,2] In this work we investigate how the chain length of the bis(alkylsulfonyl)imide anion and the 1-alkyl-3-methylimidazolium cation affect the thermodynamics of ILs. The structures of the studied ILs are presented in Figure 1.

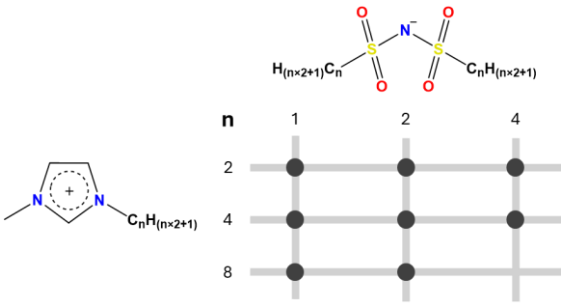


Figure 1: Structure and grid of the studied IL pairs.

Differential scanning calorimetry (DSC) revealed that bis(methylsulfonyl)imide-based ILs present higher glass transition temperatures than their bis(trifluoromethylsulfonyl)imide analogs. Furthermore, melting also occurs at higher temperature. The bis(alkylsulfonyl)imide-based ILs were found to have a significantly lower thermal stability than their fluorinated analogs, as revealed by thermogravimetric analysis (TGA). The heat capacity of the ILs was determined at T = 298.15 K and as a function of temperature using drop calorimetry[1] and differential scanning microcalorimetry.[2] The elongation of the alkyl chain of the cation produces a similar effect on the heat capacity of the liquid phase, at T = 298.15 K, to that found in previous works. However, the elongation of the alkyl chain of the anion seems to produce a smaller effect.

Acknowledgements
This work was supported by the Fundação para a Ciência e Tecnologia (FCT) (funded by national funds through the FCT/MCTES (PIDDAC)) to CIQUP, Faculty of Science, University of Porto (Project UIDB/00081/2020), IMS-Institute of Molecular Sciences (LA/P/0056/2020). RMAS is grateful to FCT for the award of his PhD grant (U1/BD/153093/2022). AIMCLF is also financed by national funds through the FCT-I.P., in the framework of the execution of the program contract provided in paragraphs 4, 5 and 6 of art. 23 of Law no. 57/2016 of 29 August, as amended by Law no. 57/2017 of 19 July.

References

1. F. Philippi *et al.*, *Chem. Sci.* 2020, **11**, 6405.
2. F. Philippi *et al.*, *Chem. Sci.* 2022, **13**, 9176.
3. L. Santos *et al.*, *J. Chem. Thermodyn.* 2011, **43**, 1818-1823.
4. R. Silva *et al. J. Phys. Chem. B* 2024, **128**, 3742-3754.

Membranes functionalized with non-volatile solvents for gas separation

POSTER_P6.7 - Ionic Fluids and Deep Eutectic Solvents

Beatriz F. Esteves[1,*], Bruna R. M. Ferreira[1], Ricardo T. Pais[1], Filipe H. B. Sosa[1], and Pedro J. Carvalho[1]

[1]*CICECO – Aveiro Institute of Materials, University of Aveiro, Aveiro, Portugal*

[*]*beatriz.est@ua.pt*

Over recent decades, greenhouse gas (GHG) emissions have risen, leading to an increase in their atmospheric concentrations and amplifying the natural greenhouse effect. This has resulted in adverse impacts on Earth's ecosystems and climate. The annual GHG emissions are approximately 50 billion tons of CO_2 equivalents, comprising 73.7% carbon dioxide (CO_2), 18.9% methane (CH_4), 4.7% nitrous oxide (N_2O), and 2.7% fluorinated gases.[1] Many technologies, including absorption, adsorption, and electrochemical reduction, have been employed to mitigate these pollutants. However traditional abatement technologies face several drawbacks, including high energy demand, low efficacy, solvent toxicity and size requirements.[2] These limitations underscore the need for more efficient and environmentally friendly GHG mitigation approaches.
Non-volatile solvents, particularly Ionic Liquids (ILs) and Deep Eutetic Solvents (DES) have emerged as promising alternatives to conventional solvents, due to their attractive properties, including negligible vapor pressure, high thermal stability, and tuneable properties.[3] However, the direct implementation of non-volatile solvents in conventional separation units faces obstacles, including the need for large separation units and high energy demands for solvent recovery.[4] To address these challenges, we proposed the development of a Gas-Liquid Membrane Contactor (GLMC) with hollow-fiber membranes constituted by polyetherimide (PEI) with a thin layer of Pebax® functionalized with non-volatile solvents. This novel approach aims to optimise the balance between the sorption capacity and selectivity of the solvent with the modularity, compactness, and scalability inherent in membrane technology. The GLMC modules will be modelled and described with Fick and Stefan-Maxwell equation foreseeing a better understanding of the systems aiming at an accurate implementation in a process simulator Aspen Plus for realistic scale-up/technical evaluations.

Acknowledgements
The present study was developed in the scope of the Project "Agenda ILLIANCE" [C644919832-0000035 | Project n.º46], financed by PRR – Plano de Recuperação e Resiliência under the Next Generation EU from the European Union and the project CICECO Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MEC(PIDDAC). The authors acknowledge Arkema for kindly supplying Pebax®1657 and 1074. B.F.E. and R.T.P. acknowledges FCT for their Ph.D. Grant 2024.02809.BDANA and 2020.07796.BD, respectively.

References

1. EDGAR - The Emissions Database for Global Atmospheric Research, https://edgar.jrc.ec.europa.eu/report_2024, (accessed 12 January 2025).
2. N. Islam, H. Warsi Khan, A. A. Gari, M. Yusuf and K. Irshad, *Fuel* 2022, **330**, 125540.
3. Y. Xu, R. Zhang, Y. Zhou, D. Hu, C. Ge, W. Fan, B. Chen, Y. Chen, W. Zhang, H. Liu, G. Cui and H. Lu, *Chemical Engineering Journal* 2023, **463**, 142298.
4. M. T. Mota-Martinez, P. Brandl, J. P. Hallett and N. Mac Dowell, *Mol Syst Des Eng* 2018, **3**, 560-571.

Biopolymeric membrane using deep eutectic solvent for gas separation

POSTER_P6.8 - Ionic Fluids and Deep Eutectic Solvents

Bruna R. M. Ferreira[1,*] Beatriz F. Esteves[1], Ricardo T. Pais[1], Filipe H. B. Sosa[1], Pedro J. Carvalho[1]

[1] *CICECO – Aveiro Institute of Materials, Chemistry Department, University of Aveiro*

**brunaf@ua.pt*

Air pollution was declared the second largest risk factor of mortality in 2021 and World Health Organization claims that 99% of all people are exposed polluted air.[1-2] Although atmospheric air pollution is a big concern, poor indoor air quality is even more relevant to human health as the world population spends about 90% of their lifetime indoors.[3] Room ventilation is a key factor to ensure healthy breathable air but itself alone isn't enough to guarantee healthy air therefore, the development of new, sustainable, technical and economical technologies for air treatment is of key relevance. Established techniques like mechanical or electronic filtration and adsorption or emerging technologies like photocatalytic oxidation or plasma air disinfection present important drawbacks such as high energy consumption, release and fostering of more hazardous pollutants and short lifespans. The use of greener solvents for membrane preparation has been proposed to address the typical use of highly toxic solvents. Between water-based solvents, ionic liquids and deep eutectic solvents (DES) offer advantages like ease of preparation, low toxicity and high solubility and selectivity. It is yet a challenge to implement those non-volatile solvents in classic separation systems as there's a need for large separation units and high energy demands for solvent recovery.[4] Membrane separation stands as an approach that offers great potential, presenting advantages such as modularity, scalability and compactness. A manipulation of the formulation adjusts the permeability and selectivity of the fuctionalized structure to ensure a superior performance depending on the application invisioned. In this study, the advantages of membranes and greener solvents are coupled to form highly selective compact membranes that can be used continuously with no required regeneration and, therefore, being a lower energy intensive separation technique. In the present investigation, polyetherimide supported Pebax® membranes with a DES and lignin as additives to enhance the membranes separation capabilities are tested as a solution for indoor air purification purposes. The prepared membranes were tested using carbon dioxide, oxygen and nitrogen; the addition of the DES when compared to the pristine formulation lowered the membranes selectivity towards all gases and allowed easier oxygen and nitrogen transport across the membrane.

Acknowledgements

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/ 50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MEC (PIDDAC). Filipe H. B. Sosa acknowledges FCT for the researcher contract CEECIND/07209/2022 under the Scientific Employment Stimulus - Individual Call 2022. The authors acknowledge Arkema for kindly supplying Pebax® 1074.

References

1. Health Effects Institute. State of Global Air 2024. Special Report. Boston, MA: Health Effects Institute.
2. World Health Organization, "Billions of people still breathe unhealthy air: new WHO data," 2022.
3. Faculty of Public Health "Air Pollution and Climate Change." Internal Report, 2021.
4. M. T. Mota-Martinez, P. Brandl, J. P. Hallett and N. Mac Dowell, *Mol Syst Des Eng* 2018, **3**, 560-571.

Understanding salicylic acid solubility in eutectic solvents: From predictions to experimental results and molecular simulations

POSTER_P6.9 - Ionic Fluids and Deep Eutectic Solvents

Bárbara C. Jesus[1], Hannyah Remetula[1], Maria Gonzalez-Miquel[3], Alice Martins[4], Nuno Galamba[2], Isabel M. Marrucho[1,*]

[1]*Centro de Química Estrutural - Institute of Molecular Sciences, and Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa*
[2]*Biosystems and Integrative Sciences Institute, Faculdade de Ciências, Universidade de Lisboa*
[3]*Departamento de Ingeniería Química Industrial y del Medio ambiente, ETS Ingenieros* Industriales, *Universidad Politécnica de Madrid*
[4]*MARE – Marine and Environmental Sciences Centre, ARNET – Aquatic Research Network, Polytechnic of Leiria*

[*]*isabel.marrucho@tecnico.ulisboa.pt*

Eutectic solvents (ES) have shown great potential in extracting phenolic compounds from natural matrices, namely seaweeds. Portuguese invasive seaweeds are underexplored and promoting their exploitation is not only economically important but also relieves their environmental burden.[1] It is well known that seaweeds present several phenolic compounds (PCs), and species belonging to *Sargassaceae* family are recognized to have particularly high quantity.[2]

In previous work[2], we showed that Proline:1,2-Propanediol (1:4) has a high extraction efficiency and selectivity towards salicylic acid (SA), an abundant PC in *Sargassum muticum.* The present work focuses on understanding this phenomenon through solubility studies. COSMO-RS was used to obtain activity coefficients and solubilities values of salicylic acid in Proline:1,2-Propanediol for different ES ratios and with different water contents. Furthermore, a design of experiments was performed to determine the experimental conditions, ES ratio and water content, to achieve the maximum SA solubility. It was curious to observe that for each DES ratio, a maximum water content was found, indicating the hydrotropic character of the ES.[3] The solubility of SA in aqueous solutions of each of the pure compounds that compose the ES were also evaluated to understand which of the two compounds, proline or 1,2-propanediol, rules this hydrotropic behavior.

Other ES, such as Proline:1,3-Propanediol and Proline:1,2-Butanediol were also tested previously[2] tested as extraction solvents of SA *Sargassum muticum.* Despite their lower SA extraction efficiencies when compared to Proline:1,2-Propanediol, these ES were also here used to understand the influence of small structural differences in the hydrogen bond donor in the SA solubility. Molecular dynamics simulations were also carried out to further understand this behaviour at the molecular level.

Acknowledgements
Centro de Química Estrutural (UIDB/00100/2020 and UIDP/00100/2020) and Institute of Molecular Sciences (LA/P/0056/2020) are funded by FCT. This work acknowledges Comunidad Autónoma de Madrid (Spain) through projects "SUSTEC P2018/EMT-4348" and "Multiannual Agreement with UPMadrid in the line Excellence Programme for University Professors, in the context of the V PRICIT (Regional Programme of Research and Technological Innovation)". MARE—Marine and Environmental Sciences Centre (UIDP/04292/2020 and UIDB/04292/2020), and to Associate Laboratory ARNET (LA/P/0069/2020) are also funded by FCT. Bárbara C. Jesus is financed by FCT under a PhD Studentship (2023.00421.BD).

References

1. A. G. Pereira, M. Fraga-Corral, P. Garcia-Oliveira, C. Lourenço-Lopes, M. Carpena, M. A. Prieto, J. Simal-Gandara, *Marine Drugs* 2021, **19**, 178.
2. B. C. Jesus, B. Saenz De Miera, R. Santiago, A. Martins, R. Pedrosa, M. Gonzalez-Miquel, I. M. Marrucho, *RSC Sustainability* 2023, **1**, 1245-1258.
3. B. Soares, A.J.D. Silvestre, P.C. Rodrigues Pinto, C.S.R. Freire, J.A.P. Coutinho, *ACS Sustain Chem Eng* 2019, **7**, 12485-12493.

Phase transition of cationic surfactant CTAB-water binary system: Effects of long-chain alcohol, carboxylic acid, and carboxylate additives

POSTER_P7.1 - Soft Matter, Colloids, and Complex Fluids

Kosei Yoshida*, Hal Suzuki

Department of Chemistry, Kindai University, Higashiosaka, Osaka, 577-8502, Japan

*2433310148y@kindai.ac.jp

Surfactant-water binary systems form various molecular assemblies depending on their concentration and temperature, including micelles (spherical and rod-like), lyotropic liquid crystals (nematic, hexagonal, etc.), and gels. The gel phase has potential applications in cosmetic and healthcare products, such as body creams and hair conditioners, due to its unique viscoelastic properties. Cetyltrimethylammonium bromide (CTAB: $[CH_3(CH_2)_{15}N(CH_3)_3]Br$) is a widely used cationic surfactant, and the CTAB-water binary system exhibits various molecular assemblies including the gel phase. However, the gel phase of CTAB-water system is thermodynamically metastable; it can be obtained by supercooling micelles or lyotropic liquid crystals but easily transforms into a more stable crystalline phase.[1] To obtain a stable gel phase, the addition of a third component is necessary, but the mechanism is not yet fully understood.

In this study, to explore the effect of additives on the thermodynamic stability of the CTAB-water gel phase, we investigated the phase behavior of CTAB-water-additive ternary system using differential scanning calorimetry (DSC). The additives used were hexadecanol ($C_{16}H_{33}OH$), palmitic acid ($C_{15}H_{31}COOH$), and sodium palmitate ($C_{15}H_{31}COONa$). The concentration of CTAB in water was fixed at 14 wt. %, and the molar ratio x of the additive to CTAB was varied from 0.000 to 0.331.

Fig. 1 shows the DSC curves (cooling scan) at the transition from rod-like micelles to gel phase. In all three systems, the transition peak shifts to a higher temperature with increasing x. For the $C_{16}H_{33}OH$ and $C_{15}H_{31}COOH$ systems, the transition peak broadens at $x > 0.03$, and the transition enthalpy $\Delta_{trs}H$ slightly increases with x. In contrast, for the $C_{15}H_{31}COONa$ system, new transition peaks appear sequentially as x increases, and $\Delta_{trs}H$ decreases. These results indicate that the gel phase is stabilized by the additives, but the stabilization mechanisms differ between the $C_{16}H_{33}OH/C_{15}H_{31}COOH$ and $C_{15}H_{31}COONa$ systems.

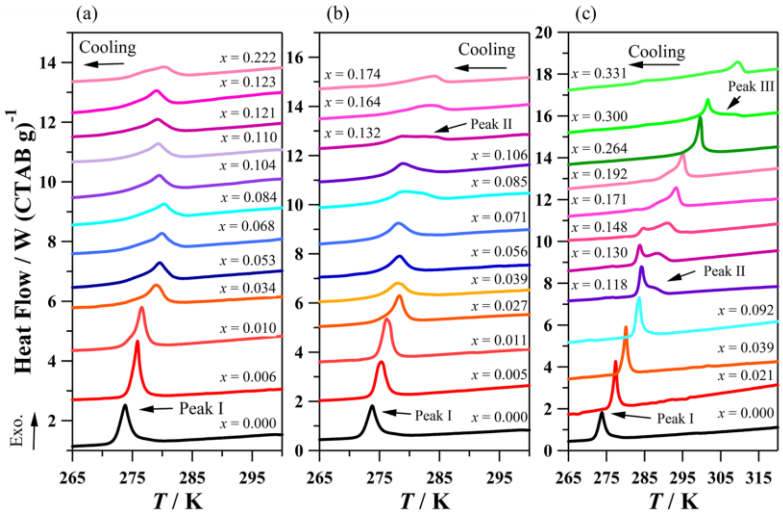


Fig. 1 DSC curves on the cooling scan for (a) CTAB-H_2O-$C_{16}H_{33}OH$, (b) CTAB-H_2O-$C_{15}H_{31}COOH$, and (c) CTAB-H_2O-$C_{15}H_{31}COONa$.

References

1. T. Yamamoto, Y. Yagi, T. Hatakeyama, T. Wakabayashi, T. Kamiyama, H. Suzuki, *Colloids and Surfaces A* 2021, **625**, 126859.

Soft dynamics of water and solute in solutions of polyhydroxy compounds: inelastic and quasielastic neutron scattering and terahertz spectroscopy study

POSTER_P7.2 - Soft Matter, Colloids, and Complex Fluids

Luke L. Daemen[1], Alexander I. Kolesnikov[1], Eugene Mamontov[1], J. Axel Zeitler,[2] Evgenyi Shalaev[3,*]

[1]Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA
[2] Department of Chemical Engineering, University of Cambridge, UK. [3]AbbVie, Irvine, CA, USA

*evgenyi.shalaev@abbvie.com

Frozen aqueous solutions containing carbohydrates and other polyhydroxycompounds (PHC) are ubiquitous in food and biological drugs. During the cooling of dilute solutions, water crystallization is usually incomplete, with a freeze-concentrated solution (FCS) coexisting with hexagonal ice. In concentrated solutions, crystalline ice does not form even at temperatures below 100K, and the system remains in an amorphous state. The mechanism of the incomplete liquid water-to-crystalline ice transformation has not been unequivocally established yet. It has been proposed that the prevention of the formation of crystalline ice is related to the confinement of water molecules in a sugar matrix, with sugar molecules forming rigid walls below its Tg.[1]
In the present study, inelastic and quasielastic neutron scattering (INS and QENS, respectively) are used to investigate vibrational dynamics and diffusional (rotational and translational) mobility of both matrix (glycerol, sorbitol, sucrose) and water molecules at temperatures 5 to 320 K and two solute concentrations. The experiments are performed with VISION, SEQUOIA and BASIS instruments at the Oak Ridge National Laboratory, USA. The neutron scattering data are complemented with results obtained using terahertz spectroscopy and differential scanning calorimetry. Preliminary analysis of the QENS results reveal intriguing difference in the water and solute behavior between three PHC systems tested. At 298 K, for example, water average jump length appears to be similar to sucrose fixed jump length, while decoupling between water and the matrix is observed in glycerol/water mixture. This observation indicates microphase segregation and clustering of solute molecules in glycerol and possibly sorbitol systems, which is different from sucrose/water solution. Temperature trends are also different between three systems studied, with major change observed in glycerol/water systems between 228 and 258K and sucrose/water between 258 and 298K, whereas sorbitol demonstrates more gradual changes between 228 and 298K (Figure 1). Terahertz spectroscopy data for the water/glycerol system linked the change in the neutron scattering patterns with transformation from harmonic to anharmonic regime, which marks onset of molecular relaxation as measured by infrared active dipoles. The study provides additional inputs to understanding of factors which limit water-to-crystalline ice conversion, including water diffusion, confinement of water within a solute matrix, and the solidification of the matrix below its calorimetric Tg.

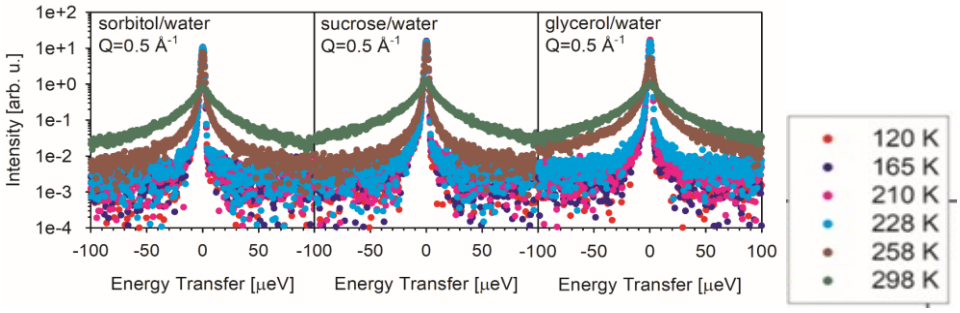


Figure 1: Examples of QENS spectra with BASIS instrument for 70% PHC+30% water at 120K to 298K.

Acknowledgments
This research used resources at the Spallation Neutron Source, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory. ES is AbbVie employee and may own AbbVie stock. AbbVie did not provide financial funding for this study. AbbVie contributed to the design, analysis, and interpretation of the data, and wrote, reviewed, and approved the presentation.

References

1. E. Shalaev, A. K. Soper. *J Phys Chem B* 2016, **120**, 7289-96.

Heat capacity measurements of 2,5-dibromothiophene and 2,5-dichlorothiophene

POSTER_P7.3 - Soft Matter, Colloids, and Complex Fluids

Kaito Nagata[1], Mai Nakamura[1], Rie Kuwashima[2], Mariko Noguchi[1], Hiroki Fujimori[1,2,*]

[1]*College of Humanities and Sciences, Nihon University, Tokyo, 156-8550, Japan*
[2]*Graduate School of Integrated Basic Sciences, Nihon University, Tokyo, 156-8550, Japan*

[*]*fujimori.hiroki@nihon-u.ac.jp*

Thiophene-based materials have been known as the material which indicates the glass transition in the crystalline phase by the freezing of molecular reorientation. It has been reported that their glass transitions were observed by calorimetric measurements. Table 1 shows the glass transition temperatures in the stable crystalline phases of some of the thiophene-based materials.[1-4]

2,5-Dibromothiophene (BBT) and 2,5-dichlorothiophene (CCT) are the di-substituted compounds of thiophene. In CCT the glass transition was observed in the stable crystalline phase.[4] On the other hand, in BBT the glass transition was not observed in the crystalline phase, but instead a first-order phase transition was observed at 235.26 K. In the present study, heat capacity measurements using by an adiabatic calorimeter were performed for BBT, CCT, and their solid-solution system. We discuss the relationship between the glass transition in CCT and the phase transition in BBT.

Table 1. Glass transition temperatures in the stable crystalline phases of thiophene-based materials.

Sample	T_g / K
Thiophene[1]	42
2-Bromothiophene[2]	120
2-Chlorothiophene[3]	164 and 186
2,5-Dichlorothiophene[4]	138

References

1. P. Figuière, H. Szwarc, M. Oguni and H. Suga, *J. Chem. Thermodyn.* 2024, **17**, 949.
2. H. Fujimori and M. Oguni, *J. Phys. Chem. Solids* 1993, **54**, 271.
3. H. Fujimori and M. Oguni, *J. Phys. Chem. Solids* 1993, **54**, 607.
4. H. Fujimori, K. Matsuda, A. Todoroki, T. Asaji and M. Oguni, *J. Non-Cryst. Solids* 2006, **352**, 4790.

Volumetric study of zirconia (45 nm) + water nanofluid: thickness, molar volume and density of the nanolayer

POSTER_P7.4 - Soft Matter, Colloids, and Complex Fluids

A. Queirós[1,2], M. F. Coelho[2], T. P. Iglesias[1,*]

[1] *Departamento de Física Aplicada, Facultad de Ciencias, Universidad de Vigo, 36310 Vigo, Spain*
[2] *Politécnico do Porto, Instituto Superior de Engenharia do Porto, 4200-072 Porto, Portugal*

**tpigles@uvigo.gal*

Nanofluids are colloids of nanoparticles dispersed in base fluids. In this work we carry out a study on the volumetric properties of zirconia (45 nm) + water nanofluid. Its density was measured at temperatures between 298.15 and 348.15 K and concentrations below 2 % in volume, because this is considered low enough that nanoparticles act individually to affect the properties of the system.[1] From density the coefficient of thermal expansion was calculated. This quantity can be of interest from the applied point of view. From the fundamental point of view the nanolayer thickness, t_v, was calculated following the theoretical model of Iglesias et al.[2] In this model t_v is calculated through the molar volume of mixing which is defined as $\Delta V_m = V_m - (x_p V^*_p + (1 + x_p) V^*_b)$ where V^*_b is the molar volume of the base fluid and V_m is the nanofluid molar volume calculated using the nanofluid density. From the nanolayer thickness, the nanolayer density and its molar volume were calculated following the model mentioned above. The knowledge of these properties could be of interest to know how nanoparticles and base fluids interact and might help to understand how nanoparticles disperse in the base fluid and how this affects the nanofluid stability over time, with temperature and with nanoparticle concentration.

Acknowledgments
This work was funded by the European Union H2020-MSCA-RISE- 2019 PEPSA-MATE (872233) and Consellería de Cultura, Educación e Universidade, Xunta de Galicia, Spain (Grant ED431B 2024/27).

References

1. An introduction to Interface & Colloids. The bridge to nanoscience, John C. Berg, World Scientific, New Jersey, 2010.
2. T.P. Iglesias, A. Queiros and M.F. Coelho, *J. Mol. Liq*. 2024, **393**, 123537.

Enhancing nimesulide solubility with sodium benzoate: A solvatochromic study to elucidate hydrotropic mechanisms

POSTER_P7.5 - Soft Matter, Colloids, and Complex Fluids

Nelson Nunes[1,2*], Martim Chorão[3], Ruben Leitão[1,2], Filomena Martins[1,3]

[1]*Centro de Química Estrutural, Faculdade de Ciências, Institute of Molecular Sciences, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal*
[2]*Departamento Engenharia Quimica, Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa, R. Conselheiro Emidio Navarro, 1959-007 Lisboa, Portugal;*
[3]*Departamento de Química e Bioquímica, Faculdade de Ciências Universidade de Lisboa, Ed. C8, Campo Grande, 1749-016 Lisboa, Portugal*

**nelson.nunes@isel.pt*

The limited aqueous solubility of Active Pharmaceutical Ingredients (APIs) remains a significant challenge in drug formulation, directly impacting bioavailability. Strategies to improve solubility, such as co-solvency, complexation, and micellar solubilization, are well-documented.[1] A less common approach is the use of hydrotropes which are also an alternative to enhance water solubility of poorly soluble drugs. The mechanism of action of hydrotropes is still not fully understood with different hypotheses proposed in the literature.[2] This study focuses on nimesulide (Figure 1), a widely used acidic nonsteroidal anti-inflammatory drug exhibiting particularly low water solubility (0.01 mg/mL) and aims to investigate its solubilization improvement using different concentrations of sodium benzoate used as a model hydrotrope.[3] To elucidate the underlying mechanism, we characterized the sodium benzoate solutions making use of five solvatochromic probes, (4-nitroaniline, 4-nitrophenol, *N*,*N*-dimethyl-4-nitroaniline, 4-nitroanisole, and Reichard's dye), which allow the calculation of Kamlet-Taft solvent parameters, namely, π^*, α, β. These parameters were then correlated with solubility data to identify dominant solute-solute-solvent interactions driving solubilization. Additionally, we completed this analysis with further solvent structural characterization of the hydrotrope solutions through density, sound velocity, viscosity, refractive index and conductance measurements, complementing previous studies,[3] thus providing a more comprehensive understanding of the mechanism at play and offering insights into optimizing nimesulide formulation for improved therapeutic efficacy.

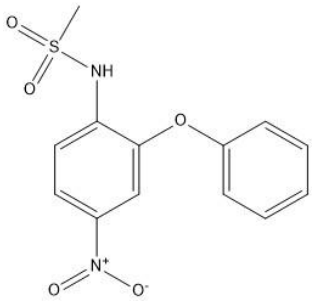


Figure 1: Nimesulide structure.

Acknowledgements
This research was funded by the Fundação para a Ciência e a Tecnologia (FCT), Portugal. Centro de Química Estrutural is a Research Unit funded by FCT through projects UIDB/ 00100/2020 (https://doi.org/10.54499/UIDB/00100/2020) and UIDP/00100/2020 (https://doi.org/10.54499/UIDP/00100/2020). Institute of Molecular Sciences is an Associate Laboratory funded by FCT through project LA/P/0056/2020 (https://doi.org/10.54499/LA/P/0056/2020).

References

1. M.A. El Hamd, R. H. Obaydo, D. Nashed, M. El-Maghrabey, H. M. Lofty, *Talanta Open* 2025, **11**, 100391.
2. A. M. Cláudio, M. C. Neves, K. Shimizu, J. N. Lopes, M. Freire, J. P. Coutinho, *Green Chem.* 2015, **17**, 3948-3963.
3. S. Agrawal, S. S. Pancholi, N. K. Jain and G. P. Agrawal, *Int. J. Pharm.* 2004, **274**, 149-155.

Phase behavior and rheological properties of thermoresponsive hydrogels

POSTER_P7.6 - Soft Matter, Colloids, and Complex Fluids

Rui L. Machado[1], Elsa C. Loureiro[1], Isabel S. Oliveira[1], Sandra G. Silva[2], Eduardo F. Marques[1,*]

[1]*CIQUP (Centre of Research in Chemistry), IMS (Institute of Molecular Sciences), Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre, 4169-007 Porto, Portugal*

[2]*LAQV-REQUIMTE (Associated Laboratory for Green Chemistry of the Network of Chemistry and Technology), Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Rua do Campo Alegre, 4169-007 Porto, Portugal*

[*]*efmarque@fc.up.pt*

Polymer/surfactant (P/S) mixtures have garnered significant interest as effective platforms for stimuli-sensitive drug delivery[1,2], in particular hydrogel-based systems where polymers act as scaffolds for various embedded nanostructures (e.g., vesicles, micelles, tubes).[3] However, deeper insight into the self-assembly, thermodynamics, and nano-/micro scale organization of these P/S systems is still warranted. In this work, we explore the colloidal properties of two P/S mixtures formed by an amino acid-derived surfactant, 14Lys10, and an amphiphilic triblock copolymer, either Pluronic F127 or P84 (having distinct hydrophobic/hydrophilic balances), as depicted in Fig. 1. Light microscopy, differential scanning microcalorimetry, rheology and dynamic light scattering provide a comprehensive picture of the physicochemical properties of the systems. P/S molecular interactions significantly reduce the surfactant characteristic tube-to-vesicle melting temperature, while also decreasing the structural integrity of the 3D tube network. These interactions only become critical above the polymer *cmc*. After melting of the surfactant tubes, the formation of both mixed P/S vesicles and P/S micelles takes place. A global molecular mechanism for the observed phenomena is proposed.

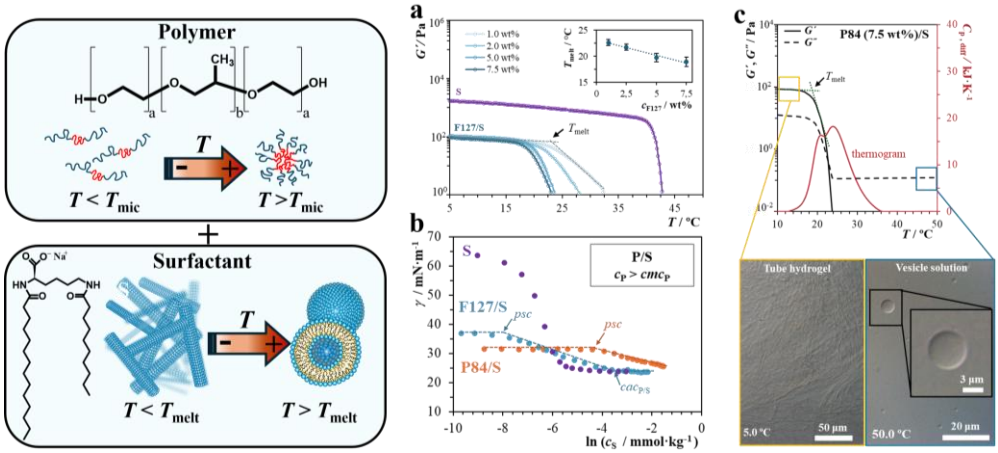


Figure 1: Thermal behavior of the block-copolymers and amino acid surfactant. **a**, Evolution of storage modulus with increasing temperature; **b.** surfactant self-assembly in a polymer solution: **c.** Structural, rheological, and thermal behavior of a P/S mixture.

Acknowledgements

Financial support from Fundação para a Ciência e Tecnologia (FCT) through project 2022.05543.PTDC-Smart4Vir, through CIQUP via grant UID/QUI/0081/2020 (https://doi.org/10.54499/UIDB/00081/2020) and IMS via grant LA/P/0056/2020 (https://doi.org/10.54499/LA/P/0056/2020). Elsa C. Loureiro acknowledges support through a research scholarship from project 2022.05543.PTDC-Smart4Vir.

References

1. M. Gradzielski, *Langmuir*, 2022, **38**, 13330-13343.
2. I. S. Oliveira, J. P. N. Silva, M. J. Araújo, A. C. Gomes and E. F. Marques, *J. Mol. Liq.* 2021, **322**, 114540.
3. R. L. Machado, A. C. Gomes and E. F. Marques, *J. Mol. Liq.* 2024, **416**, 126453.

New fluorinated surfactant-free microemulsions: Erasing the border between colloids and simpler fluids

POSTER_P7.7 - Soft Matter, Colloids, and Complex Fluids

Ricardo A. A. Luís, Tiago M. Eusébio, José Santos Pereira, Diogo Machacaz, Pedro Morgado and Eduardo J. M. Filipe*

Centro de Química Estrutural – Institute of Molecular Sciences, Instituto Superior Técnico, Universidade de Lisboa

**efilipe@tecnico.ulisboa.pt*

Detergent-less or surfactant-free microemulsions (SFMEs) are ternary mixtures composed of two immiscible fluids and a third one, which promotes the solubilization of the three components. The third component, often known as hydrotrope, is typically a small molecule like ethanol or propanol. This unique type of emulsion is important to many applications, such as drug delivery, and can be found in many daily life products.
In this work, a new type of SFMEs involving a perfluorinated compound is presented, featuring the presence of coexisting aqueous, fluorinated and hydrogenated domains. The system was studied using different experimental techniques and complemented with molecular dynamic simulations. The ternary liquid-liquid equilibrium phase diagram was determined, and the interfacial tension of the coexisting phases was measured. The surface tension of solutions within the monophasic region were also measured at constant water/ethanol volume fraction and found to display a typical surfactant behavior, enabling the determination of a critical aggregation concentration. The existence of aggregates was demonstrated by Dynamic Light Scattering, and their size was estimated. Finally, atomistic molecular dynamics simulations provide a detailed description of the structure of the aggregates at the molecular level and of the organization of the liquid-vapor interface.

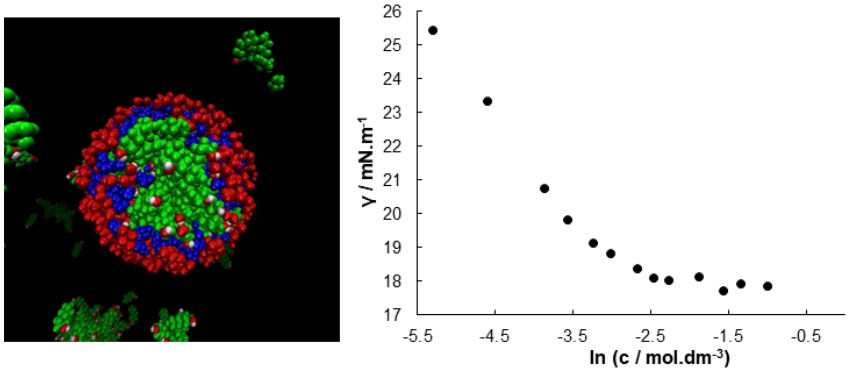


Figure 1. Left – Snapshot of a fluorinated aggregate, with the fluorinated core in green and the ethanol, in blue, and water, in red, at the surface of the aggregate. Right - Experimental surface tension as a function of the logarithm of the concentration of 1H,1H-Perfluoroheptan-1-ol at a constant water/ethanol volume ratio of 1.15 and 297.15 K.

Aneotropy: Unusual interfacial behavior of mixtures of hydrogenated and fluorinated substances

POSTER_P7.8 - Soft Matter, Colloids, and Complex Fluids

Teresa Pires, Diogo Machacaz, Pedro Morgado, Eduardo J. M. Filipe*

Centro de Química Estrutural – Institute of Molecular Sciences, Instituto Superior Técnico, Universidade de Lisboa

**efilipe@tecnico.ulisboa.pt*

The well-known mutual phobicity between hydrogenated and fluorinated chains gives rise to unexpected and intriguing behaviour in the properties of their mixtures. Indeed, mixtures of hydrogenated and perfluorinated substances display large anomalies in phase equilibria, volumetric, dynamic and conformational properties.[1] Despite all efforts to understand this phenomenon at the fundamental level, its origin is still not known.

This peculiar behaviour extends to the interfacial properties of the mixtures, in particular the occurrence of a rare and not fully understood phenomenon named aneotropy, characterized by the existence of minima (or maxima) on the surface tension versus composition curve of liquid mixtures.

In recent research, it was shown for the first time that mixtures of hydrogenated and fluorinated alcohols also display aneotropy.[2] In the present work the subject is further explored and extended to mixtures of fluorinated alcohols and hydrogenated amines, particularly primary and tertiary amines. New experimental data has been obtained for the liquid density, liquid-vapor surface tension. Other pertinent thermodynamic properties have also been measured and calculated, such as the excess molar volumes of the mixtures. Furthermore, atomistic molecular simulations of the bulk and interface have be conducted to better understand the organization of the liquid mixture and the detailed orientation and distribution of molecules at the interface.

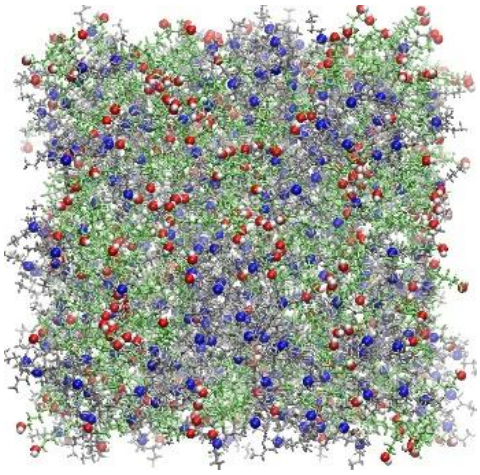


Figure 1. Snapshot of a MD simulation depicting the bulk of an equimolar binary mixture of (tributylamine + 1H,1H-perfluoroheptanol). Nitrogen atoms are shown in blue, oxygen atoms in red, the fluorinated chains in light green, and the alkyl chains in grey.

References

1. P. Morgado, L.F.G. Martins, E.J.M. Filipe, *Phys. Chem. Chem. Phys.* 2019, **21**, 3742-3751.
2. J. Justino, M. Teixeira, D. Machacaz, P. Morgado, L. F. Vega, E. J. M. Filipe, *Journal of Molecular Liquids* 2024, **393**, 123684.

Critical aggregation concentration of crude oil asphaltene

POSTER_P8.1 - Surfaces, Interfaces, and Confinement

Gabriel M. N. Costa[1], Gustavo V. Olivieri[1], Ricardo B. Torres, Ronaldo G. Santos[1,*]

[1] *University Center FEI, São Bernardo do Campo, São Paulo, Brazil*

[*] *rgsantos@fei.edu.br*

Asphaltenes fraction represents the crude oil molecules with the highest molar mass, polarity, and interfacial activity. Asphaltenes cause difficulties and costs in petrochemical processes by production decreasing and the need of maintenance caused by its facility of aggregation and adsorption on solid surface, increasing the effective diameter of pipelines, complicating the oil extraction because of interactions with the reservoir rock and clogging of separators. Maltene exhibits an important role in the solubility of asphaltenes in crude oil, preventing aggregative processes. This work describes the influence of asphaltene and maltene interactions in the aggregative process of asphaltenes. Specifically, the study describes the influence of maltenes on the critical aggregation concentration (CAC), and asphaltene monolayers. Drops of asphaltene-maltene solutions were subjected to static and oscillating tensiometry tests to analyze CAC and dilatational interfacial rheology, respectively. Asphaltene-maltene monolayer films were submitted to oscillatory tests in the Langmuir trough for analysis of the influence of maltenes on the modulus of elasticity. The results showed that maltenes could increase the CAC up to a value of 0.1318 g/L, postponing the aggregative process of asphaltenes, in addition to decreasing the modulus of elasticity of pulsating drops. The asphaltene-maltene monolayer films and droplet surfaces containing asphaltene were found to be substantially elastic. It has been proved that the effect of maltene - asphaltene interactions were strong enough to change the solubility of asphaltenes in crude oil and the modulus of elasticity of interfacial films.

Keywords: crude oil, Langmuir film, thermodynamics, phase behavior.

Acknowledgments
The authors gratefully acknowledge the support from the São Paulo Research Foundation (FAPESP) by means the Grant #2018/06486-6. Petrobras is recognized for the kind gift of crude oil samples used in this study.

References

1. W. Loh, R. S. Mohamed, R. G. Santos, *Encyclopedia of Surface and Colloid Science* 2007, **1**, 1-18.
2. C.B. Kabbach, R.G. Santos, *Energy & Fuels* 2018, **32**, 2811-2818.

Properties of interfacial films containing crude oil asphaltenes

POSTER_P8.2 - Surfaces, Interfaces, and Confinement

Mayara A. R. Neves[1], Gustavo V. Olivieri[1], Ricardo B. Torres, Ronaldo G. Santos[1,*]

[1] University Cen
ter FEI, São Bernardo do Campo, São Paulo, Brazil

*rgsantos@fei.edu.br

Molecules having interfacial activity can adsorb on interfaces promoting the occurrence of important phenomena such as emulsification and foaming, wettability, and adsorption. These interfacial phenomena are present in several oilfield operations. This work describes the phase behavior of interfacial films containing petroleum amphiphiles, assessing thermodynamic and rheological aspects. The investigation aims to contribute to the studies of petroleum stability by describing interfacial rheological behavior and thermodynamics. The experimental methodology includes the extraction and characterization of the SARA fractions and the analysis of the properties of SARA films. A Langmuir Trough was used to obtain the surface pressure curves. The elasticity modulus values show that saturate and aromatic fractions have similar behavior for compression and expansion. The asphaltene film's surface pressure - area isotherm exhibits substantial hysteresis, indicating a high interaction between the molecules. Asphaltene isotherms display a sharp surface pressure drop under area expansion, so the film cannot return to its initial estate. In addition, the saturate film dissipated less energy in the hysteresis cycle than the other films, which is related to its weaker molecular interaction. The maximum surface pressure obtained for the asphaltene - resin mixtures was 80.52 $mN.m^{-1}$ for the compression process and 65.96 $mN.m^{-1}$ for the expansion process, both for a mixture containing 60 wt.% of asphaltene. The excess areas obtained for the asphaltene - resin mixtures indicate that the molecular interactions are most repulsive during the area-decreasing process. The interfacial behavior is directly related to the excess Gibbs energy and the Gibbs energy change of mixing asphaltenes - resins.

Keywords: crude oil, Langmuir film, thermodynamics, phase behavior.

Acknowledgments
The authors gratefully acknowledge the support from the São Paulo Research Foundation (FAPESP) by means the Grant #2018/06486-6. Petrobras is recognized for the kind gift of crude oil samples used in this study.

References

1. W. Loh, R. S. Mohamed, R. G. Santos, *Encyclopedia of Surface and Colloid Science* 2007, **1**, 1-18.
2. M. A. R. Neves, R. G. Santos, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 2021, **618**, doi.org/10.1016/j.colsurfa.2021.126423

Thin films of organic semiconductor materials: Structural, morphological, and thermodynamic study of polyphenylanthracenes

POSTER_P8.3 - Surfaces, Interfaces, and Confinement

Jiaqi Yan[1], Artur F. M. Farinha, Carlos F. R. A. C. Lima[1], Luís M. N. B. F. Santos[1], and José C. S. Costa[1,*]

[1]*CIQUP, Institute of Molecular Sciences (IMS), Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Rua do Campo Alegre s/n, P4169-007 Porto, Portugal*

**jose.costa@fc.up.pt*

Thin films of organic semiconductor materials (OSCs) have a significant impact on modern industries, demonstrating great potential for applications in flexible electronic devices such as organic solar cells (OPVs) and organic light-emitting diodes (OLEDs).[1,2]

This study focuses on the structural, morphological, and thermodynamic properties of two polyphenylanthracenes (PPAs): 1,2,3,4-tetraphenylantracene (1,2,3,4-TPhA) and decaphenylanthracene (DPhA). Differential scanning calorimetry (DSC) and the Knudsen effusion methodology were used to evaluate the phase transition thermodynamics of these OSCs. Thin films were fabricated by physical vapor deposition (PVD), and their morphology was assessed using scanning electron microscopy (SEM). UV-Vis spectroscopy was employed to evaluate the optical properties and derive the optical band gap for both solution and thin film states. The interplay between the supramolecular structure, aromatic interactions, and the fusion and sublimation equilibria in these PPAs was compared to those observed in polyphenylnaphthalenes and polyphenylbenzenes.[3,4] The introduction of phenyl groups to the acene moieties leads to greater intramolecular constraints, which result in significant changes in molecular properties and cohesive energy.

Regarding thin film formation, DPhA exhibits markedly different morphological properties compared to 1,2,3,4-TPhA. While 1,2,3,4-TPhA displays a crystalline morphology, DPhA forms a completely amorphous structure, as evidenced by SEM and supported by DSC. This pronounced difference can be attributed to their molecular structures: the lower degree of phenyl substitution in 1,2,3,4-TPhA allows for greater molecular planarity and effective intermolecular π–π stacking, which promotes crystallinity. In contrast, the extensive phenyl substitution in DPhA introduces significant steric hindrance and torsional strain, disrupting π-stacking and favoring the formation of amorphous films during vapor deposition. The comparative analysis of 1,2,3,4-TPhA and DPhA highlights the critical influence of molecular structure on the morphology and thermal behavior of vapor-deposited thin films. The observed differences in crystallinity, driven by phenyl substitution patterns, directly impact the potential of these materials in organic electronic devices.

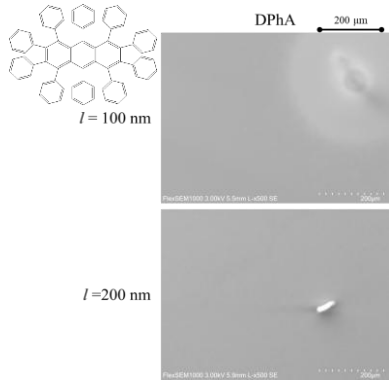


Figure 1: SEM images of vapor-deposited DPhA thin films (amorphous).

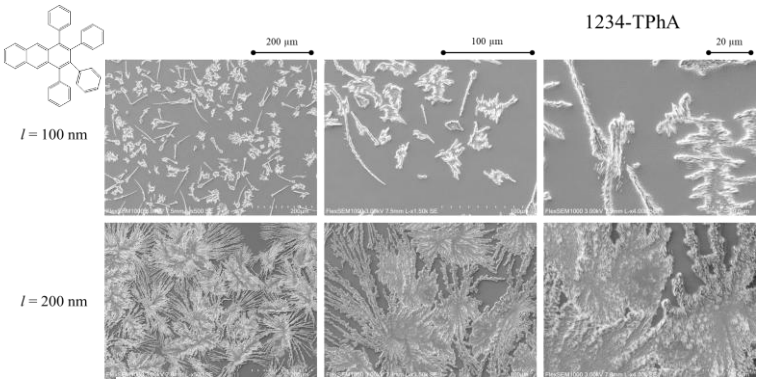


Figure 2: SEM images of vapor-deposited 1,2,3,4-TPhA thin films (crystalline).

Acknowledgements

This work was supported by the Fundação para a Ciência e Tecnologia (FCT) (funded by national funds through the FCT/MCTES (PIDDAC)) to CIQUP, Faculty of Science, University of Porto (Project UIDB/00081/2020: DOI 10.54499/UIDP/00081/2020), and IMS-Institute of Molecular Sciences (LA/P/0056/2020). A.F.M. Farinha thanks the FCT and the European Social Fund (ESF) for the award of a Ph.D. Research Grant (ref. 2022.11342.BD: DOI 10.54499/2022.11342.BD).

References

1. N. Lu, L. Li, D. Geng, M. Liu, *Organic Electronics* 2018, **61**, 223-234.
2. J. C. S. Costa, R. J. S. Taveira, C. F. R. A. C. Lima, A. Mendes, L. M. N. B. F. Santos, *Opt. Mater.* 2016, **58**, 51-60.
3. C. F. R. A. C. Lima, A. S. M. C. Rodrigues, L. M. N. B. F. Santos, *J. Phys. Chem. A* 2017, **121**, 2475-2481.
4. C. F. R. A. C. Lima, M. A. A. Rocha, B. Schröder, L. R. Gomes, J. N. Low, L. M. N. B. F. Santos, *J. Phys. Chem. B* 2012, **116**, 3557-3570.

Influence of alkyl chain length on the morphology of pyridinium-based ionic liquid films deposited by vacuum thermal evaporation

POSTER_P8.4 - Surfaces, Interfaces, and Confinement

Soraia R. M. R. Silva[1], João Pereira[1], Luís M. N. B. F. Santos[1], and José C. S. Costa[1,*]

[1]*CIQUP, Institute of Molecular Sciences (IMS), Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Portugal*

[*]*jose.costa@fc.up.pt*

Ionic liquids (ILs) have attracted growing attention due to their unique properties, such as thermal stability, low vapor pressure, and high ionic conductivity.[1,2] Among them, imidazolium-based ILs have been extensively studied, particularly for their interfacial behavior and film formation.[3,4] In contrast, pyridinium-based ILs, though offering advantages such as higher thermal stability, lower cost, and functional properties like low ecotoxicity, have only recently begun to be explored.[5] Despite their promising applications, such as catalysis[6] and CO_2 capture[7], their thin-film behavior, particularly under vacuum deposition, remains largely uninvestigated.

In this study, pyridinium-based ILs with the NTf_2^- anion were deposited by vacuum thermal evaporation onto ITO — a transparent conductive oxide-coated glass — and gold substrates. Cations with alkyl chains ranging from C_2 to C_9 were selected to evaluate the influence of chain length on film morphology. The resulting films were analyzed by scanning electron microscopy (SEM).

The SEM images revealed that increasing the alkyl chain length leads to greater coalescence on ITO surfaces and, in the case of gold, even more pronounced wetting behavior. Notably, ILs with C_8 and C_9 chains exhibited a distinct behavior, with intensified wetting resulting in the formation of a coalesced film on the gold substrate. In contrast, the other ILs formed droplets, among which an interesting odd–even effect was observed: those with even-numbered alkyl chains tended to form larger droplets.

In conclusion, this study demonstrates that the alkyl chain length of pyridinium-based ionic liquids significantly influences film morphology. As the chain length increases, wettability becomes more pronounced, particularly on gold substrates, highlighting the strong affinity between long alkyl chains and the gold surface. The observed odd–even effect further underscores the subtle structural factors that govern interfacial behavior. These findings offer valuable insights into the design and optimization of pyridinium-based ILs in surface-related applications and suggest that, while their behavior parallels that of imidazolium-based counterparts, it also exhibits distinctive characteristics.

Acknowledgements

The authors thank the Portuguese Foundation for Science and Technology (FCT) for the financial support to CIQUP, Faculty of Science, University of Porto (Project UIDB/00081/2020: DOI 10.54499/UIDP/00081/2020), and IMS-Institute of Molecular Sciences (Grant LA/P/0056/2020), Faculty of Science, University of Porto.

References

1. J. Lopes, A. Pádua, *The Journal of Physical Chemistry B* 2006, **110**, 3330-3335.
2. R. Hayes, G. Warr, R. Atkin, *Chem Rev* 2015, **115**, 6357-6426.
3. J. Costa, A. Alves, M. Bastos, L. Santos, *Phys. Chem. Chem. Phys.* 2022, **24**, 13343-13355.
4. M. Teixeira, L. Santos, J. Costa, *Colloids Interfaces* 2022, **6**, 46.
5. S. Men, D. Mitchell, K. Lovelock, P. Licence, *ChemPhysChem* 2015, **16**, 2211-2218.
6. A. Moosavi-Zare, M. Zolfigol, M. Zarei, A. Zare, V. Khakyzadeh, *Journal of Molecular Liquids* 2013, **186**, 63-69.
7. N. Yunus, M. Mutalib, Z. Man, M. Bustam, T. Murugesan, *Chemical Engineering Journal* 2012, **189-190**, 94-100.

Crystalline film growth of pentacene and perylene via ionic liquid-assisted VLS mechanism followed by IL removal

POSTER_P8.5 - Surfaces, Interfaces, and Confinement

Catarina S. Viegas, Artur F. M. Farinha, Luís M. N. B. F. Santos, and José C. S. Costa*

CIQUP/Institute of Molecular Sciences (IMS), Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre s/n, 4169–007 Porto, Portugal

**jose.costa@fc.up.pt*

Crystalline thin films of organic semiconductors (OSCs) play a crucial role in multilayer optoelectronic devices, including perovskite solar cells, where materials like pentacene and perylene can serve as efficient charge transport layers. High crystallinity in these layers significantly enhances charge mobility; however, achieving such order while maintaining clean interfaces remains a challenge.

In this work, we report the use of an ionic liquid (IL) layer to promote the vapor–liquid–solid (VLS) growth of highly crystalline pentacene and perylene films. Both the OSCs and the IL were deposited via thermal evaporation under vacuum[1], ensuring precise control over film thickness and interface. This method builds on previous findings showing that ILs can guide the ordered crystallization of OSCs on surfaces[2-4]. However, a key limitation has been the presence of residual IL after deposition, which may hinder device performance.

To address this, we developed a simple and effective post-deposition treatment, in which the IL is diluted in isopropanol and subsequently removed, preserving the crystalline structure of the films. Optical microscopy and scanning electron microscopy (SEM, Figure 1) confirm the high degree of crystallinity and removal of the IL, while energy-dispersive X-ray spectroscopy (EDS) verifies the successful elimination of IL residues.

Originally developed in the context of perovskite solar cell fabrication, where perovskite layers are themselves deposited by dual-source thermal evaporation[1], this strategy can be generalized to other OSC-based systems where clean, ordered interfaces are critical. Our results highlight a practical route for integrating IL-assisted crystallization into device fabrication, particularly in systems involving surface-mediated growth.

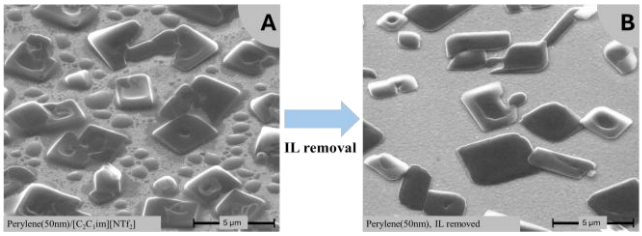


Figure 1: SEM images of perylene (50 nm) films deposited via thermal evaporation over a thin film of $[C_2C_1im][NTf_2]$ (droplets). Image A shows the as-deposited sample, showing perylene crystals surrounded by IL, while image B depicts the same sample after IL removal by isopropanol treatment, revealing well-defined and clean perylene crystallites on the substrate.

Acknowledgements

This work was supported by the Fundacão para a Ciência e Tecnologia (FCT) (funded by national funds through the FCT/MCTES (PIDDAC)) to CIQUP, Faculty of Science, University of Porto (Project UIDB/00081/2020: DOI 10.54499/UIDP/00081/2020), and IMS-Institute of Molecular Sciences (LA/P/0056/2020)). A.F.M. Farinha also thanks the FCT and the European Social Fund (ESF) for the award of a Ph.D. Research Grant (ref. 2022.11342.BD: DOI 10.54499/2022.11342.BD).

References

1. J.C.S. Costa, R.M. Rocha, I.C.M. Vaz, M.C. Torres, A. Mendes, L.M.N.B.F. Santos, *Journal of Chemical & Engineering Data* 2015, **60**, 3776-3791.
2. J.C.S. Costa, R.M. Campos, Â.C.M. Castro, A.F.M. Farinha, G.N.P. Oliveira, J.P. Araújo, L.M.N.B.F. Santos, *CrystEngComm* 2024, **25**, 913-924.
3. A.F.M. Farinha, G.N.P. Oliveira, J.P.Araújo, L.M.N.B.F. Santos, J.C.S. Costa, *Crystal Growth & Design* 2025, **25**, 612-623.
4. S.R.M.R. Silva, R.M. Carvalho, O. Bondarchuk, G.N.P. Oliveira, J.P. Araújo, M. Bastos, L.M.N.B.F. Santos, J.C.S. Costa, *Langmuir* 2025, **41**, 9086-9099.

Ionic liquid-mediated vapor growth of thienoacenes for molecular electronics

POSTER_P8.6 - Surfaces, Interfaces, and Confinement

Soraia R. M. R. Silva[1,*], Luís M. N. B. F. Santos[1], and José C. S. Costa[1]

[1] *CIQUP, Institute of Molecular Sciences (IMS), Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Portugal*

**soraiareis21@gmail.com*

Organic semiconductors (OSCs) are promising for electronic devices due to their flexibility, chemical versatility, low-cost processing, and high charge carrier mobility.[1-3] Their performance is strongly influenced by molecular packing, intermolecular interactions, and crystallinity.[3] Molecular design strategies focus on optimizing OSC structures to promote favorable packing arrangements and efficient charge transport. Thienoacenes-based OSCs benefit from the presence of sulfur atoms, which enhance intermolecular interactions and solid-state ordering.[4]

This study investigates the thermal behavior and the supramolecular and thermodynamic properties of selected thienoacenes using methods such as Knudsen effusion, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). Additionally, their thin film formation was explored via ionic liquid (IL)-assisted vapor deposition using vacuum thermal evaporation. The interaction between OSCs and ILs plays a crucial role in controlling molecular ordering during deposition, as observed by scanning electron microscopy (SEM).[5-7] Thienoacenes were deposited onto both short- and long-alkyl chain ionic liquids to evaluate their influence on crystallinity. These findings establish correlations between volatility, molecular ordering, and thin film morphology.

TGA revealed that four-ring thienoacenes exhibit greater thermal stability than their three-ring counterparts, with alkylation further enhancing stability. DSC successfully characterized the melting and crystallization behavior of all compounds. Alkylated thienoacenes displayed phase transitions indicative of a liquid-crystalline behavior. Knudsen effusion provided vapor pressure data, enabling the derivation of sublimation thermodynamic properties and allowing a reproducible control of the experimental variables used to form thin films by vacuum thermal evaporation.

Thin film deposition studies demonstrated that the deposition rate and evaporation temperature influenced the film morphology and crystallinity. The deposition of thienoacenes onto an IL was found to enhance the film crystallinity significantly. Notably, a long-chain IL further improves crystallization, resulting in larger, more horizontally grown crystals – an ideal morphology for electronic applications such as organic field-effect transistors (OFETs).

In conclusion, understanding thermodynamic properties is essential for optimizing thin film deposition and enhancing electronic device performance. Furthermore, the use of ionic liquids was shown to improve the crystallinity of organic semiconductors, leading to better device functionality.

Acknowledgments

The authors thank the Portuguese Foundation for Science and Technology (FCT) for the financial support to CIQUP, Faculty of Science, University of Porto (Project UIDB/00081/2020: DOI 10.54499/UIDP/00081/2020), and IMS-Institute of Molecular Sciences (Grant LA/P/0056/2020), Faculty of Science, University of Porto.

References

1. W. Jiang, Y. Li, and Z. Wang, *Chemical Society Reviews* 2013, **42**, 6113-6127.
2. C. Wang, H. Dong, L. Jiang, and W. Hu, *Chemical Society Reviews* 2018, **47**, 422-500.
3. V. Coropceanu, J. Cornil, D. da Silva Filho, Y. Olivier, R. Silbey, and J. Brédas, *Chemical Reviews* 2007, **107**, 926-952.
4. K. Takimiya, S. Shinamura, I. Osaka, and E. Miyazaki, *Advanced Materials* 2011, **23**, 4347-4370.
5. J. Costa, R. Campos, A. Castro, A. Farinha, G. Oliveira, J. Araújo, and L. Santos, *CrystEngComm* 2023, **25**, 913-924.
6. A. Farinha, G. Oliveira, J. Araújo, L. Santos, and J. Costa, *Cryst. Growth Des.* 2025, **25**, 612-623.
7. S. R. M. R. Silva, R.M. Carvalho, O. Bondarchuk, G.N.P. Oliveira, J.P. Araújo, M. Bastos, L.M.N.B.F. Santos, J.C.S. Costa, *Langmuir* 2025, **41**, 9086-9099.

Inclusion complex of gallates with cyclodextrins: thermodynamic study and antioxidant activity

POSTER_P8.7 - Surfaces, Interfaces, and Confinement

Sonia Losada-Barreiro[1,*], Tamara Martínez-Senra[1], Fátima Paiva-Martins[2], Carlos Bravo-Díaz[1]

[1] *Universidade de Vigo, Departamento de Química Física, 36310, Vigo, Spain*

[2] *REQUIMTE/LAQV, Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, Campo Alegre 687, Porto, Portugal*

[*] *sonia@uvigo.es*

Properties of the inclusion complexes of gallates with hydroxypropyl- β -cyclodextrin (HP- β -CD), were investigated. The stoichiometry and thermodynamic parameters for the complexation process (stability constants *K*, Gibbs free energy change ΔG, enthalpy change ΔH and entropy change ΔS) were determined using phase-solubility and fluorescence spectra analysis.
The thermodynamic studies indicated that the inclusion reactions between gallates and the cyclodextrins are enthalpy-driven processes. The antioxidant activity of gallates and their inclusion complexes were determined by the scavenging of stable radical DPPH$^{\bullet}$. The results showed that the complexed gallates have similar efficiency than free gallates. The results may be of interest to the food industry because inclusion of phenolic antioxidants, which are widely employed to minimize the oxidation of lipid-based foods, can substantially improve their efficiency.

Acknowledgments
Financial support of the following institutions is acknowledged:
MICIU/AEI/Grant PID 2022-136443OB-I00 and "ERDF/EU", Universidade de Vigo.
T. M.-S. thanks Spain-Ministry of Science and Innovation for a FPU research training grant.

Graph neural network framework for robust ionic liquid property prediction

POSTER_P9.1 - Modelling and Simulation

Adrian Racki[1,*], Kamil Paduszyński[1]

[1]*Department of Physical Chemistry, Faculty of Chemistry, Warsaw University of Technology, 00-664 Warsaw, Poland*

[*]*adrian.racki2.dokt@pw.edu.pl*

Accurate prediction of ionic liquid properties remains a challenge. Traditional approaches rely either on molecular descriptors that are often impractical to compute or on modern natural language processing transformations of SMILES codes, which, although broadly applicable to arbitrary molecules, require extensive datasets that are frequently unavailable in practice. In this work, we introduce a graph neural network (GNN) architecture designed to overcome these limitations. Utilizing an extensive, up-to-date database encompassing properties such as viscosity, density, and melting temperature, we systematically compare different feature sets to evaluate potential enhancements in predictive performance. Our results demonstrate that the proposed GNN model not only achieves superior predictive accuracy relative to existing methods but also retains the versatility to be applied to any molecular input, underscoring the promising role of GNNs in the advancement of computational material property prediction.

Acknowledgements
The research was funded by the NChem.5 project at the Faculty of Chemistry, Warsaw University of Technology.

Shifting thermodynamic equilibria with membrane technology: Enhancing CO_2 conversion in catalytic processes

POSTER_P9.2 - Modelling and Simulation

Q. Smejkal[1], S. Wohlrab[2,*]

[1]EnProCo Berlin GmbH, Volmerstr. 7A, 12489 Germany
[n]Leibniz Institute for Catalysis, e.V. (LIKAT), Albert-Einstein-Straße 29A, 18059 Rostock, Germany

*sebastian.wohlrab@catalysis.de

The efficiency of catalytic processes is often limited by thermodynamic equilibrium. Many of the different CO_2 hydrogenation routes are affected by this fact. The main reason is the formation of water as a by-product in these reactions. In our research work we are studying how membranes can be used to eliminate water *in situ* in order to modify the reaction equilibria and increase conversion efficiency.
In Fischer-Tropsch syntheses with CO_2[1,2], the formation of water not only prevents the hydrogenation of CO_2, but also affects the formation of higher hydrocarbons. Also, in the synthesis of methanol from CO_2[3,4], the accumulation of water shifts the equilibrium in favor of the reactants, which reduces the yield of the target product and even favors secondary reactions. By integrating membrane technologies, and in case of CO_2 conversion an integrated water removal, the reaction equilibrium can be shifted towards the desired products and conversion rates are considerably improved.
Here, a theoretical case study on Fischer-Tropsch synthesis is presented[5], showing that the use of water-selective membranes allows a considerable increase in CO_2 conversion from 36% to over 60%. Furthermore, the initial high selectivity for hydrocarbons is maintained. Our calculations reveal the minimum requirements for a membrane suitable for CO_2-Fischer-Tropsch: 40% of the reaction water has to be removed and less than 10% hydrogen permeation should occur.
Similar effects are observed in experimental CO_2 esterifications, where the continuous removal of water increases the yield of dialkyl carbonate[6]. The thermodynamic basis of this improvement is Le Chatelier's principle. By removing a reaction product (in this case, water), the equilibrium shifts towards increased product formation. Our experimental and modeling data confirm this approach.
Our contribution shows the potential of a membrane-assisted reaction technology. The theoretical and experimental results indicate that the development of selective membranes could boost the industrial use of CO_2 as future feedstock.

Acknowledgements
We would like to thank the Federal Ministry for Economic Affairs and Energy (BMWi) for funding the project CO2OL (03EE5060B) and Project Management Jülich (PtJ) for coordinating it.

References

1. E. Kraleva, H. Lund, J. Weiß, S. Bartling, H. Atia, Z. Cherkezova-Zheleva, D. Paneva, S. Wohlrab, U. Armbruster, *Appl. Catal. A: General* 2024, **683**, 119857.
2. A. Fedorov, P. A. Graefe, A. Perechodjuk, R. Rauch, S. Wohlrab, D. Linke, *Appl. Catal. A: General* 2024, **680**, 119749.
3. M. G. Mohammed, N. A. Hashim, W. M. A. W Daud, U. W. Hartley, M. K. Aroua, S. Wohlrab, *Int. J. Hydrogen Energy* 2024, **77**, 936-957.
4. N. Ortner, D. Zhao, H. Mena, J. Weiß, H. Lund, S. Bartling, S. Wohlrab, U. Armbruster, E. V. Kondratenko, *ACS Catalysis* 2023, **13**, 60-71.
5. Q. Smejkal, A. Bagherzadeh, E. Kraleva, A. Zanina, U. Armbruster, S. Wohlrab, *Appl. Catal. O: Open* 2025, **204**, 207045.
6. J. Wang, Z. Hao, S. Wohlrab, *Green Chem.* 2017, **19**, 3595-3600.

Predicting imidazolium-based ionic liquid phase equilibria via SAFT-VR Mie parameter correlations with molecular volume

POSTER_P9.3 - Modelling and Simulation

Cleiton S. Beraldo[1], Xiaodong Liang[2], Luis A. Follegatti-Romero[1,*]

[1]*Laboratory of Separation and Purification Engineering (LaSPE), Department of Chemical Engineering (PQI), Polytechnic School (EP), University of São Paulo (USP), São Paulo–SP, Brazil*
[2] *Center for Energy Resources Engineering (CERE), Department of Chemical and Biochemical Engineering, Technical University of Denmark, DK–2800 Kgs. Lyngby, Denmark*

**follegatti@usp.br*

This study introduces a predictive method based on the SAFT-VR Mie (Statistical Associating Fluid Theory of Variable Range Mie potentials) equation of state to estimate CO_2 solubility in imidazolium-based ionic liquids (ILs). In this approach, ILs are modeled as associating compounds using the 3B association scheme. SAFT molecular parameters are first fitted to experimental pure liquid density data for a training set of ILs and then correlated with their molecular volumes (Figure 1). This correlation is subsequently applied to a new set of ILs, where molecular volumes are determined using the COSMO (Conductor-like Screening Model) quantum chemistry approach. The predicted SAFT parameters are then used to estimate CO_2–IL phase equilibria, making the method fully predictive. The results demonstrate high accuracy, with an average absolute deviation of 6% in CO_2 solubility predictions. Notably, this approach eliminates the need for binary interaction parameters.

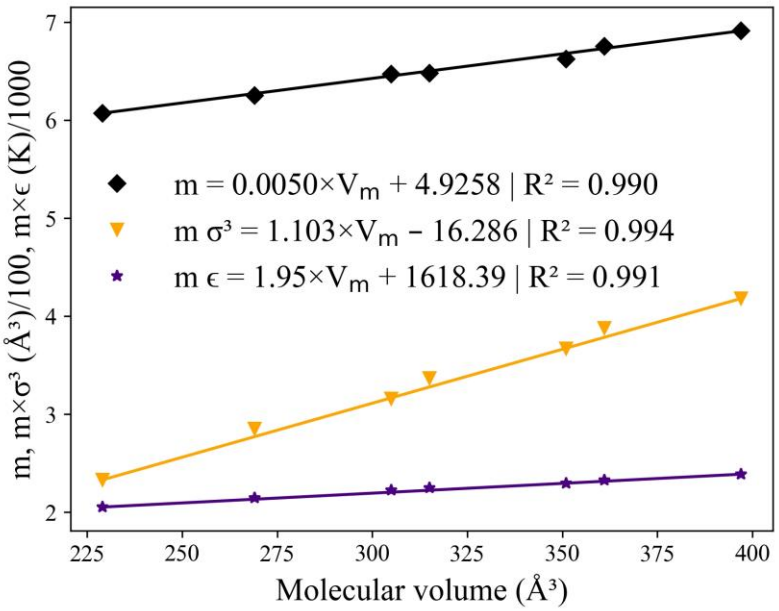


Figure 1: The correlated SAFT molecular parameters with molecular volumes.

Acknowledgments
This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), Brazil – Finance Code 001, and the São Paulo Research Foundation (FAPESP), Brazil – Process Number 2024/10537-6. Luis A. Follegatti-Romero sincerely appreciates the support from the São Paulo Research Foundation (FAPESP) under grant 2019/22085-4 and from Petronas (Petroliam Nasional Berhad) for Project No. ANP 23708-1. Xiaodong Liang gratefully acknowledges funding from the Independent Research Fund Denmark (Case No. 3105-00024B). Grant CNPq/MCTI/FNDCT Nº 22/2024 number 443839/2024-7.

Entropic order upon self-assembly: Antiferroic three-state potts model on *reo* net

POSTER_P9.4 - Modelling and Simulation

Kazuya Saito*

Research Center for Thermal and Entropic Science, Graduate School of Science, Osaka University and Center for Computational Sciences, University of Tsukuba

**kazuya@chem.tsukuba.ac.jp*

As exemplified by the coincidence of uniaxial symmetry of nematic liquid crystals and the pronounced anisotropy of molecules (after averaging molecular details),[1,2] the resulting order upon the symmetry breaking in a macroscopic ensemble, such as self-assembled states, is usually consistent with the symmetry of the constituent entities. In this presentation, we discuss and show a simple example that contradicts this intuition.

Monte Carlo simulations of the antiferromagnetic three-state Potts model on the tripartite ***reo*** net, consisting of corner-sharing regular octahedrons, yields an occurrence of a phase transition from the disordered phase to a partially ordered phase, where the ordering is perfect on a single sublattice. This state can be regarded as the self-assembly of isotropic octahedral (sixfold branched) junctions with three diagonal endpoint pairs of different colors. The observed partially ordered phase represents the perfect order along a single axis, as shown in Figure 1. An overwhelming possibility of such aggregation states is rationalized by the effect of minimal entropy, which vanishes in the thermodynamic limit. Notably, the ordering phase transition(s) of the first order mimics a switch of self-assembly in these simulations. We will also report some additional results of the simulation, including the possibility of a metastable isotropic order, which is more in line with intuition. Further details can be found in the reference.[4]

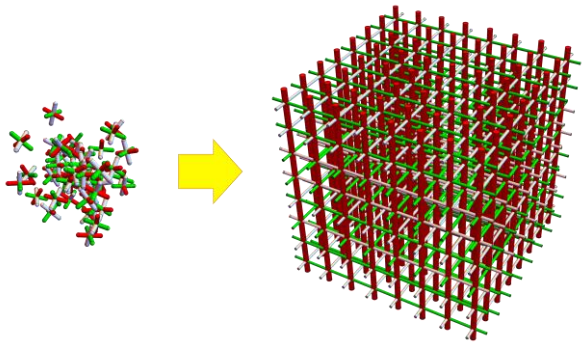


Figure 1: Self-assembly of octahedral junctions always includes an axis of complete order (the vertical red strings in this illustration).

Acknowledgments
This work was supported by JSPS KAKENHI, Transformative Research Areas (A) "Materials Science of Meso-Hierarchy" No. 24H01694.

References

1. L. Onsager, *Ann. N.Y. Acad. Sci.*1949, **51**, 627.
2. W. Maier and A. Saupe, *Z. Naturforsch. A* 1958, **13**, 564.
3. Reticular chemistry structure resource at http://rcsr.net/
4. K. Saito, arXive:2503.0081.

The non-isothermal compositional grading problem specifying the overall composition of the mixed migrating streams

POSTER_P9.5 - Modelling and Simulation

R. O. Espósito[1,*], L. G. Fofano[1], P. H. De Paulo[1], F. W. Tavares[2]

[1] *Petrobras - Petróleo Brasileiro S.A./Reservoir Engineering*
[2] *Federal University of Rio de Janeiro, School of Chemistry*

[*] *esposito@petrobras.com.br*

The variable-set specification from the traditional compositional-grading (CG) problem is modified to consider the overall integrated composition of an 1D-column reservoir instead of the sampling-point reference-level (local) composition. This kind of specification may be much more useful for decision-making in bidding processes, non-perforated achieved fields or even investigation of trap-filling developments in geological time. Guessing a local composition at the reference level, the CG problem is called at each iteration by an outer optimizer which objective-function compares the square difference between the depth-along integration of distributed mole fractions with the desired global composition previously set, which comes from moving-stream studies performed by basin-system geologists. The optimized configuration can give some insights on GOC occurrence, oil-zone and condensate quality, GORs, PVT properties, hydrocarbons and contaminants sources and other representative parameters for the investigation purposes.

Paving the way to a sustainable future: COSMO-RS as a tool to identify eutectic solvents for selective polymer dissolution

POSTER_P9.6 - Modelling and Simulation

Ana M. Ferreira*, Mariana I. S. Aguiar, José Pedro Wojeicchowski, João T. S. Martins, Simão Vidinha Pandeirada, Andreia F. Sousa João A. P. Coutinho

CICECO – Aveiro Institute of Materials, Department of Chemistry, University of Aveiro (UA), 3810-193, Aveiro, Portugal

**ana.conceicao@ua.pt*

Global synthetic polymer production exceeds 350 million tons annually, with limited recycling leading to a predicted 12,000 tons of plastics in landfills by 2050. While dissolution and precipitation techniques could enhance recycling, most methods still rely on conventional organic solvents. Eutectic solvents (ES) offer a promising alternative but present challenges due to the wide variety of hydrogen bond acceptors (HBAs) and donors (HBDs).

This study aimed to identify selective and effective ES for dissolving massively produced fossil-based polymers such as polyethylene (PE), poly(ethylene terephthalate) (PET), polypropylene (PP), and poly(vinyl chloride) (PVC), as well as alternative commercial bio-based polymers like poly(lactic acid) (PLA), using the COnductor-like Screening MOdel for Realistic Solvents (COSMO-RS). COSMO-RS was used to calculate infinite dilution activity coefficients for 40 HBAs and 59 HBDs, resulting in 2,360 eutectic mixtures at a 1:1 molar ratio at 100 °C. Predictions were validated through solubilization tests. Results showed that hydrophobic ES, particularly those with long-chain alcohols as HBDs, effectively dissolved PP and PE. For PET and PLA, ES containing phenolic monoterpenes as HBAs exhibited strong dissolution capabilities.

These findings underscore the importance of selecting suitable ES for developing sustainable solutions for complex polymer mixtures and multilayer films.

Acknowledgements

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020 (DOI 10.54499/UIDB/50011/2020), UIDP/50011/2020 (DOI 10.54499/UIDP/50011/2020) & LA/P/0006/2020 (DOI 10.54499/LA/P/0006/2020), financed by national funds through the FCT/MCTES (PIDDAC). This work is funded by national funds through FCT – Fundação para a Ciência e a Tecnologia, I.P., under the project GREEN-PATH (Ref. 2023.15169.PEX, DOI 10.54499/2023.15169.PEX). MISA acknowledges FCT for the Ph.D.grant PRT/BD/154714/2023. AMF, APT and AFS acknowledge FCT for the research contracts CEECIND/00361/2022 (DOI 10.54499/2022.00361.CEECIND/CP1720/CT002), CEECIND/01867/2020 and CEECINSTLA/00002/2022, respectively.

Inherent single-point calibration for quantitative Raman analysis of hydrogen's isomeric composition

POSTER_P10.1 - Instrumentation and Methods

Fabian Luther[1,*], Guinevere M. Sellner[2], Markus Richter[1,2,3], Paul L. Stanwix[2]

[1]*Professorship of Applied Thermodynamics, Chemnitz University of Technology, 09107 Chemnitz, Germany*
[2]*Fluid Science & Resources, School of Engineering, University of Western Australia, WA 6009, Australia*
[3]*Leibniz University Hannover, Institute of Thermodynamics, An der Universität 1, 30823 Garbsen, Germany*

[*]*Fabian.Luther@mb.tu-chemnitz.de*

The global effort to reduce emissions and decarbonize the energy sector has led to the pursuit of carbon-free energy carriers, with hydrogen emerging as one of the most promising alternatives. However, its effective utilization, storage, and transport–especially in liquified form–requires accurate monitoring of composition and conversion kinetics of hydrogen's isomer states, para- and orthohydrogen. Indirect measurements based on thermal conductivity or speed of sound have historically been the most commonly employed techniques for this purpose, while, Raman spectroscopy, a direct measurement approach, has gained increasing popularity more recently. However, it is consistently reported, that isomeric compositions directly derived from raw Raman spectra do not agree with the expected results, underlining the need for system calibration.

Here, we present a novel and straightforward calibration method for Raman spectroscopy systems, enabling direct hydrogen isomer composition measurements based on the inherent nature of hydrogen's vibrational states.[1] The approach requires only one measured reference dataset at a known isomer composition and temperature, allowing an easy integration for most systems and applications. The acquired experimental data is calibrated against theoretical calculations of the overall hydrogen isomer composition and relative occupations of specific molecular states. Ultimately, the method provides line-by-line scaling coefficients (calibration coefficients) for each individual hydrogen peak. The technique can be applied for both rotational and vibrational transitions of equilibrium hydrogen down to cryogenic temperatures and almost pure para-hydrogen compositions.

The presented method was validated through experiments conducted in cooperation with University of Technology Dresden and Forschungszentrum Jülich using an advanced ortho-parahydrogen catalyst test facility as described by Eisenhut.[2] This setup enabled precise control of the isomeric composition, allowing the method to be rigorously tested across a wide range of conditions. The accuracy of the Raman measurements is strongly dependent on the specific instrumentation and measurement settings used. Nevertheless, across different systems with varying levels of precision, the maximum deviation in the measured isomeric composition from the estimated reference value remained well below 0.7% o-H_2—often significantly lower—across the full temperature and composition range. A comprehensive uncertainty analysis confirmed full agreement between experimental results and theoretical predictions, demonstrating the robustness of the calibration approach. Consequently, the presented calibration method represents a significant advancement in measurement accuracy and methodology compared to the results obtained from uncorrected spectra or conventional scaling approaches.

Acknowledgments
The authors would like to acknowledge the support from Eisenhut from the University of Technology Dresden for letting us conduct Raman validation measurements using his ortho-parahydrogen catalyst test facility.

References

1. F. Luther, G. M. Sellner, M. Richter and P. L. Stanwix, *International Journal of Hydrogen Energy* 2025, **102**, 778-789.
2. S. Eisenhut and C. Haberstroh, *IOP Conf. Ser.: Mater. Sci. Eng.* 2024, **1301**, 012058.

AdsorptionCAL – calibration and optimization of a Calvet microcalorimeter based gas-adsorption system

POSTER_P10.2 - Instrumentation and Methods

Alexandre C. P. M. Alves*, Manuel C. Torres, Francisco S. Carpinteiro, José C. S. Costa, and Luís M. N. B. F. Santos

CIQUP, Institute of Molecular Sciences (IMS), Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Porto, Portugal

**alexandrecostapalves@gmail.com*

The **AdsorptionCal** system was designed for the simultaneous or individual measurements of gas adsorption/desorption through three different instruments: Quartz crystal microbalance (QCM), Vacuum Microbalance (VMB), and Calvet LV 4C (MS80) calorimeter. A main gas line that allows the control and measurement of the pressure with high precision can be connected individually to each instrument. The Calvet calorimeter allows the measurement of the heat of adsorption/desorption processes with high sensitivity, reaching a detection limit (10 times the noise level) of 5 μW. This model has 4 cells and 2 pairs of measurement cells (sample and reference), which allows for 2 independent and simultaneous measurements (Fig. 1-A). The experimental setup can work at different conditions, from ambient temperature to 200° C, very high pressures (up to 350 bar), and high vacuum. The coefficient of sensitivity of the Calvet microcalorimeter was evaluated by electrical calibration using a customized calibration cell identical to the adsorption cell. Two independent VEE Pro software were developed for data acquisition and data analysis (Fig 1-B) and include real-time visualization and signal correction of the thermal inertia by application of the Tian equation.

A

B

Figure 1: A- Calvet LV 4C (MS80) calorimeter used in this project. B- Software application for data acquisition and real time analysis developed in VEE Pro.

Acknowledgments
This work was supported by the Fundação para a Ciência e Tecnologia (FCT) (funded by national funds through the FCT/MCTES (PIDDAC)) to CIQUP, Faculty of Science, University of Porto (Project UIDB/00081/2020: DOI 10.54499/UIDP/00081/2020), IMS-Institute of Molecular Sciences (LA/P/0056/2020)) A.C.P.M.A. also thanks the FCT and the European Social Fund (ESF) for the award of a Ph.D. Research Grant (ref. 2022.11108.BD).

Experimental unit for absorption of gaseous mixtures in ionic liquids at high pressures

POSTER_P10.3 - Instrumentation and Methods

Laura Montenegro Richard[1], Edgar Recavarren Rios[1], Claudio Augusto Oller do Nascimento[1], Leonardo Hadlich de Oliveira[1,*]

[1]*Department of Chemical Engineering, Polytechnic School of the University of São Paulo, Brazil*

**hadlich@usp.br*

Widely applied methods for separating gas mixtures are cryogenic distillation, membranes, adsorption, and chemical/physical absorption.[1] Physical absorption of gases is one of the most cost-effective methods used in industry to separate hydrocarbons.[2] The solute solubility in the liquid and the selectivity of the separation between gaseous components are key factors that determine the efficiency of the absorption process.[3] Selecting the right solvent is crucial in separation processes, since a poorly selective solvent will inevitably require additional separation steps. For this reason, ionic liquids[4] are used, as they are considered suitable solvents due to their low vapor pressure. Among the liquids used as absorbents, ionic liquids stand out as an alternative to problems associated with the degradation and high energy consumption required for regenerating amine-based solutions.[5] In recent years, various industrial CO_2 separation units (such as batch mode, tray columns, packed columns, membranes, etc.) and physical-chemical absorbents[6] have been considered. In this work, an experimental unit (Figure 1) was developed for the absorption of gas mixtures in ionic liquids using a high-pressure bubble column. This unit comprises different equipment, accessories, valves, transducers, and tubing of 1/16' diameter. Lak tests under different conditions were conducted to verify the absence of helium gas leaks in the entire system: a)1 h at pressures of 5 and 30 bar with the column both empty and filled with 55 mL of water; b) 1 h at flow rates of 1 mL/min at pressures of 5 and 30 bar, with the column both empty and filled with 55 mL of water. In all cases, no gas leakage was detected, as the pressure remained constant. It was also confirmed that the check valve and backpressure valve are working properly. This unit will be used for the separation of various CO_2 + CH_4 gas mixtures by absorption in different ionic liquids, aiming to provide gas-liquid equilibrium ternary diagrams that are unpublished in literature.

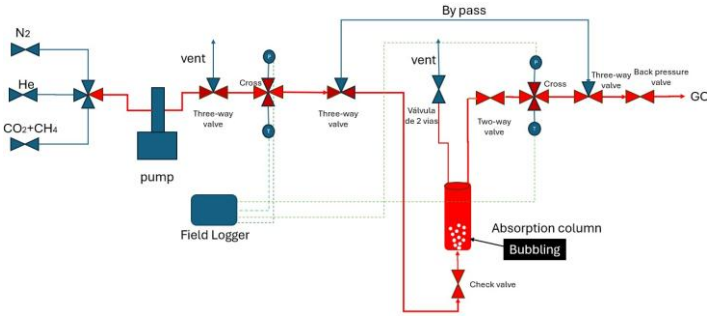


Figure 1: High-pressure mixed gas absorption unit operation flow sheet

Acknowledgements

The authors would like to acknowledge Petronas (process FUSP 403902), FAPESP (process 2022/10714-0) CAPES (processes 88887.020216/2024-00 and 88887.147523/2025-00).

References

1. Abdulabbas, T. Mohammed and T. Al-Hattab, *Heliyon* 2024, **10**, e29069,1-16.
2. Y. Zhang, X. Zhao, Q. Yang, Z. Zhang, Q. Ren and H. Xinglnd. *Eng. Chem. Res.* 2017, **56**, 7336-7344.
3. W. Cabrera, M. Espinoza, D. Lazo, A. Ulloa, W. León, *Ciencia Latina 2024*, **8**, 8712-8737.
4. M. Ramdin, A. Amplianitis, T. W. De Loos and T. J. H. Vlugt, *Fluid Phase Equilibria* 2014, **375**, 134-142.
5. X. Zhang, S. Zhanga, D. Baoa, Y. Huanga, X. Zhanga, *Bioresource Technology* 2015, **175**, 135-141.
6. A. Elhambakhsh and P. Keshavarz, *Energy Fuels* 2025, **39**, 19-38.

Novel small-volume electrical conductivity cell for ionic fluids

POSTER_P10.4 - Instrumentation and Methods

Carlos F. P. Miranda*, Luís M. N. B. F. Santos

CIQUP, Institute of Molecular Sciences (IMS)- Departamento de Química e Bioquímica, Faculdade de Ciências da Universidade do Porto, Rua do Campo Alegre S/N, Porto, Portugal

**carlospesqueiramiranda@gmail.com*

This work presents the development and test of a small-volume (140 µL) coin-type cell used in measurements of electrical conductivity of ionic fluids (Figure 1). This cell is part of a measuring apparatus composed by a Precision LCR meter (20 Hz - 500 kHz) from Keysight (model E4980AL, a customized air bath thermal chamber based on Peltier heat/cooling and a dedicated data acquisition & analysis software application. The core of the coin cell is a PEEK block that acts as both the sample container and the electrode spacer. The electrodes are pressed against the core part and the O-rings by two opposing aluminium plates, ensuring the geometry and sealing of the effective measuring compartment. The top and bottom of the cell are connected to a flow line allowing the sample to be introduced by injection. Additionally, this feature makes it possible to apply vacuum and to flow gaseous nitrogen for sample degasification and cell cleaning. The cell constant was experimental verified by measuring the resistance, at different temperatures, of aqueous 0.1 and 0.01 molal KCl solutions.[1]

The performance and accuracy of the cell was evaluated by measuring the electrical conductivity of some common ILs, including the NIST recommended reference ionic liquid, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, $[C_6C_1im][NTf_2]$.[2] Several types of electrodes were tested: stainless steel AISI 316, stainless steel AISI 316 with titanium nitride (TiN) coating, platinum (Pt), nickel (Ni), titanium (Ti), and Ti with TiN coating. The results were compared with the data previously obtained using a dip-in cell based on a commercial Metrohm conductivity cell (model MTO-6.0908.110).

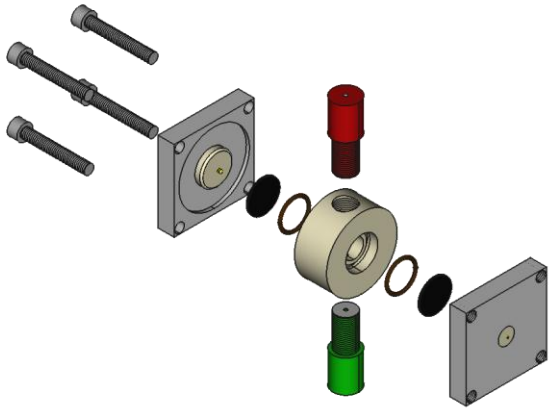


Figure 1: Exploded 3D-view of the coin cell.

Acknowledgements

This work was supported by the Fundacão para a Ciência e Tecnologia (FCT) through the FCT/MCTES (PIDDAC) to CIQUP, Faculty of Science, University of Porto (Project UIDB/00081/2020), IMS-Institute of Molecular Sciences (LA/P/0056/2020). Carlos F. P. Miranda is grateful to FCT for his research grant (Reference: 2020.05717.BD).

References

1. K. W. Pratt et al., *Pure Appl. Chem.* 2001, **73**, 1783-1793.
2. X. Paredes et al., *J. Phys. Chem. Ref. Data* 2020, **49**, 043101-51.

AUTHOR INDEX

LIST OF PARTICIPANTS

Aaron Scurto, University of Kansas, United States
Adriaan Bruinhorst, University Clermont Auvergne, France
Adrian Racki, Warsaw University of Technology, Poland
Alejandro Moreau, University of Valladolid, Spain
Aleksey Pimerzin, Gubkin Russian State University of Oil and Gas, Russia
Alex Illesca, University of Concepción, Chile
Alexandre Alves, University of Porto, Portugal
Alexandre Jorge, University of Coimbra, Portugal
Aline Zambom, University of Aveiro, Portugal
Ana Cunha, University of Campinas, Brazil
Ana Ferreira, University of Aveiro, Portugal
Ana Luísa Silva, University of Porto, Portugal
Ana Pereira, University of Porto, Portugal
Anastasiia Maslechko, Odessa National University, Ukraine
André Araújo, Norleq, Portugal
André Gomes, University of Lisbon, Portugal
Antoni Maciejewski, Warsaw University of Technology, Poland
Antonio Sellitto, University of Salerno, Italy
Arthur Nascimento, University of Campinas, Brazil
Artur Farinha, University of Porto, Portugal
Ashish Verma, Indian Institute of Technology of Ropar, India
Atsuko Uchida, Nihon University, Japan
Atsumi Miyake, Yokohama National University, Japan
Baba Ahmed, ARKEMA, France
Bárbara Jesus, University of Lisbon, Portugal
Bastián González, University of Concepción, Chile
Beatriz Esteves, University of Aveiro, Portugal
Behnaz Asadzadeh, Aalto University, Finland
Bernd Rathke, University of Bremen, Germany
Brian Woodfield, Brigham Young University, United States
Bruna Ferreira, University of Aveiro, Portugal
Bruno Pinheiro, University of Porto, Portugal
Bruno Ramos, University Centre of the FEI, Brazil
Caleb Narasigadu, North-West University, South Africa
Cara Schwarz, Stellenbosch University, South Africa
Carla Ferreira, University of Porto, Portugal
Carlos Bernardes, University of Lisbon, Portugal
Carlos Lima, University of Porto, Portugal
Carlos Miranda, University of Porto, Portugal
Catinca Secuianu, Politehnica University of Bucharest, Romania
Christoph Schick, University of Rostock, Germany
Christopher Piske, Polytechnic Institute of Bragança, Portugal
Claudia Sousa, University of Porto, Portugal
Cleiton Beraldo, University of São Paulo, Brazil
Cornelia Bandas, INCEMC - Timisoara, Romania
Costas Patrickios, University of Cyprus, Cyprus
Dinis Abranches, University of Aveiro, Portugal
Dmitriy Moreira, University of Porto, Portugal
Eduardo Filipe, University of Lisbon, Portugal
Eduardo Marques, University of Porto, Portugal
Eric May, University of Western Australia, Australia
Eva Muehlegger, Technical University of Dortmund, Germany
Evgenyi Shalaev, AbbVie Inc, United States
Fabian Luther, Chemnitz University of Technology, Germany
Fernanda Barbosa, Norleq, Portugal
Fernanda Pelaquim, University of Campinas (CEPETRO), Brazil
Filipe Ribeiro, University of Porto, Portugal
Filipe Sosa, University of Aveiro, Portugal

Filipe Sousa, MT Brandão, Portugal
Flavia Braga, University of Aveiro, Portugal
Frederico Tavares, Federal University of Rio de Janeiro, Brazil
Fufang Yang, École Normale Supérieure de Lyon, France
Fuyu Jiao, University of Western Australia, Australia
Gabriel Camilo, University of Aveiro, Portugal
Gabriel Teixeira, University of Aveiro, Portugal
Gabriela Biliuta, "Petru Poni" Institute of Macromolecular Chemistry, Romania
Gennady Gor, New Jersey Institute of Technology, United States
Guillaume Depraetère, École Normale Supérieure de Lyon, France
Guinevere Sellner, University of Western Australia, Australia
Gustavo Olivieri, University Centre of the FEI, Brazil
Hadrián Montes-Campos, University of Santiago de Compostela, Spain
Hal Suzuki, Kindai University, Japan
Helena Passos, University of Porto, Portugal
Hiroki Fujimori, Nihon University, Japan
Ibuki Tanizawa, Kindai University, Japan
Inês Vaz, University of Aveiro, Portugal
Isabel Oliveira, University of Porto, Portugal
Isabella Cordova, University of Aveiro, Portugal
Isabella Souza, University of Aveiro, Portugal
Ivo Rietveld, University of Rouen Normandy, France
Jean-Luc Daridon, University of Pau, France
Jean-Noël Jaubert, University of Lorraine, France
Jiaqi Yan, University of Porto, Portugal
Jinsoo Kim, Kyung Hee University, South Korea
Joana Costa, Specanalítica, Portugal
Joana Dias, University of Coimbra, Portugal
João Cappelle, Specanalítica, Portugal
João Carvalheira, Paralab, Portugal
João Coutinho, University of Aveiro, Portugal
João Fabian, University of Aveiro, Portugal
Jorge Ávidos, Specanalítica, Portugal
Jorge Gonçalves, University of Porto, Portugal
Jorge Pereira, University of Coimbra, Portugal
José Costa, University of Porto, Portugal
José Fonseca, Aveva, United States
Juan Roa, University of Valladolid, Spain
Julien Joliat, University of Lorraine, France
Kai Langenbach, TU Dortmund University, Germany
Karsten Müller, University of Rostock, Germany
Kazuya Saito, University of Tsukuba, Japan
Ken Kroenlein, Citrine Informatics, United States
Kosei Yoshida, Kindai University, Japan
Krzysztof Cwynar, University of Silesia in Katowice, Poland
Kuveneshan Moodley, University of KwaZulu-Natal, South Africa
Laurent Zoppi, Mettler Toledo, France
Leonardo de Oliveira, University of São Paulo, Brazil
Leslie Woodcock, University of Algarve, Portugal
Letícia Souza, University of São Paulo, Brazil
Liam Tenardi, University of Western Australia, Australia
Ligia de Souza, NETZSCH, Germany
Lillian Ladu, Imperial College London, United Kingdom
Lourdes Vega, Khalifa University, United Arab Emirates
Luan Corso, Polytechnic Institute of Bragança, Portugal
Lucas Zini, Polytechnique Montréal, Canada
Luis Romero, University of São Paulo, Brazil
Luís Santos, University of Porto, Portugal
Luis Varela, University of Santiago de Compostela, Spain
Luísa Amaral, University of Porto, Portugal
Mafalda Valente, MT Brandão, Portugal
Magdalena Bendová, University of Chemistry and Technology Prague, Czechia
Manuel M. Piedade, University of Lisbon, Portugal

Mara Freire, University of Aveiro, Portugal
Marc Tshibangu, Mangosuthu University of Technology, South Africa
Marcin Smiglak, Poznan Science and Technology Park, Poland
Margarida Bastos, University of Porto, Portugal
Margarida Gomes, École Normale Supérieure de Lyon, France
Margarida Pinhão, University of Aveiro, Portugal
María Saquete, University of Alicante, Spain
Maria Sequeira, University of Lisbon, Portugal
Mariko Noguchi, Nihon University, Japan
Mark Barwood, University of Western Australia, Australia
Mark Thies, Clemson University, United States
Marko Popović, University of Belgrade, Serbia
Markus Richter, Leibniz University Hannover, Germany
Markus Sekulla, Chemnitz University of Technology, Germany
Marta Figueiras, Norleq, Portugal
Martín Lema, University of Santiago de Compostela, Spain
Martin Trusler, Imperial College London, United Kingdom
Marzena Dzida, University of Silesia in Katowice, Poland
Maysa Nesti, University Centre of the FEI, Brazil
Melusi Danisa, Durban University of Technology, South Africa
Micha Polak, Ben-Gurion University, Israel
Miguel Barros, Gravimeta, Portugal
Miguel Jorge, University of Strathclyde, United Kingdom
Mikołaj Więckowski, Warsaw University of Technology, Poland
Min-Su Kim, Korea Institute of Industrial Technology, South Korea
Mirjana Minceva, Technical University of Munich, Germany
Moisés Neto, Federal University of Technology - Paraná, Brazil
Mónia Martins, Polytechnic Institute of Bragança, Portugal
Mónica Corea, National Polytechnic Institute, Mexico
Murilo Alcantara, University of Aveiro, Portugal
Natália Cordeiro, University of Porto, Portugal
Nelson Nunes, Polytechnic Institute of Lisbon, Portugal
Nicolas Schaeffer, University of Aveiro, Portugal
Nivaar Brijmohan, University of KwaZulu-Natal, South Africa
Nuria Botella, University of Alicante, Spain
Olga Ferreira, Polytechnic Institute of Bragança, Portugal
Olivia Fandino, IFREMER, France
Osvaldo Chiavone, Federal University of Rio Grande do Norte, Brazil
Pedro Carvalho, University of Aveiro, Portugal
Quan Shi, Chinese Academy of Sciences, China
Rachid Hadjadj, University of Lorraine, France
Raj Akshat, Birla Institute of Technology Mesra, India
Raluca Baron, "Petru Poni" Institute of Macromolecular Chemistry, Romania
Raul Santos, University of Porto, Portugal
Ricardo Castro, University of Porto, Portugal
Ricardo Pais, University of Aveiro, Portugal
Ricardo Reis, Soquímica, Portugal
Ricardo Torres, University Centre of the FEI, Brazil
Riko Siewert, University of Rostock, Germany
Riku Seiki, University of Tsukuba, Japan
Rita Carvalho, University of Aveiro, Portugal
Rodrigo Silva, University of Porto, Portugal
Rodrigo Tomaz, Soquímica, Portugal
Roxana Pasca, Iuliu Hatieganu University of Medicine and Pharmacy, Romania
Rui Machado, University of Porto, Portugal
Rui Zhang, Thermo-Calc Software AB, Sweden
Sahar Nasrallah, Technical University of Munich, Germany
Sebastian Wohlrab, Leibniz Institute for Catalysis, Germany
Sergey Verevkin, University of Rostock, Germany
Shaoheng Wang, University of Hamburg, Germany
Simão Cardoso, Paralab, Portugal
Simão Pinho, Polytechnic Institute of Bragança, Portugal
Sofia Cunha, MT Brandão, Portugal

Sonia Barreiro, University of Vigo, Spain
Soraia Silva, University of Porto, Portugal
Stephan Knappe, NETZSCH, Germany
Sungjun Lee, Korea Research Institute of Standards and Science, South Korea
Taichi Abe, National Institute for Materials Science, Japan
Takashi Tokumasu, Tohoku University, Japan
Teresa Iglesias, University of Vigo, Spain
Tom Hughes, Monash University, Australia
Vanessa Vieira, University of Aveiro, Portugal
Vito Cimmelli, University of Basilicata, Italy
Vojtěch Štejfa, University of Chemistry and Technology, Prague, Czechia
Wanying Wu, University of Western Australia, Australia
Xiong Xiao, University of Western Australia, Australia
Yasuhiro Nakazawa, Osaka University, Japan
Yong Park, Kyonggi University, South Korea
Yongchai Kwon, Seoul National University of Science and Technology, South Korea
Yoshitomo Furushima, Toray Industries Europe GmbH, Germany