24th ESAT

EUROPEAN SYMPOSIUM ON APPLIED THERMODYNAMICS

June 27- July 1, 2009
Santiago de Compostela, Spain

BOOK OF ABSTRACTS

Editors: Alberto Arce and Ana Soto

GROUP OF SEPARATION PROCESSES AND PHASE EQUILIBRIA
CHEMICAL ENGINEERING DEPARTMENT
SCHOOL OF ENGINEERING
UNIVERSITY OF SANTIAGO DE COMPOSTELA

CD ROM
Included

PII-44

Vapour pressures and osmotic coefficients of binary mixtures of 1-ethyl-3-methylimidazolium ethylsulfate with alcohols at 323.15 K

N. Calvar(1)*, B. González*(2)*, E. A. Macedo*(1)

(1) LSRE - Laboratory of Separation and Reaction Engineering,
Associate Laboratory LSRE/LCM, Department of Chemical Engineering
Faculty of Engineering, University of Porto
Rua Dr Roberto Frias s/n 4200-465 Porto, Portugal
(2)Group of Advanced Separation Processes, Departament of Chemical Engineering,
Universidad de Vigo, Edif. Isaac Newton
Lagoas-Marcosende 36310, Vigo, España

Abstract

Osmotic coefficients of binary mixtures containing alcohols (ethanol, 1-propanol, 2-propanol) and the ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate were determined at 323.15 K. Vapour pressure and activity coefficients of the studied systems were calculated from experimental data. The extended Pitzer model modified by Archer, and the modified NRTL model (MNRTL) were used to correlate the experimental data, obtaining standard deviations lower than 0.012 and 0.031, respectively. The mean molal activity coefficients and the excess Gibbs free energy of the studied binary mixtures were calculated from the parameters obtained with the extended Pitzer model of Archer

Introduction

Ionic liquids (ILs) find a wide range of application as alternatives to the organic solvents for different processes, and they are being used as separation agents with very promising results. Thermodynamic properties of mixtures containing ionic liquids are of great interest, and namely osmotic and activity coefficients.

In this work, experimental data of osmotic and activity coefficients together with the vapour pressures of the binary mixtures containing ethanol, 1-propanol, and 2-propanol with the ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate ($EMimESO_4$) are presented. The vapour pressure osmometry (VPO) technique was employed for the determination of the experimental data. In spite of the numerous advantages of this technique, such as its high accuracy, being less time-consuming than other techniques used for VLE, and the fact that small amounts are enough for the experiments, it is scarcely used in mixtures containing ionic liquids [1-6].

To correlate the experimental data, the extended Pitzer model modified by Archer [7, 8], and one local composition model, the modified NRTL (MNRTL) [9] are used. The extended Pitzer model of Archer is capable of reproducing satisfactorily the experimental osmotic coefficients. The mean molal activity coefficients and excess

Gibbs free energies were calculated adopting the parameters obtained with this model

Experimental

Chemicals. The ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate (EMimESO$_4$) was synthesised and purified in our laboratory according to previously published procedure [10]. The water content was determined using a 756 Karl Fischer coulometer, and it was lower than $3 \cdot 10^{-4}$. Ethanol used in this work was supplied by Merck with mass fraction purity > 0.999, 1-propanol was purchased by Sigma-Aldrich with mass fraction purity > 0.999, and 2-propanol was supplied by Riedel-de Haën with mass fraction purity > 0.998. The alcohols were degassed ultrasonically and dried over molecular sieves type 4 Å, supplied by Aldrich, and kept in an inert argon atmosphere. Their maximum water mass fraction was $2 \cdot 10^{-6}$.

Apparatus and Procedure. The vapour pressure osmometry measurements were performed using a Knauer K-7000 vapour pressure osmometer (VPO). The osmometer consists of two thermistors that are placed in a cell where the gas phase is saturated with solvent vapour. These thermistors measure resistance differences caused by changes in the temperature (ΔT). This ΔT is measured in terms of ΔR, the difference in the resistances of the two thermistors.

Results and Discussion

Experimental. The osmotic coefficients, ϕ, of the solutions of molality m can be expressed as:

$$\nu \phi m = k \Delta R \qquad (1)$$

where ν is the number of ions into which the electrolyte dissociates.
The calibration factors k were calculated using binary mixtures of NaCl with ethanol and LiBr with 1-propanol and 2-propanol of different known molalities, and obtaining their ΔR.
From the experimental osmotic coefficients, the activity and vapour pressures of the different solutions can be calculated using the standard following thermodynamic relations:

$$\phi = -\ln a_s / \nu m M_s \qquad (2)$$

$$\ln a_s = \ln (p/p^*) + (B_s - V_s^*)(p - p^*) / RT \qquad (3)$$

where a_s is the activity of the solvent, M_s is the molecular weight of the solvent, T is the absolute temperature, R is the universal gas constant, p is the vapour pressure of the solution, and p^* is the vapour pressure of the pure solvent. B_s and V_s^* are the second virial coefficient and molar volume of the pure solvent, respectively. The necessary data on the second virial coefficients, B_s, molar volumes, V_s^*, densities, d_s, relative permittivities, ε, and Antoine constants, A, B, and C, for the different solvents were taken from literature, together with the calculated values of the Debye-Hückel constants, A_ϕ. The uncertainty for the experimental osmotic coefficients and for the calculated activity coefficients were < ± 0.006 and < ± 0.02, respectively.

The vapour pressure depression, Δp, versus molality for the binary mixtures of the different alcohols and the ionic liquid $EMimESO_4$ at T = 323.15 K is plotted in figure 1a. The vapour pressure depression was calculated attending to the next equation:

$$\Delta p = p^{*} - p \tag{4}$$

where p is the vapour pressure of the mixtures, and p^{*} is the pure solvent vapour pressure.

The vapour pressure depression is a property directly related to the solute-solvent interactions, and from figure 1 these interactions can be deduced:

2-propanol + IL > ethanol + IL > 1-propanol + IL

It can be deduced that, of the studied alcohols, 2-propanol presents stronger solute-solvent interactions than ethanol, and ethanol stronger interactions than 1-propanol, in their mixtures with this ionic liquid.

The osmotic coefficients, activities and vapour pressures for the three binary mixtures studied in this work at T = 323.15 K are summarized in table 1. The osmotic coefficients versus molality of the studied systems are plotted in figure 1b. As usual, osmotic coefficients decrease with increasing concentration of ionic liquid, showing non-ideality because of the ion-association interactions.

As can be observed from figure 1b, in binary mixtures containing 2-propanol, the osmotic coefficient values are higher than the ones obtained in mixtures with 1-propanol at low composition solutions, while when the concentration increases at molalities higher than 1 $mol \cdot kg^{-1}$, the trend is the opposite.

Thermodynamic modelling. The model of Pitzer with Archer's ionic-strength dependence of the third virial coefficient [7, 8] has been used for aqueous electrolytes and for nonaqueous electrolytes, including systems containing ionic liquids [1-3] with good accuracy. In this work, the set of parameters b= 3.2, $\alpha_1 = 2\ kg^{1/2}\ mol^{-1/2}$, $\alpha_2 = 7\ kg^{1/2}\ mol^{-1/2}$, $\alpha_3 = 1\ kg^{1/2}\ mol^{-1/2}$ was adopted. Ion-interaction parameters obtained from the correlation for the studied systems are summarized in table 2, together with the obtained standard deviations. Experimental and calculated osmotic coefficients are compared in figure 1b. As can be observed from this figure, the extended Pitzer model of Archer correlates the experimental osmotic coefficients with very high accuracy.

In local composition models the activity coefficient is a summation of two terms: a long-range (LR) and a short-range (SR) contributions. The Pitzer-Debye-Hückel (PDH) equation [11] has been used as the long-range term in this work. The short-range contribution for the activity coefficient of the solvent for the MNRTL model has been developed by Jaretun and Aly [9]. The model parameters and the corresponding standard deviations for the six studied systems at T = 323.15 K are presented in table 3. Comparing the standard deviations given in tables 2 and 3, in general the Archer extension of Pitzer model gives slightly better results for the majority of the studied systems.

From the parameters obtained with the Archer extension of Pitzer model, mean molal activity coefficients [11] were calculated. The validity of the mean molal activity coefficient calculations depends on the capacity of the model to describe the osmotic coefficients in the diluted region. In figure 2a, the calculated $\gamma_{\pm}$ for the studied

systems at T = 323.15 K are presented. The values of mean molal activity coefficients decrease according to: 2-propanol > 1-propanol > ethanol.
The excess Gibbs free energy, G^E, can be expressed in terms of osmotic and activity coefficients. In figure 2b the excess Gibbs free energy for the binary systems containing $\mathrm{EMimESO_4}$ are plotted The values of the excess Gibbs free energy decrease in the same order of the values of mean molal activity coefficients.

Acknowledgements

The authors are grateful for the scholarship from Fundação para a Ciência e a Tecnologia (FCT, Portugal) (ref: SFRH/BDP/37775/2007), LSRE financing by FEDER/POCI/2010, and to the Xunta de Galicia (Ángeles Alvariño program) for financial support.

References

[1] B. González, N. Calvar, A. Domínguez, E. A. Macedo, J. Chem. Thermodyn. (2008), 40, 1346-1351.
[2] N. Calvar, B. González, A. Domínguez, E. A. Macedo, J. Chem. Thermodyn. (2009), 41, 11-16.
[3] N. Calvar, B. González, A. Domínguez, E. A. Macedo, J. Chem. Thermodyn. (2009) doi: 10.1016/j.jct.2008.12.021
[4] H. Shekaari, M. T. Zafarani-Moattar, Fluid Phase Equilib. (2007), 254, 198-203.
[5] R.L. Gardas, D.H. Dagade, J.A.P. Coutinho, K.J. Patil, J. Phys. Chem. B (2008), 112, 3380-3389.
[6] H. Shekaari, S.S. Mousavi, J. Chem. Thermodyn. (2009), 41, 90-96.
[7] D. G. Archer, J. Phys. Chem. Ref. Data, (1991), 20, 509-555.
[8] D. G. Archer, J. Phys. Chem. Ref. Data, (1992), 21, 793-829.
[9] A. Jaretun, G. Aly, Fluid Phase Equilib. (1999), 163, 175-193.
[10] E. Gómez, B. González, N. Calvar, E. Tojo, A. Domínguez, J. Chem. Eng. Data (2006), 51, 2096-2102.
[11] K. S. Pitzer, Activity Coefficients in Electrolyte Solutions, CRC Press, Florida, 1991.

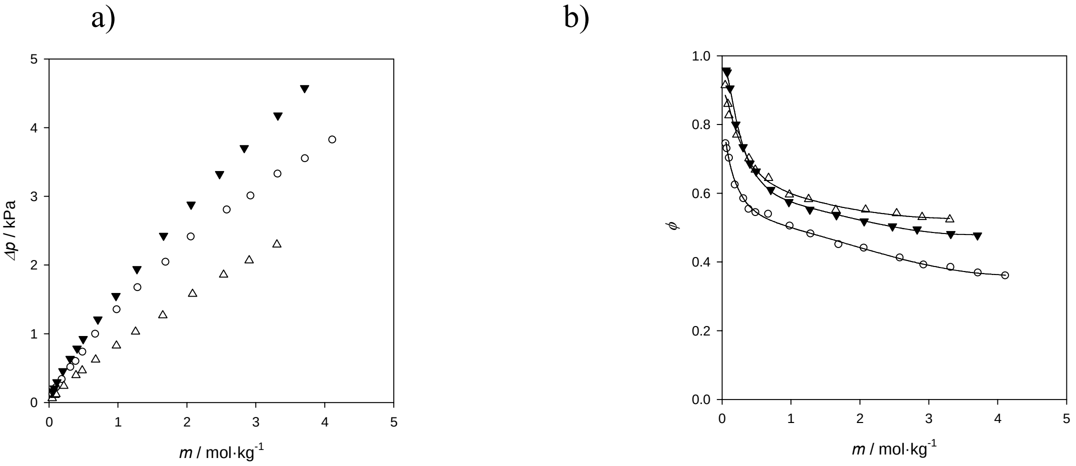
a) b)

Figure 1. a) Vapour pressure depression, Δ*p*, plotted against molality (○) ethanol, (△) 1-propanol, and (▼) 2-propanol with EMimESO$_4$ at 323.15 K; b) Experimental osmotic coefficients, ϕ_1, plotted against molality of the studied binary mixtures: a) (○) ethanol, (△) 1-propanol, and (▼) 2-propanol with EMimESO$_4$ at T = 323.15 K. Solid line (—): Extended Pitzer Model of Archer

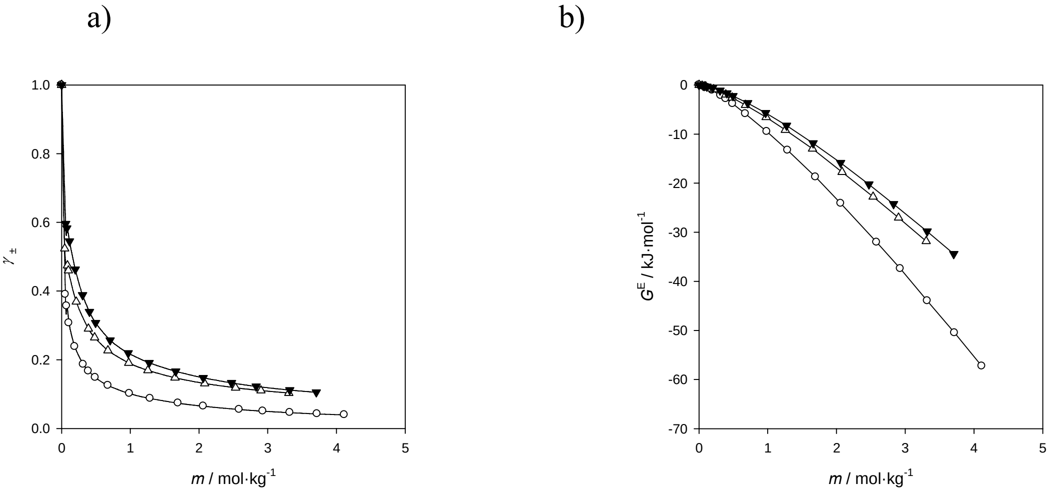
a) b)

Figure 2. a) Mean molal activity coefficients, $\gamma_{\pm}$, calculated from the extended Pitzer model of Archer parameters, plotted against molality: (○) ethanol, (△) 1-propanol, and (▼) 2-propanol with EMimESO$_4$ at 323.15 K.; b) Excess Gibbs free energy, G^E, plotted against molality: (○) ethanol, (△) 1-propanol, and (▼) 2-propanol with EMimESO$_4$ at T = 323.15 K.

Table 1. Osmotic coefficients, ϕ_1, activities, a_1, and vapour pressures, p, of binary mixtures {solvent (1) + 1-ethyl-3-methylimidazolium ethylsulfate (EMimESO$_4$) (2)} at T = 323.15 K

m / (mol · kg^{-1})	ϕ_1	a_1	p / kPa
{Ethanol (1) + EMimESO$_4$ (2)}			
0.0565	0.744	0.996	29.361
0.0734	0.729	0.995	29.329
0.1084	0.701	0.993	29.267
0.1932	0.623	0.989	29.145
0.3175	0.584	0.983	28.969
0.3923	0.553	0.980	28.883
0.4921	0.543	0.976	28.746
0.6773	0.538	0.967	28.485
0.9888	0.504	0.955	28.130
1.2900	0.481	0.944	27.809
1.6972	0.450	0.932	27.438
2.0633	0.440	0.920	27.070
2.5861	0.411	0.907	26.678
2.9298	0.391	0.900	26.474
3.3224	0.384	0.889	26.155
3.7188	0.367	0.882	25.933
4.1154	0.359	0.873	25.660
{1-Propanol (1) + EMimESO$_4$ (2)}			
0.0464	0.914	0.995	12.040
0.0854	0.860	0.991	11.995
0.0991	0.826	0.990	11.982
0.2144	0.770	0.980	11.862
0.3907	0.702	0.968	11.705
0.4826	0.668	0.962	11.637
0.6749	0.644	0.949	11.479
0.9772	0.596	0.932	11.274
1.2548	0.583	0.916	11.072
1.6504	0.551	0.896	10.834
2.0823	0.552	0.871	10.522
2.5319	0.541	0.848	10.244
2.9028	0.531	0.831	10.035
3.3062	0.524	0.812	9.805
{2-Propanol (1) + EMimESO$_4$ (2)}			
0.0601	0.957	0.993	23.426
0.0757	0.952	0.991	23.385
0.1148	0.905	0.988	23.294
0.2001	0.800	0.981	23.135
0.3055	0.734	0.973	22.954
0.4052	0.686	0.967	22.804
0.4942	0.664	0.961	22.665
0.7072	0.610	0.949	22.382
0.9702	0.575	0.935	22.040
1.2750	0.553	0.919	21.648
1.6603	0.536	0.899	21.163
2.0610	0.518	0.880	20.710
2.4737	0.504	0.861	20.266
2.8311	0.495	0.845	19.887
3.3196	0.482	0.825	19.413
3.7067	0.478	0.808	19.013

Table 2. Parameters of modified extended Pitzer model of Archer for binary mixtures at T = 323.15 K, together with the obtained standard deviations, (σ)

$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	$C^{(0)}$	$C^{(1)}$	σ
{Ethanol (1) + EMimESO$_4$ (2)}					
0.42552	-0.95540	5.61754	-0.00681	-0.72020	0.006
{1-Propanol (1) + EMimESO$_4$ (2)}					
0.10884	1.51383	20.13045	-0.00045	-0.10302	0.012
{2-Propanol (1) + EMimESO$_4$ (2)}					
0.52267	0.86827	33.68204	-0.01046	-0.72845	0.007

$\sigma = \left[\sum_{i}^{n_{dat}} \left(\phi_{i,\exp} - \phi_{i,calc} \right)^2 / n_{dat} \right]^{1/2}$, where n_{dat} is the number of experimental data

Table 3. Parameters of the MNRTL model for binary mixtures at T = 323.15 K, together with the standard deviations, (σ)

$\tau_{\mathrm{ca,m}}$	$\tau_{\mathrm{m,ca}}$	$\omega_{\mathrm{ca,m}}$	$\omega_{\mathrm{ca,m}}$	σ
{Ethanol (1) + EMimESO$_4$ (2)}				
0.901	-0.010	2.614	-7.531	0.031
{1-Propanol (1) + EMimESO$_4$ (2)}				
4.665	-0.006	6.010	-19.898	0.014
{2-Propanol (1) + EMimESO$_4$ (2)}				
1.057	-0.012	3.552	-7.804	0.006