Fluid Phase Equilibria 567 (2023) 113717

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.journals.elsevier.com/fluid-phase-equilibria

Predicting the ionicity of ionic liquids in binary mixtures based on solubility data

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ARTICLE INFO

Keywords:
Ionic liquids
Thermodynamic modelling
PDH+UNIQUAC
Ionicity

ABSTRACT

Ionic liquids (ILs) are ionic compounds which are liquid at room temperature and pressure, and can be applied in many fields, such as industrial synthesis, catalysis, electrochemistry, and liquid-liquid separations. To enhance the description of mixtures containing ILs and, consequently, to allow a more rigorous evaluation of the feasibility of chemical processes, it is important to study properties such as the ionicity (α) of ionic liquids, *i.e.*, the fraction of dissociated molecules. However, experimental determinations of ionicity (also known as dissociation degree or dissociation extent) are time-consuming and require the handling of expensive equipment, so the prediction of this property as a function of the system's composition using thermodynamic modelling is of great relevance. For that purpose, the UNIversal QUAsi-Chemical (UNIQUAC) model was combined with the Pitzer-Debye-Hückel (PDH) equation, which is often referred as PDH+UNIQUAC, and it was used to predict the ionicity of ILs in binary mixtures based on liquid-liquid equilibria (LLE) data. The results were compared with the available experimental data from literature and low deviations were observed, validating thereafter the developed approach. In total, the IL ionicity was predicted, as function of composition, for fourteen ionic liquid / solvent (water or 1-butanol) binary systems. Further, a sensitivity analysis was performed to evaluate the influence of the LLE uncertainties on ionicity (α), and it was concluded that α was not significantly affected by small deviations, for which the methodology proposed in this work was considered robust. The prediction of IL ionicity with composition using PDH+UNIQUAC thermodynamic modelling was considered a breakthrough, since very accurate results were achieved without the need of undergoing complex experiments.

1. Introduction

The society of the 21st century has been forcing a growing environmental awareness in both scientific community and industry, leading to the replacement of hazardous organic solvents by more eco-friendly counterparts. Ionic liquids (ILs), due to their favourable chemical and physical properties, have emerged as relevant greener alternatives [1]. Even though ILs were considered as "unbreakable" molecules for many years [2], nowadays it is known that they can dissociate in solution, *i.e.*, they are electrolytes [3]. Consequently, it is crucial to study the ionicity (also known as dissociation degree or dissociation extent) of ILs to thoroughly characterise the electrolyte systems and to quantify the fraction of dissociated species in solution. In this study, the ionicity term will be used as a synonym of dissociation degree despite its sometimes more comprehensive meaning.

Due to their unique properties, ionic liquids can be used in many industrial applications, such as separation processes, electrochemistry, and wastewater and gas treatments [4]. However, some of these applications require the handling of labile species, such as vitamins and proteins, which are generally sensitive to large ionic strengths. Consequently, it is important to quantify the dissociation of ionic liquids to avoid product denaturation and to increase the process yield. Moreover, the study of this property in binary mixtures is important to control some intricately related chemical and physical properties, such as viscosity, density, surface tension, volatility, solubility, and chemical reactivity [5].

Even though some experimental determinations of IL ionicity can be found in literature [5,6], they are generally complex and time-consuming, so the development of alternative approaches using thermodynamic modelling to predict this property is crucial. In

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https://doi.org/10.1016/j.fluid.2022.113717
Received 6 October 2022; Received in revised form 16 December 2022; Accepted 26 December 2022
Available online 30 December 2022

literature, some works have already delved into this problematic, such as the one of Lin *et al.* [7], which modelled the dissociation of ionic liquids in three aqueous systems using the electrolyte-Non-Random Two-Liquid (eNRTL) model, obtaining a very good description of the experimental results. Moreover, Lee and Lin [8] compared 3 ionicity values: $\alpha = 0$, $\alpha = 0\,35$ and $\alpha = 1$ to describe some binary systems containing ionic liquids using the Conductor-like Screening Model for Segment Activity Coefficient (COSMO-SAC) model. Finally, Marques *et al.* [9] studied 13 aqueous systems and qualitatively evaluated the ionicity of ionic liquids using the Universal Quasi-Chemical (UNIQUAC) model and UNIQUAC combined with the Pitzer-Debye-Hückel equation (commonly known as PDH+UNIQUAC).

In this work, continuing a previous study of the research group [9], the PDH+UNIQUAC model was employed to quantitatively evaluate the ionicity of ionic liquids (ILs) in binary mixtures based on liquid-liquid equilibria (LLE) data. This approach is expected to enhance the description of mixtures containing ILs and to reduce the need for experimental determinations, allowing, for example, to direct experimental efforts to the most likely successful systems in the liquid-liquid extraction of biomolecules, which are very sensitive to large ionic strengths, sparing valuable time and resources.

2. Model presentation

2.1. PDH+UNIQUAC model

The Universal Quasi-Chemical (UNIQUAC) model was chosen since it has proven applicability to electrolyte systems [10] (despite not being originally developed for these systems [11]), and since the research group has sustained experience with this model [9,12,13]. It is a local composition and excess Gibbs energy model [11], which accounts for short-range interactions, *i.e.*, the ones established between neutral particles in contact [14], and can be applied to mixtures with asymmetrical molecules, *i.e.*, different sizes and shapes [11]. Since this model is widely reported in literature [9,12], its equations will not be presented.

The Pitzer-Debye-Hückel (or PDH) equation was developed in 1980 [14] and it is one of the most popular equations to describe long-range forces [2,9,15], *i.e.*, the ones established between ions of opposite charges. It is an improvement to the Debye-Hückel equation since it can be used for solutions with higher ionic strengths [16], and has successfully been used to model systems with charged species, such as aqueous systems containing sodium chloride (NaCl) and potassium chloride (KCl) [16]. The symmetric electrolyte reference state convention is used in this equation [17].

In a mixture, following the symmetric convention [18], and the Lewis-Randall rule, the activity coefficient of species i (γ_i) can be derived from the molar excess Gibbs energy (G^E) using the standard thermodynamic relation [19]:

$$R T \ln(\gamma_i) = \left(\frac{\partial n_T G^E}{\partial n_i}\right)_{T,\ P,\ n_j} \tag{1}$$

where R is the ideal gas constant, T is the absolute temperature, P is pressure, γ_i is the activity coefficient of species i, n_i and n_j are the number of moles of species i and j, and n_T is the total number of moles.

The UNIQUAC model can be combined with the PDH equation, which is often referred as PDH+UNIQUAC. In this model, the activity coefficient of species i (γ_i) is calculated by deriving Eq. (1) into:

$$\ln \gamma_i = \ln \gamma_i^{\mathrm{UNIQUAC}} + \ln \gamma_i^{\mathrm{PDH}} \tag{2}$$

where $\gamma_i^{\mathrm{UNIQUAC}}$ and γ_i^{PDH} refer to the activity coefficients from the UNIQUAC model and from the PDH equation, respectively.

In the UNIQUAC model, the τ_{ij} parameter between the components i and j is calculated by [11]:

$$\tau_{ij} = e^{\frac{\Delta u_{ij}}{T}} \tag{3}$$

where Δu_{ij} is the UNIQUAC binary interaction parameter.

In this work, a linear dependence of the Δu_{ij} parameter with temperature was considered [20]:

$$\Delta u_{ij} = a_{ij}^* + b_{ij}^* \cdot T \tag{4}$$

where a_{ij}^* and b_{ij}^* are adjustable parameters between species i and j. The a_{ij}^* and b_{ij}^* parameters were adjusted in the intervals [50,50] and [5,5], respectively, following previous works in this field [21–23].

The long-range term of the activity coefficients (γ_i^{PDH}) is calculated by the Pitzer-Debye-Hückel (PDH) equation in the symmetric convention [17].

$$\ln \gamma_i^{\mathrm{PDH}} = z_i^2 \cdot A_{\mathrm{DH},x} \left[\frac{2}{\rho}\ln\left(\frac{1+\rho\sqrt{I_x}}{1+\rho\sqrt{\frac{z_i^2}{2}}}\right) + \sqrt{I_x}\ \frac{1}{1+\rho\sqrt{I_x}}\ \frac{2\,I_x}{z_i^2}\right] \tag{5}$$

where z_i is the electrical charge of the species i, ρ is the closest approach parameter, $A_{\mathrm{DH},x}$ is the Debye-Hückel parameter, and I_x is the ionic strength, which is calculated by [24]:

$$I_x = \frac{1}{2}\sum_{i=1}^{N_{\mathrm{ions}}} x_i z_i^2 \tag{6}$$

where N_{ions} is the number of ion species present in solution and x_i is the mole fraction of species i.

The $A_{\mathrm{DH},x}$ parameter is calculated by [24]:

$$A_{\mathrm{DH},x} = \frac{1}{3}\sqrt{2\pi\ \frac{N_A\ \rho_{\mathrm{ms},x}}{M_{\mathrm{ms}}}}\left(\frac{e^2}{4\pi\ \varepsilon_0\ \varepsilon_{\mathrm{ms}}\ k_B\ T}\right)^{1\,5} \tag{7}$$

where N_A is the Avogadro's constant, $\rho_{\mathrm{ms},x}$ is the molar density of the mixed solvent, e is the electronic charge, M_{ms} is the molecular mass of the mixed solvent, ε_0 is the vacuum permittivity, k_B the Boltzmann constant, $\varepsilon_{\mathrm{ms}}$ is the dielectric constant of the mixed solvent and T is the absolute temperature.

The molecular mass of the mixed solvent (M_{ms}) can be calculated by the weighted arithmetic mean given by [17]:

$$M_{\mathrm{ms}} = x'_{\mathrm{IL}} M_{\mathrm{IL}} + x'_{\mathrm{solv}} M_{\mathrm{solv}} \tag{8}$$

where x'_{IL} and x'_{solv} are the salt-free mole fractions of the ionic liquid and of the solvent, and M_{IL} and M_{solv} the respective molecular masses. Salt-free nomenclature only considers undissociated ionic liquid and solvent molecules. Although ionic liquids are also solvents, the nomenclature used in this work does not refer to ionic liquids as solvents.

The molar density of the mixed solvent ($\rho_{\mathrm{ms},x}$) is calculated based on the molar density of the solvent ($\rho_{\mathrm{solv},x}$) and of the ionic liquid ($\rho_{\mathrm{IL},x}$) [25].

$$\rho_{\mathrm{ms},x} = \frac{1}{\frac{x'_{\mathrm{solv}}}{\rho_{\mathrm{solv},x}} + \frac{x'_{\mathrm{IL}}}{\rho_{\mathrm{IL},x}}} \tag{9}$$

where w'_{solv} and x'_{IL} are the salt-free mole fraction of the solvent and of the ionic liquid, respectively.

Similarly, the density of the mixed solvent (ρ_{ms}) is calculated using an analogous expression and based on the salt-free mass fraction of solvent (w'_{solv}) and ionic liquid (w'_{IL}), and on their densities (ρ_{solv} and ρ_{IL}, respectively):

$$\rho_{\mathrm{ms}} = \frac{1}{\frac{w'_{\mathrm{solv}}}{\rho_{\mathrm{solv}}} + \frac{w'_{\mathrm{IL}}}{\rho_{\mathrm{IL}}}} \tag{10}$$

The dielectric constant of mixed solvent (ε_{ms}) can be calculated from Oster's mixing rule [26], which allows to better predict the dielectric constant of the mixture.

$$\varepsilon_{ms} = \varepsilon_1 + \left(\frac{(\varepsilon_2 \quad 1)(2\varepsilon_2 \quad 1)}{2\varepsilon_2} \quad (\varepsilon_1 \quad 1)\right) \frac{x_2'}{\rho_{ms,x}} \rho_{ms} \tag{11}$$

where ε_1 and ε_2 refer to the dielectric constants of two generic solvents and x_2' is the salt-free mole fraction of solvent 2.

For a given solvent, the electrical charge (z_i) is zero and Eq. (5) is reduced to:

$$\ln \gamma_m^{PDH} = \frac{2\ A_{DH,x}\ I_x\ \sqrt{I_x}}{1 + \rho\sqrt{I_x}} \tag{12}$$

In Eqs. (5) and (12), the closest approach parameter (ρ) appears, which is a dimensionless parameter related to the distance between the centres of the IL's cation and anion. Pitzer [16] studied the closest approach parameter in systems containing strong electrolytes (such as NaCl and KCl) and assumed that it should be adjusted between 8 and 15, but the value of 14.9 is more commonly used for monocharged ions [16]. However, in this work, in order to preserve the physical meaning of this parameter, the equation proposed by Pitzer and Simonson [27] (Eq. (13)) was adopted, following previous works [9,12,13] which obtained good results in the qualitative evaluation of the ionicity of ionic liquids [9] and in the prediction of the tie-lines of Aqueous Two-Phase Systems (ATPS) [12,13].

$$\rho = a\left(\frac{2\ e^2\ N_A\ \rho_{ms}}{M_{ms}\ \varepsilon_0\ k_B\ \varepsilon_{ms}\ T}\right)^{0.5} \tag{13}$$

a is the hard-core collision diameter, *i.e.*, it is the sum of the radii of the IL-cation and IL-anion without solvation.

The radii of the IL-cation and IL-anion can be approximated by their respective van der Waals radii (r_w), which can be calculated from the van der Waals volume (V_w), *i.e.*, the impenetrable volume of an atom or molecule [28].

$$V_w = \frac{4}{3}\pi\ r_w^3 \tag{14}$$

V_w was correlated with the relative van der Waals molecular volume (r_i) using the well-known equation [11]:

$$V_w = r_i \cdot 15\ 17 \cdot 10^6 \tag{15}$$

2.2. Thermodynamic modelling

In this work, the ionic liquids were assumed to exist in their neutral state (IL = CA) and in their dissociated species (IL-cation: C^+, and IL-anion: A). All the studied ILs dissociate into 1–1 electrolytes, so their ions are monocharged and a simple equilibrium reaction can describe the dissociation process (Eq. (16)), and the ionicity (α) can be calculated by Eq. (17):

$$CA\ (aq) \rightarrow C^+(aq) + A\ (aq) \tag{16}$$

$$\alpha = \frac{\text{Number of dissociated molecules}}{\text{Number of total molecules}} \tag{17}$$

In this work, a new algorithm was developed to apply the thermodynamic modelling using PDH+UNIQUAC. First, the mole fraction of the ionic liquid (x_{IL}^0) and of the solvent ($x_{solv}^0 = 1 \quad x_{IL}^0$) were determined without considering the dissociation reaction. Afterwards, the mole fraction of the solvent (x_{solv}), neutral ionic liquid (x_{IL}), IL-cation (x_C) and IL-anion (x_A) were calculated considering the dissociation process using Eqs. (18) to (20).

$$x_{solv} = \frac{x_{solv}^0}{1 + \alpha\, x_{IL}^0} \tag{18}$$

$$x_{IL} = \frac{(1 \quad \alpha)\ x_{IL}^0}{1 + \alpha\, x_{IL}^0} \tag{19}$$

$$x_C = x_A = \frac{\alpha\ x_{IL}^0}{1 + \alpha\ x_{IL}^0} \tag{20}$$

The different compositions were iterated until the objective function (O F) given by Eq. (21) was minimised following a quasi-Newtonian method.

$$O\ F\ = \sqrt{100\left(\frac{\sum_{i=1}^{N_{species}} {}^{1}\sum_{j=1}^{N} x_{i,j}^{P,exp} \quad x_{i,j}^{P,pred})^2 + x_{i,j}^{R,exp} \quad x_{i,j}^{R,pred})^2}{2N \cdot N_{species}}\right)} \tag{21}$$

where N is the number of equilibrium points, $N_{species}$ is the number of species present in solution, $x_{i,j}^P$ and $x_{i,j}^R$ refer to the mole fraction of species i for the j LLE point for the IL-poor and IL-rich phases, respectively, and the superscripts exp and pred refer to the experimental and predicted compositions.

Moreover, to ensure the validity of the obtained compositions and parameters, the isoactivity criterium, a general phase equilibrium condition between the two liquid phases, was taken into consideration. The algorithm used to predict the ionicity of the ionic liquids is summarised in Fig. 1.

The developed algorithm started by using the experimental LLE mole fractions as an initial estimation and a first set of IL ionicity values (α) equal to zero for the whole range of composition was assumed. Then, the mole composition of neutral ionic liquid, IL-cation, IL-anion, and solvent (x_{IL}, x_C, x_A and x_{solv}, respectively) were calculated using Eqs. (18) to (20), and the PDH+UNIQUAC model was applied. In this model, different values of the UNIQUAC binary interaction parameters (a_{ij}^* and b_{ij}^*) were considered for the previously determined set of IL ionicity values and mole fractions in order to achieve the minimum objective function (iterative process I). Following, a set of IL ionicity values was calculated using a quasi-Newtonian method, and the O F was recalculated (iterative process II). When all sets of IL ionicity values allocated by the algorithm were tested, another set of mole fractions of IL (x_{IL}^0) was calculated using again the quasi-Newtonian method, and the whole procedure described previously was repeated (iterative process III). Afterwards, the code yielded the matrix with the lowest O F and the results were plotted as function of the recalculated IL mole fraction (x_{IL}^0), which was obtained using Eq. (19).

In this work, the dielectric constants (ε) for pure compounds (ionic liquids and solvents) were assumed to be constant for the studied range of temperatures, since for most compounds there was no available data in literature. Moreover, to apply the proposed thermodynamic model, it was necessary to determine the ions' radii, which were approximated by the relative van der Waals molecular volume (r_i). This parameter, together with the relative van der Waals surface area parameter (q_i), was estimated by the Bondi's group contribution method, which assumes the

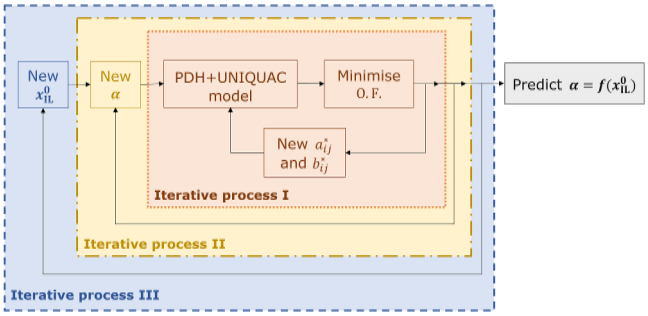

Fig. 1. Algorithm used to determine the degree of dissociation (α) of ionic liquids in binary mixtures.

sphericity of the compounds [29]. Lastly, it was also considered that only the ILs can dissociate, and that the solvents' molecules are always in their neutral state.

3. Collected experimental data

In this work, the ionicity of ionic liquids as function of the system's composition was predicted for14 binary systems comprising 8 ionic liquids, shown in Table 1, and 2 solvents (water and 1-butanol). The used liquid-liquid equilibria (LLE) data is compiled in Table 2.

To predict the ionicity, experimental solubility data, density data, dielectric constants, r_i and q_i parameters and molecular masses of the ionic liquids and solvents were needed. These data were collected from literature for all the studied systems and can be found in Tables S1-S4, in the Supplementary Materials.

4. Results

4.1. Method validation

To validate the proposed methodology, the predicted ionicity of ionic liquids using PDH+UNIQUAC was compared with the experimental data available in literature, which includes 3 of the studied binary systems.

Nordness and Brennecke [5] determined the ionicity (α) of ILs in binary mixtures as function of the system's composition based on conductivity (λ), density (ρ_i) and viscosity (μ) measurements. In their work, the estimated degree of dissociation was found to agree with Pulsed-Field Gradient-Nuclear Magnetic Resonance (PFG-NMR) measurements, which is considered a very reliable experimental method to determine the degree of dissociation [6]. Moreover, Tokuda *et al.* [6] experimentally determined the ionicity for pure [C_4Mim][NTf_2] by PFG-NMR Spectroscopy.

In Fig. 2-Fig. 4, the IL ionicity (α) predicted in this work as function of the mole fraction of IL (x^0_{IL}) was compared with the data determined by Nordness and Brennecke [5] and by Tokuda *et al.* [6]. As it can be observed in Fig. 2, the predicted IL ionicity agrees with literature for the studied range of mole composition. However, in Fig. 3, two outliers exist probably due to inconsistencies in the experimental determinations, despite a good overall shape description. So, although it was not possible to predict IL ionicity in the whole composition range, the modelling results were considered similar to the available experimental data from literature, validating the proposed algorithm.

4.1.1. Sensitivity analysis

As mentioned earlier, in this work, experimental solubility data were used to predict the ionicity of ionic liquids in binary mixtures. However, the experimental determinations always have some uncertainty associated to their procedures, so a sensitivity analysis was performed in order to evaluate how the predicted ionicity changed with deviations in the solubility data. Being so, the effects of three positive (+1 %, +2 % and +5 %) and three negative (1 %, 2 % and 5 %) oscillations in the mole fraction of ionic liquid (x^0_{IL}) on the predicted IL ionicity were studied, as Figure 5 shows for the [C_4Mim][PF_6] + water system.

As Fig. 5 illustrates, a positive variation on the IL mole fraction (x^0_{IL}) caused a higher predicted IL ionicity (α) and the opposite behaviour was verified for a negative variation. Moreover, as expected, the larger the

Table 1
Studied ionic liquids, respective abbreviation used and Chemical Abstracts Service (CAS) number.

IUPAC name	Abbreviation	CAS
1-ethyl-3-methylimidazolium hexafluorophosphate	[C_2Mim][PF_6]	155371–19–0
1-butyl-3-methylimidazolium hexafluorophosphate	[C_4Mim][PF_6]	174501–64–5
1-hexyl-3-methylimidazolium hexafluorophosphate	[C_6Mim][PF_6]	304680–35–1
1-octyl-3-methylimidazolium hexafluorophosphate	[C_8Mim][PF_6]	304680–36–2
1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl)imide	[C_2Mim][NTf_2]	174899–82–2
1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl)imide	[C_4Mim][NTf_2]	174899–83–3
1-hexyl-3-methylimidazolium bis (trifluoromethylsulfonyl)imide	[C_6Mim][NTf_2]	382150–50–7
1-octyl-3-methylimidazolium bis (trifluoromethylsulfonyl)imide	[C_8Mim][NTf_2]	178631–04–4

Table 2
Liquid-liquid equilibria (or solubility) data for the studied binary systems.

Binary systems	No. of points	x^0_{IL} range of the IL-poor phase	x^0_{IL} range of the IL-rich phase	T / K range of the IL-poor phase	T / K range of the IL-rich phase	Ref.
[C_2Mim][NTf_2] + water	14	(7 66 10 5)·10 ^{4}	0 64 0 73	288 15 318 15	288 15 318 15	[30]
[C_2Mim][NTf_2] + 1-butanol	62	0 02 0 13	0 16 0 43	307 14 321 62	307 14 321 62	[31]
[C_4Mim][NTf_2] + water	14	(2 86 4 70)·10 ^{4}	0 68 0 77	288 15 318 15	288 15 318 15	[30]
[C_4Mim][NTf_2] + 1-butanol	54	0 02 0 11	0 16 0 37	286 00 296 68	286 00 296 68	[32]
[C_6Mim][NTf_2] + water	14	(0 89 1 32)·10 ^{4}	0 74 0 81	288 15 318 15	288 15 318 15	[30]
[C_6Mim][NTf_2] + 1-butanol	15	0 02 0 11	0 12 0 32	260 11 269 45	269 46 262 00	[33]
[C_8Mim][NTf_2] + water	14	(3.17–4.55) 10^{-5}	0 78 0 83	288 15 318 15	288 15 318 15	[30]
[C_2Mim][PF_6] + 1-butanol	18	(2 6 4 9)· 10 ^{3}	0 51 0 74	368 15 381 15	328 15 389 65	[34]
[C_4Mim][PF_6] + water	30	(0 9 6 3)· 10 ^{3}	0 48 0 81	278 75 362 15	278 15 348 15	[35]
[C_4Mim][PF_6] + 1-butanol	28	(3 0 4 0)· 10 ^{4}	0 68 0 87	278 15 343 15	278 15 343 15	[36]
[C_6Mim][PF_6] + water	31	(0 33 1 8) ·10 ^{3}	0 43 0 81	286 45 363 05	278 15 353 15	[35]
[C_6Mim][PF_6] + 1-butanol	28	(0 09 4 1) ·10 ^{2}	0 43 0 77	278 15 343 15	278 15 343 15	[36]
[C_8Mim][PF_6] + water	31	(0 94 5 74)·10 ^{4}	0 58 0 88	285 85 364 55	278 15 353 15	[35]
[C_8Mim][PF_6] + 1-butanol	20	(0 1 2 8)· 10 ^{2}	0 23 0 62	278 15 323 15	278 15 323 15	[36]

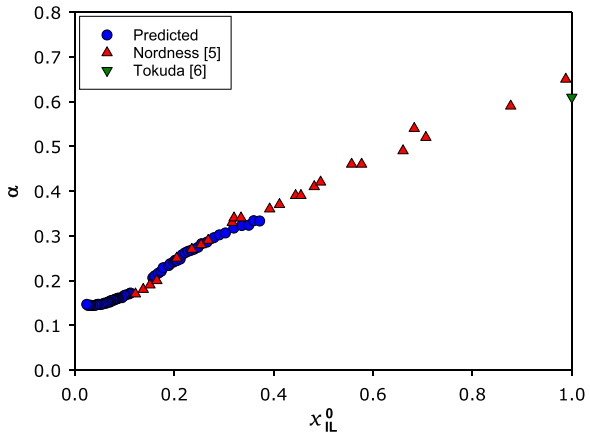

Fig. 2. Predicted IL ionicity (α) in this work and experimental values from literature [5,6] as function of the mole fraction of ionic liquid (x^0_{IL}) at atmospheric pressure for [C_4Mim][NTf_2] + 1-butanol.

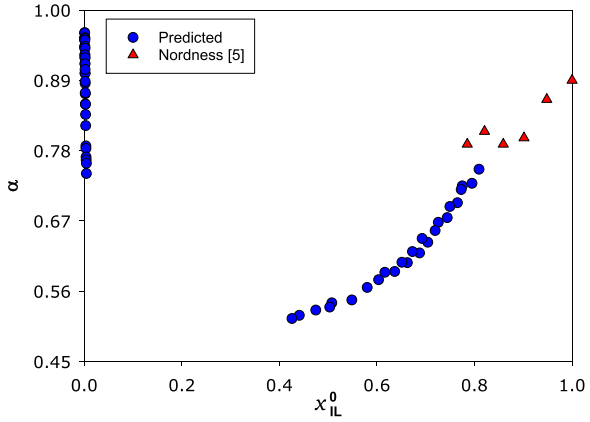

Fig. 3. Predicted IL ionicity (α) in this work and experimental values from literature [5] as function of the mole fraction of ionic liquid (x^0_{IL}) at atmospheric pressure for [C_4Mim][PF_6] + water.

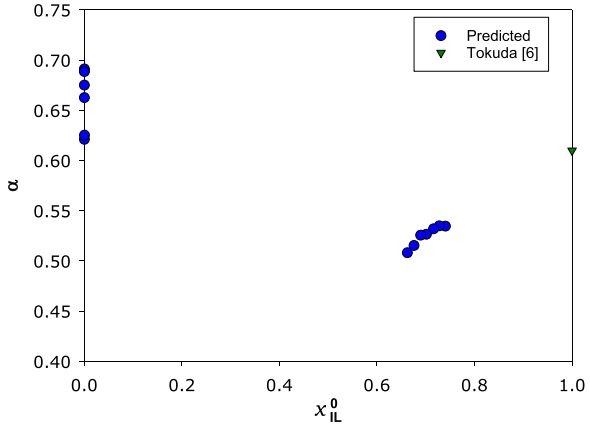

Fig. 4. Predicted IL ionicity (α) in this work and experimental values from literature [6] as function of the mole fraction of ionic liquid (x^0_{IL}) at atmospheric pressure for [C_4Mim][NTf_2] + water.

induced deviation, the larger the difference observed with the "theoretical" degree of dissociation. Given that the maximum difference verified was of 0.09 on the predicted ionicity (with an oscillation of + 5 %), the ionicity determinations were considered robust to variations in

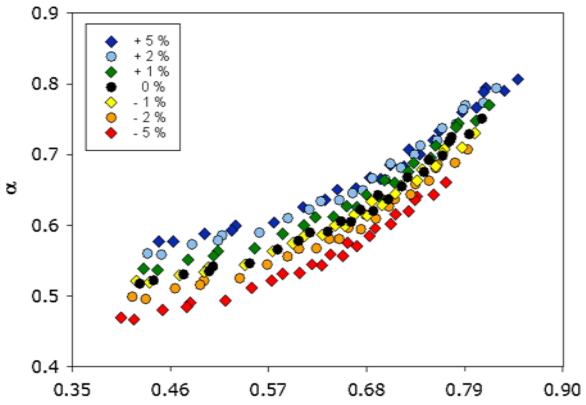

Fig. 5. Sensitivity analysis of the IL ionicity (α) as function of the mole fraction of ionic liquid (x^0_{IL}) for [C_4Mim][PF_6] + water.

the experimental data and the proposed methodology in this work was considered a reliable method to predict the ionicity of ionic liquids in binary mixtures.

4.2. Ionicity determination

After the validation, the IL ionicity was predicted for other 11 binary systems as function of mole composition. In addition, the influence of the IL-cation's alkyl chain length, solvent and IL-anion was analysed. The effect of the IL-cation's alkyl chain length for 1-alkyl-3-methylimidazolium ([C_nMim]$^+$) cations coupled with hexafluorophosphate ([PF_6]) anion in 1-butanol was assessed and it is represented in Fig. 6.

As Fig. 6 shows, a higher alkyl chain length led to a smaller ionicity (α) for the studied range of composition for the IL-rich and IL-poor phases. This can be due to the stronger van der Waals forces for larger alkyl chains, making the molecule more cohesive and the dissociation more difficult, which agrees with experimental determinations reported by other works [5,6]. Moreover, the same conclusions were obtained for the other studied binary systems to what concerns the influence of the alkyl-chain's length, as Figs. S11–13, in the Supplementary Materials, show.

On the other hand, the solvent and the IL-anion's influence on the ionicity is shown in Fig. 7. There, it can be observed that the predicted ionicity (α) is higher for water than for 1-butanol for [C_4Mim][PF_6] and [C_4Mim][NTf_2]. This is probably due to water being more polar than 1-butanol, which is translated by a higher dielectric constant, and, consequently, by an easier establishment of hydrogen bonds

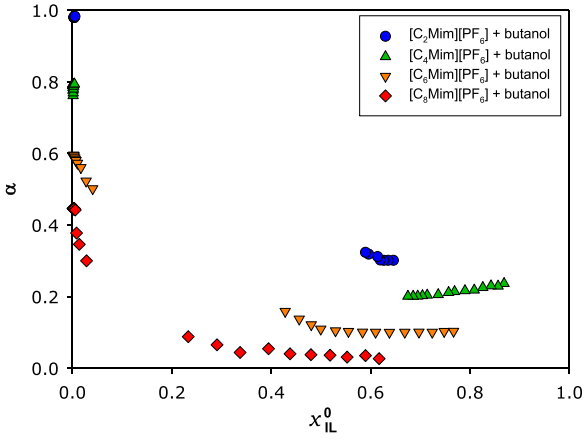

Fig. 6. Predicted IL ionicity (α) as function of the mole fraction of ionic liquid (x^0_{IL}), at atmospheric pressure for the [C_nMim][PF_6] + 1-butanol binary systems, where $n = 2, 4, 6, 8$.

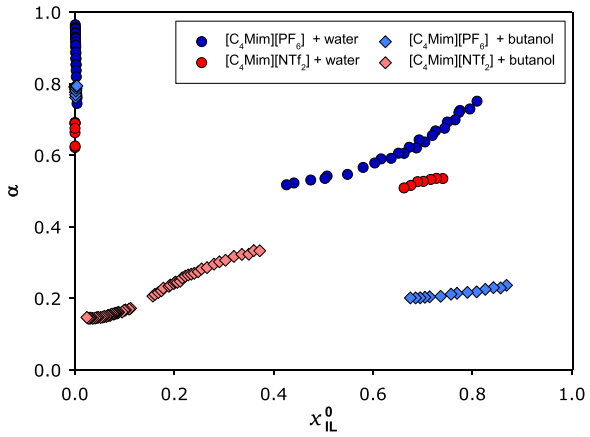

Fig. 7. Predicted IL ionicity (α) as function of the mole fraction of ionic liquid (x^0_{IL}) at atmospheric pressure for [C_4Mim][PF_6] + water, [C_4Mim][PF_6] + 1-butanol, [C_4Mim][NTf_2] + water and [C_4Mim][NTf_2] + 1-butanol.

(association), which ease the solvation of the IL-ions, separating the neutral ionic liquid into its constituents (anions and cations) and causing a higher IL ionicity. Moreover, Fig. 7 also allows to compare the [PF_6] and [NTf_2] anions: the predicted ionicity was larger for ionic liquids containing the [PF_6] anion, which, once again, can be explained by a higher polarity of the [PF_6] anion, increasing IL dissociation. The dielectric constants of the pure chemical species, which support these statements, can be seen in Table S2, in the Supplementary Materials.

Concerning the variation of the dielectric constant of the mixed solvent (ε_{ms}) with the mole fraction of ionic liquid (x^0_{IL}), it was calculated using the Oster's mixing rule [26] and can be observed in Fig. 8. ε_{ms} is higher when the solvent is water, as can be noticed when comparing the binary systems [C_4Mim][PF_6] + water and [C_4Mim][PF_6] + 1-butanol. Once again, since a higher dielectric constant of the mixed solvent is connected with a higher polarity of the mixed solvent, a higher ionicity of the ionic liquids is observed. Similarly, when comparing binary systems with different IL-anions, it was noted that the ε_{ms} is higher for the [PF_6] -based ILs, causing a higher IL ionicity. Finally, in Figs. 6-7 the predicted ionicity is higher for the IL-rich phase than for the IL-poor phase, and this phenomenon can also be explained by the dielectric constant of the mixed solvent, ε_{ms}, which is larger for the IL-poor phase.

In addition, in Figs. S14–16, in the Supplementary Materials, the influence of both solvent and IL-anion for other binary systems was studied, and the same conclusions were achieved, which agree with the experimental results reported in literature [5,6].

In this study, the prediction of the ionicity of ionic liquids in the whole composition range was not possible since it depends on the available LLE data and on the existence of two liquid phases in equilibrium, constituting a drawback of this methodology. In the future, the suggested approach could be improved if Vapour-Liquid Equilibria (VLE) and Solid-Liquid Equilibria (SLE) data are included with eventual application of equations of state (EoS).

4.3. Closest approach parameter

In this work, following previous studies of the research group [9,12,13], the closest approach parameter (ρ) was calculated as function of composition using Eq. (13) to preserve its physical meaning. As previously explained, ρ is a dimensionless parameter related to the distance between the centres of the IL-cation and IL-anion. As example, Fig. 9 illustrates the calculated closest approach parameter as function of the system's composition for [C_4Mim][PF_6] + water.

As shown in Fig. 9, in the more diluted region in ionic liquid (IL-poor phase), the closest approach parameter is higher, hinting that the mean distance of IL-counterions is higher in this phase than in the IL-rich phase. In the IL-poor phase, there are more solvent molecules per volume unit and, consequently, the anion and the cation are more diluted, increasing the distance between them. A similar behaviour of this parameter was observed for the other studied binary systems, which are presented in Table S7, in the Supplementary Materials. However, one must remember that the closest approach parameter (α) is a dimensionless parameter and that it does not allow to directly infer the distance between centres of the IL ions nor to directly predict the ionicity of ionic liquids. This way, as can be observed by comparing Fig. 7 (ionicity) and Fig. 9 (closest approach parameter) for [C_4Mim][PF_6] + water, an increasing closest approach parameter (ρ) may not imply an increasing IL ionicity (α).

Moreover, as Fig. 9 and Table S7 in the Supplementary Materials show, the closest approach parameter (ρ) generally varies between 8 and 16, which, even though mostly respecting the interval defined by Pitzer of 8 to 15 [16], is different than the most commonly used value of 14.9 [16]. For example, for more concentrated solutions in ionic liquid (IL-rich phases), which have lower values for the closest approach parameter (as seen in Fig. 9), considering ρ as 14.9 or performing an adjustment would overestimate the value of this parameter. Consequently, the PDH's contribution for the activity coefficients would present different values and the UNIQUAC model would be forced to accommodate the difference [16], which could lead to an inaccurate description of the modelled electrolyte systems.

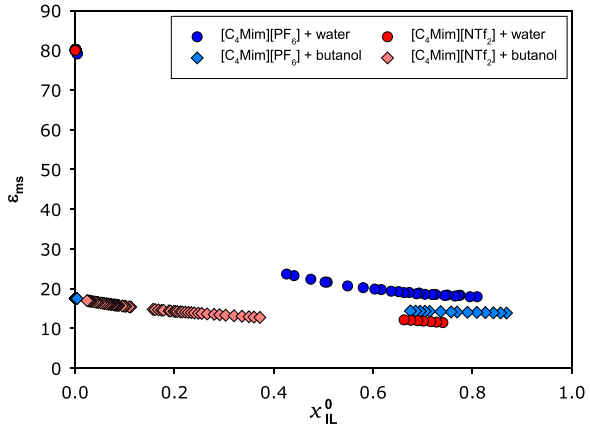

Fig. 8. Dielectric constant of the mixed solvent (ε_{ms}) as function of the mole fraction of ionic liquid (x^0_{IL}), calculated using Oster's [26] mixing rule, at atmospheric pressure, for [C_4Mim][PF_6] + water, [C_4Mim][PF_6] + 1-butanol, [C_4Mim][NTf_2] + water and [C_4Mim][NTf_2] + 1-butanol.

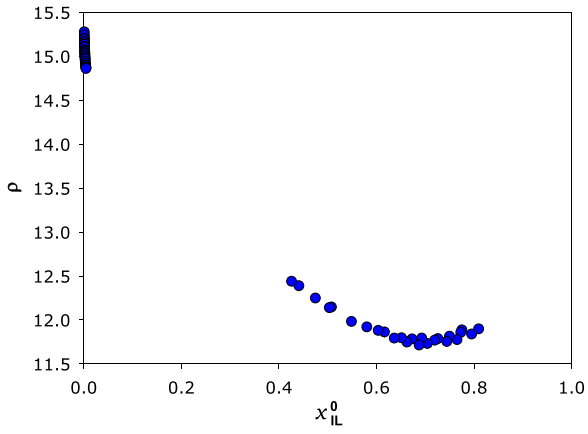

Fig. 9. Calculated closest approach parameter (ρ) as function of the mole fraction of ionic liquid (x^0_{IL}) at atmospheric pressure for [C_4Mim][PF_6] + water.

5. Conclusions

The main goal of this work was to quantitatively predict the ionicity (α) of ionic liquids (ILs) in binary mixtures as function of the system's composition based on liquid-liquid equilibria (LLE) data. For this purpose, the PDH+UNIQUAC model was chosen since it yielded reliable results in previous works of the research group with electrolytes.

The ionicity (or dissociation degree) of ionic liquids was successfully predicted for 14 binary systems, comprising 8 ILs and 2 solvents (water and 1-butanol). The predicted IL ionicity agreed with the available literature data and, therefore, the proposed methodology was validated, constituting a relevant step to reduce the need of experimental determinations in this field of thermodynamics. Moreover, even though only LLE data were used in these predictions, vapour-liquid equilibria (VLE) and solid-liquid equilibria (SLE) data could be added in the future to allow predictions in the whole composition range using, for example, a complementary equation of state.

The influence of the solvent, IL-cation and IL-anion on the ionicity of ionic liquids was evaluated and it was verified that the binary systems with larger dielectric constants (*e.g.*, aqueous systems) and smaller van der Waals forces (*e.g.*, smaller alkyl chain lengths) favoured IL dissociation. Moreover, a sensitivity analysis was conducted, which showed that the predictions of IL ionicity were not significantly affected by minor changes in mole composition, for which the methodology was considered robust to uncertainties in LLE data determination.

CRediT authorship contribution statement

Catarina Lopes: Investigation, Writing – original draft, Writing – review & editing. **Pedro Velho:** Formal analysis, Validation, Investigation, Writing – review & editing. **Eugenia A. Macedo:** Conceptualization, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Data Availability

Data will be made available on request.

Acknowledgments

This work was supported by ALiCE [LA/P/0045/2020] and LSRE-LCM [UIDB/50020/2020 and UIDP/50020/2020], funded by national funds through FCT/MCTES (PIDDAC). Catarina Lopes is grateful to the project HealthyWaters [NORTE-01-0145-FEDER-000069], supported by Norte Portugal Regional Operational Programme (NORTE 2020), under the PORTUGAL 2020 Partnership Agreement, through the European Regional Development Fund (ERDF). Pedro Velho thanks funding support from FCT [2021.06626.BD].

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.fluid.2022.113717.

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