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

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ABSTRACT

Ionic liquids (ILs) have been deeply investigated as possible substitutes for hazardous organic solvents, but their recently acknowledged ionicity, together with their generally high viscosity, has been hampering their further application. The ionicity (or degree of dissociation) of electrolytes affects properties such as viscosity, solubility and density, so it is of the utmost importance for the proper thermodynamic description of systems containing electrolytes. However, the experimental quantifications of this property are difficult to perform, which creates the need for more predictive approaches. In this work, the ionicity of 12 ionic liquids in binary mixtures composed of water, ethanol, 1-propanol or 1-butanol was predicted based on solubility data available in literature by the Pitzer-Debye-Hückel (PDH) equation combined with the UNIversal QUAsi-Chemical (UNIQUAC) model, which is often referred as PDH+UNIQUAC. The ionicity of the ionic liquids was modelled as function of mole composition for a total of 17 binary systems, comprising ILs of three chemical families: hexafluorophosphates, tetrafluoroborates, and bis(trifluoromethylsulfonyl)imides, continuing a previous work. This novel methodology provided a useful tool to estimate the ionicity of ionic liquids containing imidazolium cations without undergoing long experimental determinations, which could be applied in the design of separation processes.

1. Introduction

Ionic liquids (ILs) or liquid salts are a very broad chemical family of electrolytes with melting point below 100 °C at atmospheric pressure. Generally, they present high thermal stability, high polarity, high electrical conductivity, and a wide electrochemical window [1,2]. Moreover, it is possible to tune their intrinsic thermo-physical properties by selecting the ionic liquid counterions, for which they are known as "designer solvents" [3].

In the last years, the research for eco-friendlier solvents has been expanding, and ionic liquids are expected to play a significant role in the chemical industry as replacements for more traditional solvents such as the volatile organic compounds (VOCs), which may compromise the human and animal health [4]. This way, even though the general non-volatility of ionic liquids at room temperature hampers solvent recycling, it also made them emerge as important substitutes for VOCs as reaction media for organic and inorganic synthesis [3,5] and as separation solvents [1,6–8]. For example, ionic liquids have been used with success in the extraction of active pharmaceutical ingredients (APIs) such as anti-inflammatory drugs and antibiotics from polluted water streams [9–11], and their often high biological activity makes them strong candidates for future use in drug delivery and biomedical analytics [12]. Furthermore, other applications of ionic liquids include electrochemical devices such as lithium-ion batteries [13,14], catalysis [15,16] and novel electrolytes [2,17].

Since the application of ionic liquids in the industry is relatively recent, some of their physical and chemical properties were not yet extensively studied, for which, for example, viscosity and ionicity data are hard to find. The ionicity of ionic liquids, which corresponds to the fraction of IL molecules which is dissociated, was proven to greatly influence thermophysical properties such as density, viscosity and surface tension, so it is essential to characterise electrolyte-containing systems [18]. For example, Peng et al. [19] reported that IL-ionicity was key to enhance the intestinal absorption of macromolecular drugs such as insulin and immunoglobulin, improving API delivery in the skin, buccal membrane, and small intestine [20].

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So far, some works have already delved into the determination of IL-ionicity as function of temperature and composition from Nuclear Magnetic Resonance (NMR) measurements [21–23], molar conductivity and viscosity measurements (Walden plot) [24–27], and also combining conductivity, density and viscosity measurements with the Stokes-Einstein equation [18,28].

Noda et al. [21] quantified pure IL-ionicity using the Nernst-Einstein equation, the molar conductivity from ionic conductivity measurements and the molar conductivity determined using self-diffusion coefficients from NMR measurements. Even though this technique is regarded as one of the most trustworthy for IL-ionicity determinations, the experimental measurements are time-consuming, the method can only be applied to NMR-active nuclei, and the laboratory apparel is expensive.

An easy methodology to estimate IL-ionicity as function of temperature can be achieved with a graphical method: the Walden plot, which represents the logarithm of the molar conductivity as function of the logarithm of viscosity [24]. In this approach, which is frequently followed in literature [24–27], IL-ionicity is calculated by measuring the distance between the experimental data and a reference line, as Eq. (1) shows, which is obtained from a 0.01 M aqueous solution of potassium chloride (KCl) and which represents full dissociation [24]. The main disadvantages of this methodology are being an approximate method, only having in regard two thermophysical properties (molar conductivity and viscosity) and not considering the different shapes and sizes of the IL-counterions.

$$\alpha = 10^{\ \Delta W} \tag{1}$$

where α is IL-ionicity and ΔW refers to the vertical distance of the experimental data points from the reference line.

Nordness et al. [18] suggested a method to quantitatively estimate the ionicity of ILs in binary mixtures as function of temperature and composition. For this purpose, experimental data of electrical conductivity, density and viscosity were used with the Stokes-Einstein equation. Nevertheless, although this method is simple and reliable, it requires the use of expensive equipment and the undertaking of long laboratory experiments.

Due to the broadness of the ionic liquids' chemical family and to their wide range of applications, the thermodynamic modelling of mixtures containing ionic liquids is important to direct experimental determinations towards the most likely successful systems for a specific application. This way, by building up computational algorithms on top of easily measurable thermophysical properties, it is possible to estimate properties and parameters which would have been more expensive to determine in the laboratory. For the case of IL-ionicity in binary mixtures, previous works of the research group [29,30] have shown that it can be estimated by modelling experimental solubility data, which is commonly reported in literature, with the PDH+UNIQUAC model, *i.e.*, the Pitzer Debye Hückel (PDH) equation [31] coupled with the UNIversal QUAsiChemical (UNIQUAC) model [32].

The Pitzer Debye Hückel (PDH) equation [31] is one of the most popular terms used to describe ion-ion and ion-solvent interactions (long-range forces) and assumes the solvent as a dielectric medium [31, 33]. This equation was based on the Debye-Hückel equation [34], which was proposed around 100 years ago, and is known for accurately predicting non-ideality in the low IL-concentration region [35]. Its modification allowed to expand the validity of application to higher ionic strengths and to calculate thermodynamic properties for strong electrolytes and respective mixtures with unparalleled accuracy across a wide range of temperature and pressure [36]. For this reason, the PDH equation was incorporated in well-known non-electrolyte thermodynamic models, such as UNIQUAC [32], Non-Random Two-Liquid (NRTL) [37] and Conductor-like Screening Model for Segment Activity Coefficient (COSMO-SAC) [38].

The UNIQUAC model [32] is an extension of the Guggenheim quasi-chemical theory derived from a statistical-mechanical basis [32]. UNIQUAC is a local composition and excess Gibbs energy model and accounts for short-range interactions, *i.e.*, the ones established between contacting neutral species, by considering two contributions to the excess Gibbs energy: a combinatorial term for asymmetries in size and shape and a residual term for energetic differences [39]. Therefore, in contrast to the Guggenheim's theory, the UNIQUAC model can be applied to mixtures whose molecules have high asymmetry [40], *i.e.*, different sizes and shapes, such as ionic liquids, since it considers the intermolecular forces which make the mixing of molecules not random. So, even though UNIQUAC was not originally developed for electrolyte-containing systems, it has been used to correlate multicomponent liquid-liquid equilibria (LLE) and vapour-liquid equilibria (VLE) data with great success [41–44]. Its main drawbacks are being considered semiempirical, the questionable validity of Wilson's local composition model [45] and the overestimation of the effect of shape by the Staverman-Guggenheim combinatorial contribution [46,47].

In this work, by applying the computational algorithm developed in a previous work [29], the ionicity of 12 ionic liquids containing the imidazolium cation in 17 binary mixtures composed of water, ethanol, 1-propanol or 1-butanol was predicted based on solubility (liquid-liquid equilibria, LLE) data available in literature by the Pitzer-Debye-Hückel (PDH) equation combined with the UNIversal QUAsi-Chemical (UNIQUAC) model (PDH+UNIQUAC).

2. Thermodynamic modelling

2.1. PDH+UNIQUAC

The combination of the Pitzer-Debye-Hückel (PDH) equation with the UNIversal QUAsi-Chemical (UNIQUAC) model implies that the molar excess Gibbs free energy is given by:

$$G^{E} = G^{E,UNIQUAC} + G^{E,PDH} \tag{2}$$

where G^{E} is the molar excess Gibbs free energy, and $G^{E,UNIQUAC}$ and $G^{E,PDH}$ are the contributions from UNIQUAC and from PDH, respectively.

Then, the activity coefficient of species i (γ_i) can be derived based on equation:

$$\ln \gamma_i = \ln \gamma_i^{UNIQUAC} + \ln \gamma_i^{PDH} \tag{3}$$

where $\gamma_i^{UNIQUAC}$ and γ_i^{PDH} are the activity coefficient contributions of UNIQUAC and PDH, respectively.

The long-range electrostatic contributions to the activity coefficient (γ_i^{PDH}) are calculated from the Pitzer-Debye-Hückel (PDH) equation, which states that [48]:

$$\frac{g^{E,PDH}}{RT} = \frac{4A_{DH,x}I_x}{\rho}\ln\left(\frac{1+\rho I_x^{1/2}}{1+\rho\ I_x^{0}\ )^{1/2}}\right) \tag{4}$$

where $A_{DH,x}$ is the Debye-Hückel parameter, ρ is the closest approach parameter, I_x refers to the ionic strength and I_x^0 to the ionic strength of the pure salt (which is 0.5 for singly-charged ions).

Therefore, the differentiation of the previous equation yields the mean activity coefficient of an ionic component for the infinitely dilute reference state (unsymmetric convention) [48]:

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

where z_i is the electric charge of species i.

However, to make possible the joint application of the PDH equation (in the unsymmetric convention) and UNIQUAC (in the symmetric convention), Eq. (5) can be converted into Eq. (6), which allows to determine the mean activity coefficient of an ionic component for the

pure fused salt reference state (symmetric convention) [29,31,49]:

$$\ln \gamma_i^{\mathrm{PDH}} = z_i^2 \cdot A_{\mathrm{DH},x} \left[\frac{2}{\rho} \ln \left(\frac{1+\rho\sqrt{I_x}}{1+\rho\sqrt{\frac{z_i^2}{2}}} \right) + \sqrt{I_x} \frac{1}{1+\rho\sqrt{I_x}} \frac{2\frac{I_x}{z_i^2}}{} \right] \quad (6)$$

where the ionic strength on a mole fraction basis (I_x) is defined as:

$$I_x = \frac{1}{2}\sum_{i=1} z_i^2 x_i \quad (7)$$

where x_i is the mole fraction of species *i*.

The Debye-Hückel parameter ($A_{\mathrm{DH},x}$) is calculated by:

$$A_{\mathrm{DH},x} = \frac{1}{3}\sqrt{2\pi \frac{N_A \rho_{\mathrm{ms},x}}{M_{\mathrm{ms}}}} \left(\frac{e^2}{4\pi\, \varepsilon_0\, \varepsilon_{\mathrm{ms}}\, k_B T} \right)^{1.5} \quad (8)$$

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

To allow for a better description of the electrolytes' behaviour, the molar density and the molecular mass of the mixed solvent ($\rho_{\mathrm{ms},x}$ and M_{ms}, respectively) were considered in the thermodynamic modelling. These properties were calculated by the weighted arithmetic means given by Eqs. (9) and (10), respectively [29].

$$\frac{1}{\rho_{\mathrm{ms},x}} = \sum_i \frac{x'_i}{\rho_{i,x}} \quad (9)$$

$$M_{\mathrm{ms}} = \sum_i x'_i M_i \quad (10)$$

where x'_i is the salt-free mole fraction, $\rho_{i,x}$ is the molar density and M_i is the molecular mass. All refer to the neutral species *i*.

In this work, solubility (liquid-liquid equilibria, LLE) data of binary mixtures containing 1 ionic liquid and 1 solvent (water, ethanol, 1-propanol or 1-butanol), at atmospheric pressure, were used to estimate IL-ionicity, so the only neutral species present in each system were the molecular ionic liquid and the solvent. Moreover, the dielectric constant of the mixed solvent ($\varepsilon_{\mathrm{ms}}$) can also be calculated using a similar mole fraction-based weighted arithmetic mean [33], but, in this work, Oster's mixing rule [50] was employed, which is given by Eq. (11) [51].

$$\varepsilon_{\mathrm{ms}} = \varepsilon_1 + \left(\frac{(\varepsilon_2 \quad 1)(2\varepsilon_2 \quad 1)}{2\varepsilon_2} \quad (\varepsilon_1 \quad 1) \right) \frac{x'_2}{\rho_{2,x}} \rho_{\mathrm{ms},x} \quad (11)$$

where ε_1 and ε_2 refer to the dielectric constants of the neutral species 1 and 2, x'_2 is the salt-free mole fraction of neutral species 2, ρ_{ms} is the density of the mixed solvent and $\rho_{2,x}$ is the molar density of neutral species 2. The UNIQUAC van der Waals molecular volumes (r) [52–60], molecular masses (M) and dielectric constants (ε) [61–65] can be found in Table S1, in the Supplementary Materials, for all species. On the other hand, the densities (ρ_i) [66–78] of all species can be observed in Table S2, in the Supplementary Materials.

The closest approach parameter (ρ), from the PDH equation, is a dimensionless parameter related to the distance between the centres of the counterions of the ionic liquid [79]. In this study, this parameter was calculated using an equation developed by Pitzer and Simonson [80] and following considerations of a previous work [29], as Eq. (12) shows. The most classical approach for this parameter is an adjustment between 8 and 15 [48] and considering it independent of composition, but doing so commonly overestimates the distance between unlike charges for IL-concentrated solutions, as a previous work has shown [29].

$$\rho = a \left(\frac{2\, e^2\, N_A\, \rho_{\mathrm{ms}}}{M_{\mathrm{ms}}\, \varepsilon_0\, k_B\, \varepsilon_{\mathrm{ms}}\, T} \right)^{0.5} \quad (12)$$

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

To calculate the hard-core collision diameter (a), the van der Waals volume (V_w) was used since it represents ions as hard spheres. Other alternatives could involve, for example, the Stokes radii, but this option considers the effect of solvation on the radii, which would probably overestimate the hard-core collision diameter in the low IL-concentration region. Therefore, the van der Waals radius (r_w) was calculated from the UNIQUAC van der Waals volume parameter (r) by Eqs. (13) and (14).

$$V_w = r \cdot 15\ 17 \cdot 10^6 \quad (13)$$

where V_w is the van der Waals volume and r is the UNIQUAC van der Waals volume parameter.

$$V_w = \frac{4}{3}\pi\, r_w^3 \quad (14)$$

where r_w is the van der Waals radius.

2.2. Algorithm

The thermodynamic modelling for the estimation of IL-ionicity was based on solubility (liquid-liquid equilibria, LLE) data of binary mixtures containing 1 ionic liquid and 1 solvent (water, ethanol, 1-propanol or 1-butanol), at atmospheric pressure, and was carried out using the algorithm summarised in Fig. 1, which was proposed in a previous work of the research group [29].

The developed algorithm started by using the mole fractions of ionic liquid taken from solubility data found in literature (x_{IL}^0) as upper boundaries to iterate different compositions of molecular ionic liquid (x_{IL}), using Eqs. (15-17), and yielding the to-be-tested IL-ionicities (α), ranging from 0 to 1.

$$x_{\mathrm{solv}} = \frac{x_{\mathrm{solv}}^0}{1+\alpha x_{\mathrm{IL}}^0} \quad (15)$$

where x_{solv}^0 and x_{IL}^0 are the mole fractions of the solvent and ionic liquid reported in the literature (when no dissociation of the ionic liquids is considered), respectively, α refers to IL-ionicity and x_{solv} to the solvent's mole fraction when the IL-dissociation is taken into consideration.

$$x_{\mathrm{IL}} = \frac{x_{\mathrm{IL}}^0 (1 \quad \alpha)}{1+\alpha x_{\mathrm{IL}}^0} \quad (16)$$

where x_{IL} is the mole fraction of molecular (neutral) ionic liquid when the IL-dissociation is taken into account.

$$x_C = x_A = \frac{x_{\mathrm{IL}}^0 \alpha}{1+\alpha x_{\mathrm{IL}}^0} \quad (17)$$

Then, the calculated values of mole composition and IL-ionicity were used to predict the solubility data for the binary system under study, using the PDH+UNIQUAC model, by optimising the UNIQUAC binary interaction parameters (a_{ij}^* and b_{ij}^*), minimising Eq. (18) and using a quasi-Newtonian convergence method (iteration cycle I). To confirm the validity of the obtained binary interaction parameters, the fulfilment of the isoactivity criterium between the liquid phases was checked for all results.

$$\mathrm{O\,F} = \sqrt{100 \left(\frac{\sum_{i=1}^{N_{\mathrm{species}}} {}^{1}\sum_{j=1}^{N} \left(x_{i,j}^{\mathrm{P,exp}} \quad x_{i,j}^{\mathrm{P,pred}} \right)^2 + \left(x_{i,j}^{\mathrm{R,exp}} \quad x_{i,j}^{\mathrm{R,pred}} \right)^2}{2N \cdot N_{\mathrm{species}}} \right)} \quad (18)$$

where N refers to the number of equilibrium points, N_{species} to the

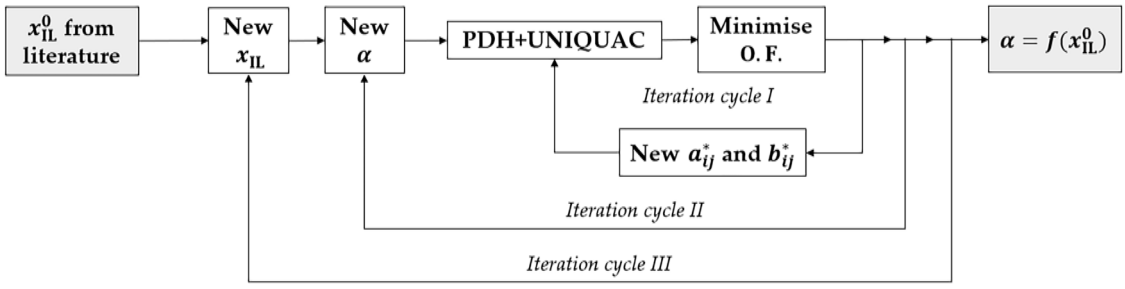

Fig. 1. Applied algorithm in the estimation of the ionicity of ionic liquids, reported in a previous work [29].

number of species present in solution, $x_{i,j}^{P}$ and $x_{i,j}^{R}$ are the mole fractions 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 mole compositions.

It must be noted that, in this work, a linear dependence of the Δu_{ij} parameter with temperature was considered, following other works [29,81]:

$$\Delta u_{ij} = a_{ij}^{*} + b_{ij}^{*} \cdot T \tag{19}$$

where a_{ij}^{*} and b_{ij}^{*} are adjustable parameters fitted in the intervals [50,50] and [5,5], respectively.

Afterwards, new IL-ionicities (iteration cycle II) and new starting mole compositions (iteration cycle III) were tested, repeating the innermost iteration cycles and searching for a minimum of the objective function (O.F.) which respected the isoactivity criterion. When both conditions were achieved, the most appropriate distribution of charged and neutral species was found, allowing to determine IL-ionicity with composition.

3. Collected experimental data

In this work, 12 ionic liquids of three different chemical families were studied, including hexafluorophosphates ([PF_6]), bis(trifluoromethylsulfonyl)imides ([NTf_2]) and tetrafluoroborates ([BF_4]). These particular ILs were chosen to assess IL-ionicity in fluorinated and imidazolium cation-based ionic liquids using LLE data available in literature. Table 1 shows the ionic liquids and binary systems studied in this work and the ones already studied in a previous work [29], which will be used for comparison purposes.

To predict the ionicity of ionic liquids in binary mixtures, the proposed methodology requires solubility (or liquid-liquid equilibria, LLE) data, which were collected from literature. Table 2 shows the number of available solubility data points, the respective ranges of IL mole fraction, as well as the temperature range of both phases. The used solubility data [73,82–89] can be found in Table S3, in the Supplementary Materials.

4. Results and discussion

Succeeding a previous work [29], in which the prediction of IL-ionicity using the PDH+UNIQUAC model was validated, IL-ionicity was determined as function of mole composition for 17 binary mixtures, comprising 12 different ionic liquids and 4 different solvents (water, ethanol, 1-propanol and 1-butanol). Moreover, the influences of the solvent, IL-cation and IL-anion on IL-ionicity were investigated. The optimised UNIQUAC binary interaction parameters (a_{ij}^{*} and b_{ij}^{*}), the predicted IL-ionicities (α), and the calculated closest approach parameters (ρ) can be found, respectively, in Tables S4, S5 and S6, in the Supplementary Materials, for all systems.

4.1. Influence of the solvent on IL-ionicity

Following the algorithm explained earlier, the ionicity as function of composition was determined for all the mentioned ionic liquids, based on the solubility data available in literature, and the influence of the solvent on IL-ionicity was analysed. Figs. 2 and 3 show that the ionicity of ILs is generally higher for lower concentrations of ionic liquid (IL-poor phase) and for more polar solvents, for the systems containing [C_4Mim][PF_6] and [C_6Mim][BF_4]. For this reason, water promotes a higher IL-ionicity than the studied alcohols, and a larger alkyl's chain length of the alcohols leads to a smaller IL-ionicity due to the lessening of the dielectric constant. Therefore, IL's dissociation mostly depends on the solvent's ability to separate the IL-ions, which can be evaluated through the dielectric constant of the mixed solvent, determined in this work by the Oster's mixing rule [50]. Solvents with high dielectric constants (and, consequently, high polarity) easily establish hydrogen bonds

Table 1
Binary systems studied in this work (●) and in a previous project following the same methodology (○) [29], together with the abbreviation and International Union of Pure and Applied Chemistry (IUPAC) name of the ionic liquids.

Ionic liquids		Solvents			
IUPAC name	Abbreviation	Water	Ethanol	Propanol	Butanol
1-hexyl-3-methylimidazolium tetrafluoroborate	[C_6Mim][BF_4]	●			●
1-octyl-3-methylimidazolium tetrafluoroborate	[C_8Mim][BF_4]	●			●
1-ethyl-3-methylimidazolium hexafluorophosphate	[C_2Mim][PF_6]		●	●	○
1-propyl-3-methylimidazolium hexafluorophosphate	[C_3Mim][PF_6]	●			
1-butyl-3-methylimidazolium hexafluorophosphate	[C_4Mim][PF_6]	○	●	●	○
1-pentyl-3-methylimidazolium hexafluorophosphate	[C_5Mim][PF_6]				●
1-hexyl-3-methylimidazolium hexafluorophosphate	[C_6Mim][PF_6]	○	●	●	○
1-octyl-3-methylimidazolium hexafluorophosphate	[C_8Mim][PF_6]	○		●	○
1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[C_2Mim][NTf_2]	○		●	○
1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[C_3Mim][NTf_2]	●			
1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[C_4Mim][NTf_2]	○			○
1-pentyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[C_5Mim][NTf_2]	●			
1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[C_6Mim][NTf_2]	○			○
1-heptyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[C_7Mim][NTf_2]	●			
1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[C_8Mim][NTf_2]	○			

Table 2
Solubility (or liquid-liquid equilibria, LLE) data for the 17 studied binary systems.

Binary system	No. of points	x^0_{IL} range of IL-poor phase	x^0_{IL} range of IL-rich phase	T range of IL-poor phase /K	T range of IL-rich phase /K	Ref.
[C_6Mim][BF_4] + water	26	(6 2 23 0)·10 ^{3}	0 15 0 38	278 15 333 15	278 15 333 15	[87]
[C_6Mim][BF_4] + 1-butanol	32	(8 5 58 2)·10 ^{3}	0 13 0 45	288 45 301 41	282 77 301 70	[82]
[C_8Mim][BF_4] + water	30	(1 6 30 5)·10 ^{3}	0 13 0 37	278 15 340 15	278 15 340 15	[87]
[C_8Mim][BF_4] + 1-butanol	26	(1 58 4 53)·10 ^{2}	0 07 0 16	276 98 279 49	276 97 279 47	[82]
[C_2Mim][PF_6] + ethanol	32	(4 4 44 1)·10 ^{3}	0 22 0 49	321 27 350 23	321 80 351 43	[83]
[C_2Mim][PF_6] + 1-propanol	16	(4 8 11 6)·10 ^{3}	0 42 0 71	342 65 364 65	325 45 368 03	[83]
[C_3Mim][PF_6] + water	14	(1 2 3 3)·10 ^{3}	0 60 0 76	288 15 318 15	288 15 318 15	[73]
[C_4Mim][PF_6] + ethanol	22	(0 3 4 7)·10 ^{2}	0 18 0 59	278 15 325 15	278 15 325 15	[84]
[C_4Mim][PF_6] + 1-propanol	28	(0 4 10 1)·10 ^{3}	0 47 0 79	278 15 343 15	278 15 343 15	[85]
[C_5Mim][PF_6] + 1-butanol	25	0 209 0 859	0 88 1 00	280 09 366 15	329 90 366 23	[89]
[C_6Mim][PF_6] + ethanol	8	(1 0 3 6)·10 ^{2}	0 18 0 37	278 15 293 15	278 15 293 15	[84]
[C_6Mim][PF_6] + 1-propanol	22	(1 8 78 5)·10 ^{3}	0 38 0 70	278 15 328 15	278 15 328 15	[85]
[C_8Mim][PF_6] + 1-propanol	16	(2 4 26 9)·10 ^{3}	0 16 0 46	278 15 307 15	278 15 307 15	[85]
[C_2Mim][NTf_2] + 1-propanol	60	(2 3 12 1)·10 ^{2}	0 14 0 38	283 65 295 20	283 65 295 20	[88]
[C_3Mim][NTf_2] + water	14	(5 15 7 01)·10 ^{4}	0 67 0 75	288 15 318 15	288 15 318 15	[86]
[C_5Mim][NTf_2] + water	14	(1 84 2 53)·10 ^{4}	0 76 0 82	288 15 318 15	288 15 318 15	[86]
[C_7Mim][NTf_2] + water	14	(4 85 7 93)·10 ^{4}	0 76 0 82	288 15 318 15	288 15 318 15	[86]

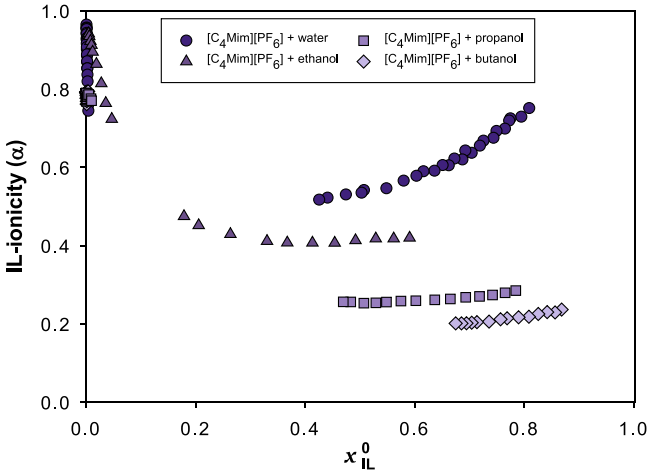

Fig. 2. Predicted ionicity (α) as a function of the IL mole fraction ($^{0}_{L}$), at atmospheric pressure, for [C_4Mim][PF_6] with: water [29], ethanol, 1-propanol or 1-butanol [29].

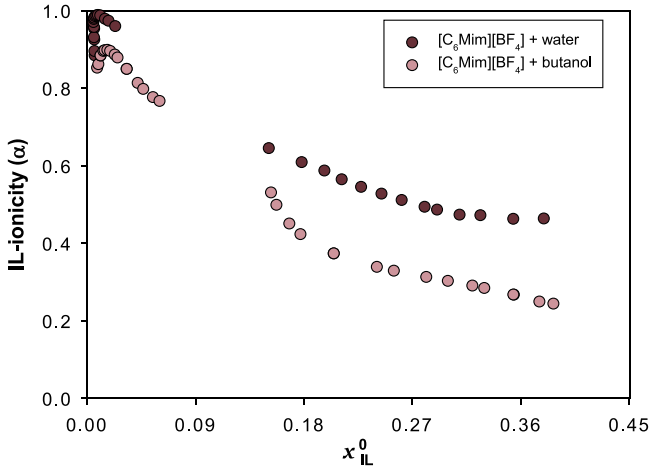

Fig. 3. Predicted ionicity (α) as a function of the IL mole fraction ($^{0}_{L}$), at atmospheric pressure, for [C_6Mim][BF_4] with water or 1-butanol.

(association) between the solvent and the IL-ions, weakening the chemical bonds between the IL-counterions. These same trends were found for [C_2Mim][NTf_2] and [C_2Mim][PF_6], which can be observed in Fig. S1, in the Supplementary Materials, and the overall conclusions agree with previous studies available in literature [18,27,90,91].

As Fig. 2 shows for the [C_4Mim][PF_6] + water binary system, IL-ionicity significantly increases with growing IL-mole fraction (IL-rich phase), and this phenomenon can be explained by the solvation of the free ions (cation (C^+) and anion (A^-)) by the ion-ion pair (CA), which leads to the formation of triplets / triple ions (*e.g.*, [ACA]$^-$ and [CAC]$^+$). The formation of these structures was also reported by some authors for high IL-content [18,28,92]. Moreover, other works reported a larger IL-ionicity for protic solvents since they contain at least one hydrogen which can connect to an electronegative atom (for example, to the IL-anion). Therefore, these solvents have a greater capacity of establishing hydrogen bonds and, consequently, to dissociate the neutral IL, increasing the IL-ionicity. However, no aprotic solvents were studied in this work, so this conclusion could not be drawn.

4.2. *Influence of the IL-cation on IL-ionicity*

Furthermore, the influence of the IL-cation on the ionicity of ionic liquids was also studied. Figs. 4–6 show that the higher the IL-cation's alkyl chain length, the smaller the IL-ionicity (α) in the tested range of composition. This can be due to the stronger electrostatic attraction between the IL-anion and the IL-cation (van der Waals forces) for longer alkyl chains, which hinders IL-dissociation. In Fig. S2, in the Supplementary Materials, the same behaviour was observed for [C_nMim][PF_6] + 1-butanol, with n = 2, 4, 5, 6 and 8.

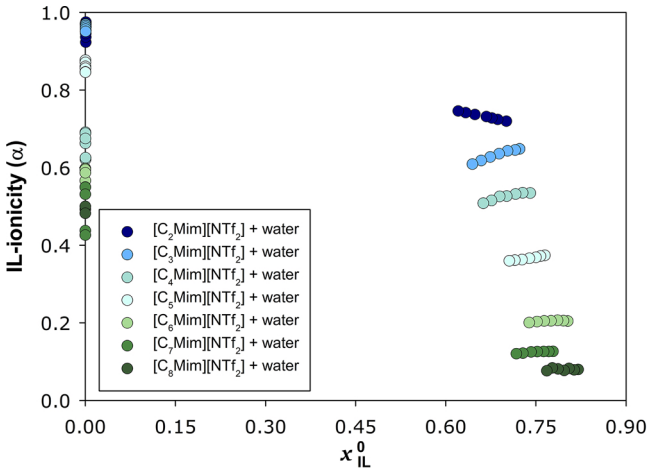

Fig. 4. Predicted IL-ionicity (α) as function of the IL mole fraction (x^0_{IL}), at atmospheric pressure, for the [C_nMim][NTf_2] + water systems, where n = 2, 4, 6, 8 [29] and n = 3, 5, 7 (this work).

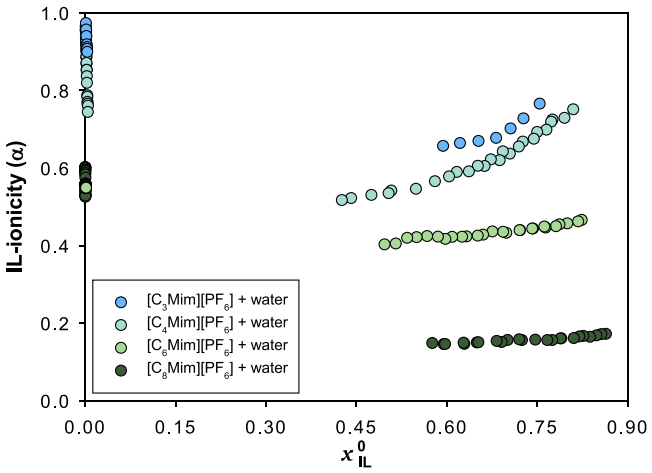

Fig. 5. Predicted IL-ionicity (α) as function of the IL mole fraction (x^0_{IL}), at atmospheric pressure, for the [C_nMim][NTf_2] + water systems, where n = 3 (this work) and n = 4, 6, 8 [29].

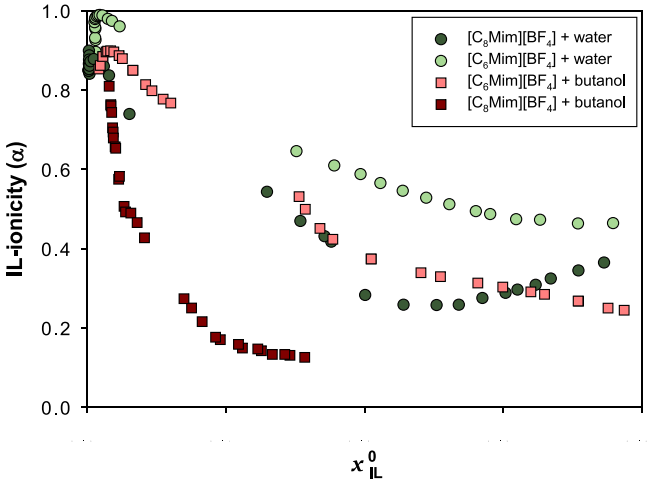

Fig. 6. Comparison of the predicted ionicity (α) as function of IL mole fraction (x^0_L) for [C_nMim][BF_4] + water or 1-butanol, with n = 6 and 8, at atmospheric pressure.

Moreover, the dielectric constants for the pure ILs are lower for longer alkyl chains, which imply less polar ILs, making the solvation process harder and lowering IL-ionicity. Analogously, a higher dielectric constant of the mixed solvent implies a higher IL-ionicity. These conclusions were also achieved by other authors using different experimental techniques, such as Pulsed-Field Gradient – Nuclear Magnetic Resonance (PFG-NMR) [93], solvatochromic measurements on ET^{30} scale [27], and density, viscosity and conductivity measurements [18, 28].

4.3. *Influence of the IL-anion on IL-ionicity*

Furthermore, the IL-anion's influence on the predicted IL-ionicity was examined and it was noticed that it was generally lower for ionic liquids containing the [NTf_2] anion, as Fig. 7 and 8 illustrate for the particular cases of $[C_8Mim]^+$-based ionic liquids with water and $[C_6Mim]^+$-based ionic liquids with 1-butanol, respectively. However, it is important to highlight that the prediction of IL-ionicity was based on solubility (liquid-liquid equilibria, LLE) data, *i.e.,* the developed algorithm relied on the existence of two liquid phases in equilibrium, so it was not always possible to compare the three IL-anions simultaneously due to differences in the IL mole fraction dominia, which limits the validity of the interpretations. In the future, this drawback may be solved by the addition of vapour-liquid equilibria (VLE) and solid-liquid equilibria (SLE) data and by the eventual inclusion of equations of state.

Moreover, given the significant hydrolysis of ionic liquids containing the tetrafluoroborate (BF_4) and hexafluorophosphate (PF_6) ions [94, 95], it must be noted that their LLE data is subject to higher uncertainties compared to, for example, ILs based on the bis(trifluoromethylsulfonyl) imide (NTf_2) ion. Hence, the observed LLE may be the result of a combination of IL-dissociation and hydrolysis, which is traduced by an accumulated IL-ionicity.

Once again, the polarity of the IL-anion (observable by the dielectric constants presented in Table S1, in the Supplementary Materials) can be used to explain the ionicity of the studied ionic liquids since a more polar IL-anion is more efficiently solvated by a polar solvent (1-butanol), enlarging the IL-ionicity. These conclusions agree with other authors, who determined the dissociation extent based on Nuclear Magnetic Resonance (NMR) measurements [96].

4.4. *Closest approach parameter*

The closest approach parameter (ρ) is a dimensionless parameter related to the distance between the centres of the IL-cation and IL-anion

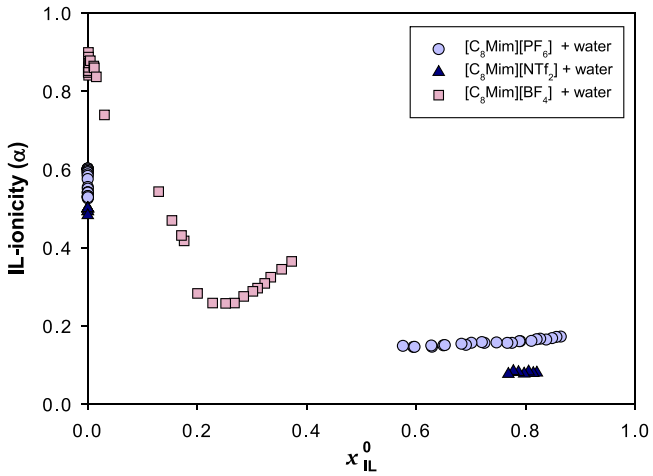

Fig. 7. Predicted IL-ionicity (α) as a function of the IL mole fraction (x^0_{IL}), at atmospheric pressure, for [C_6Mim][BF_4] (this work), [C_6Mim][PF_6] [29] and [C_6Mim][NTf_2] [29] with water.

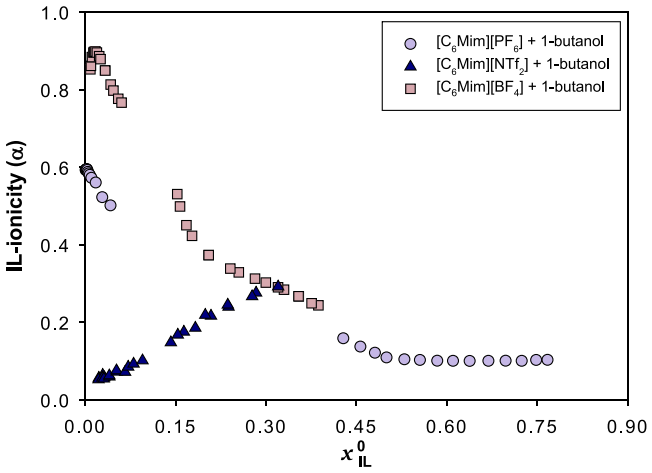

Fig. 8. Predicted IL-ionicity (α) as a function of the IL mole fraction (x^0_{IL}), at atmospheric pressure, for [C_6Mim][BF_4] (this work), [C_6Mim][PF_6] [29] and [C_6Mim][NTf_2] [29] with 1-butanol.

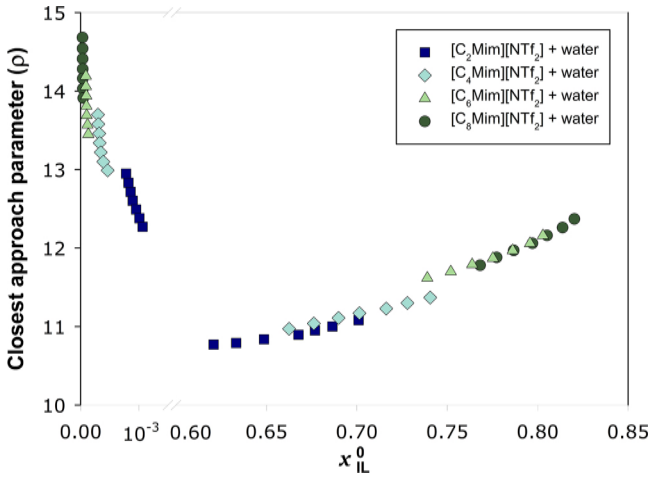

Fig. 9. Calculated closest approach parameter (ρ) as function of the mole fraction of IL (x^0_{IL}) at atmospheric pressure for [C_nMim][NTf_2] + water, with n = 3, 5, 7.

which has been mostly considered an adjustable parameter in the PDH equation, ranging from 8 to 15 [43], as suggested by Pitzer [31], or defined as 14.9 [97,98]. However, a previous work of the research group [29] demonstrated that a more accurate description of electrolyte systems could be achieved if this parameter was calculated using the approach developed by Pitzer and Simonson [80], *i.e.*, if this parameter was considered to be composition-dependant. In Fig. 9, the calculated closest approach parameter is shown for the [C_nMim][NTf_2] + water systems, and it can be observed that the closest approach parameter is generally higher for the IL-poor phase. This fact can be justified by the presence of more molecules of solvent between the IL-counterions, increasing the distance between them and enlarging the closest approach parameter. Moreover, the standard range recommended by Pitzer [31] for the closest approach parameter, *i.e.*, between 8 and 15, is generally verified in this work, as can be checked for all binary systems in Table S6, in the Supplementary Materials. However, as noted in a previous work of the research group [29], if the closest approach parameter (ρ) was used as an adjustable parameter, as is commonly done in literature, the distance between species of opposite charges for high IL-content would probably be overestimated, modifying the contribution of the Pitzer-Debye-Hückel (PDH) equation for the activity coefficients and forcing the UNIQUAC to accommodate the difference, which would cause the model to yield less specific binary interaction parameters for these systems, compromising their description.

Moreover, in Fig. S3, in the Supplementary Materials, the influence of the IL-cation's alkyl chain length on the closest approach parameter was also studied. In Figs. 9 and S3, in the Supplementary Materials, it was verified that, as expected, larger alkyl chains led to higher values of the closest approach parameter, preserving its physical meaning, which is related to the distance between the IL-counterions. Furthermore, in Fig. S4, in the Supplementary Materials, the influence of the solvent on the closest approach parameter is explored for [C_4Mim][PF_6], and it was concluded that solvents with higher dielectric constant, and consequent larger solvation power, promoted larger closest approach parameters.

5. Conclusions

The ionicity of 12 ionic liquids with imidazolium cations in 17 binary systems containing water or ethanol or 1-propanol or 1-butanol was predicted as function of the system's mole composition with the PDH+UNIQUAC model and based on solubility data (liquid-liquid equilibria, LLE) from literature.

The predicted IL-ionicity was higher for more diluted solutions in ionic liquid, which is probably due to a more significant solvation of the IL-ions. Moreover, in some binary systems, it was observed that IL-ionicity significantly increased with the IL-content for the IL-rich phase, which was explained by the formation of triplets. Furthermore, the influence of the solvent, IL-cation and IL-anion on IL-ionicity was studied and it was found that this property presented higher values for water than for the alcohols, which can be justified by the higher dielectric constant of the former. Hence, the increased polarity of solvent or IL-anions (and of the mixed solvent in general) eases ion solvation and contributes to a higher extent of dissociation of the ionic liquids. Moreover, it was observed that, the longer the length of the IL-cation's alkyl chain, the stronger the van der Waals forces between IL-counterions, which led to smaller IL-ionicities. Finally, the validity of the mentioned conclusions for other families of ionic liquids (*e.g.*, ILs without imidazolium cations or fluorine atoms) still requires evaluation.

CRediT authorship contribution statement

Pedro Velho: Investigation, Writing – original draft, Writing – review & editing, Formal analysis, Validation. **Catarina Lopes:** Investigation, Writing – original draft, 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.

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.fluid.2023.113766.

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