

An overview of the mutual solubilities of water–imidazolium-based ionic liquids systems

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Abstract

Ionic liquids (ILs) are a novel class of chemical compounds with interesting properties that are driving a lot of research in several fields. For ionic liquids to be effectively used as solvents in liquid–liquid extractions, the knowledge of the mutual solubilities between ILs and the second liquid phase is fundamental. Furthermore, while ILs cannot volatilise and lead to air pollution, even the most hydrophobic ones present some miscibility with water posturing secondary aquatic environmental risks. Despite the importance of the ILs and water systems, there are few extensive reports on their phase equilibria. The aim of this work is to discuss and understand the mutual solubilities of water and imidazolium-based ILs. The results indicate that these mutual solubilities are primarily defined by the anion followed by the cation alkyl side chain length. It was also found that the solubility of the studied ILs in water is more dependent on the ILs structural modifications than the solubility of water in those ILs. The substitution of the most acidic hydrogen in the imidazolium cation by a methyl group leads to different behaviours in both rich-phases, where the solubility of water in ILs showed to be more hydrogen bonding dependent. From the solubility results it can be concluded that the hydrophobicity of the anions increases in the order $[\text{BF}_4]^- < [\text{CH}_3(\text{C}_2\text{H}_4\text{O})_2\text{SO}_4]^- < [\text{C}(\text{CN})_3]^- < [\text{PF}_6]^- < [\text{N}(\text{SO}_2\text{CF}_3)_2]^-$ while the hydrophobicity of the cations increases, as expected, with the alkyl chain length increase.

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1. Introduction

Ionic liquids (ILs) are room temperature molten salts. They consist of large organic cations and typically smaller inorganic or organic anions. This factor tends to reduce the lattice energy of the crystalline structure of the salt and hence to lower their melting point so that they generally remain liquid at or near room temperature. Unlike molecular liquids, their ionic nature results in a unique combination of properties especially large liquidus range, negligible vapour pressures at room temperature and high solvating capacity for organic, inorganic and organometallic compounds, establishing their high potential to be exploited as “green solvents” [1,2]. Furthermore, ILs present the prospective of “designer solvents” since their physicochemical properties can be finely tuned by a criterious choice of the cation and/or the anion. As a result, these solvents can be designed for a particular application or to present a particular set of intrinsic properties. This attribute can be of substantial benefit when carrying out

Abbreviations: $[\text{C}_2\text{mim}][\text{N}(\text{SO}_2\text{CF}_3)_2]$, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; $[\text{C}_3\text{mim}][\text{N}(\text{SO}_2\text{CF}_3)_2]$, 1-methyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide; $[\text{C}_4\text{mim}][\text{N}(\text{SO}_2\text{CF}_3)_2]$, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; $[\text{C}_5\text{mim}][\text{N}(\text{SO}_2\text{CF}_3)_2]$, 1-methyl-3-pentylimidazolium bis(trifluoromethylsulfonyl)imide; $[\text{C}_6\text{mim}][\text{N}(\text{SO}_2\text{CF}_3)_2]$, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; $[\text{C}_7\text{mim}][\text{N}(\text{SO}_2\text{CF}_3)_2]$, 1-heptyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; $[\text{C}_8\text{mim}][\text{N}(\text{SO}_2\text{CF}_3)_2]$, 1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide; $[\text{C}_4\text{mim}][\text{N}(\text{SO}_2\text{CF}_3)_2]$, 1-butyl-3-methylimidazolium tetrafluoroborate; $[\text{C}_8\text{mim}][\text{BF}_4]$, 1-methyl-3-octylimidazolium tetrafluoroborate; $[\text{C}_4\text{mim}][\text{PF}_6]$, 1-butyl-3-methylimidazolium hexafluorophosphate; $[\text{C}_6\text{mim}][\text{PF}_6]$, 1-hexyl-3-methylimidazolium hexafluorophosphate; $[\text{C}_8\text{mim}][\text{PF}_6]$, 1-methyl-3-octylimidazolium hexafluorophosphate; $[\text{C}_4\text{C}_1\text{mim}][\text{PF}_6]$, 1-butyl-2,3-dimethylimidazolium hexafluorophosphate; $[\text{C}_4\text{mim}][\text{C}(\text{CN})_3]$, 1-butyl-3-methylimidazolium tricyanomethane; $[\text{C}_4\text{mim}][\text{CH}_3(\text{C}_2\text{H}_4\text{O})_2\text{SO}_4]$, 1-butyl-3-methylimidazolium 2-(2-methoxyethoxy)ethylsulfate

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liquid–liquid extractions or product separations, as the relative solubilities of the IL and the extraction phase can be adjusted to a specific goal.

In order to address ILs as designer solvents, the understanding of their structure in the presence of others solute/solvent fluids is a key feature to predict the reactivity and selectivity of systems involving these compounds. The knowledge of the ILs coordination and solvation properties, which are dependent on both the cation and the anion, is very important for the selection of a specific ionic liquid. The strong anion–cation electrostatic interaction is believed to be the major source of interaction in an IL, although the contribution that arises from polarization also needs to be taken into account. When working with imidazolium-based ILs, the hydrogen bonding between the ions also presents considerable influence in their properties, namely liquid–liquid solubilities.

In the case of imidazolium-based ILs and water mutual solubilities, the nature of the anions largely determines the macroscopic behaviour of these mixtures. For instance, $[\text{C}_4\text{mim}]^+$ -based ILs in combination with hydrophilic anions like $[\text{Cl}]^-$, $[\text{Br}]^-$, $[\text{CF}_3\text{SO}_3]^-$ or $[\text{BF}_4]^-$ are miscible with water, but those combined with $[\text{C}(\text{CN})_3]^-$, $[\text{CH}_3(\text{C}_2\text{H}_4\text{O})_2\text{SO}_4]^-$, $[\text{PF}_6]^-$ or $[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$ present phase split, at room temperature. Note, however, that if the alkyl side chain of the cation becomes sufficiently long, the IL–water system can present phase split, as is the case of $[\text{C}_8\text{mim}][\text{BF}_4]$. This intricate pattern of interactions, together with negligible vapour pressures and densities generally higher than water [3,4], can be largely exploited for liquid–liquid separation purposes using ILs in spite of traditional volatile organic liquids.

Although imidazolium-based ILs are commonly used, their microscopic nature is far from being well understood. They can act both as hydrogen bond acceptors (anion) and donors (cation) and would be expected to interact with solvents with both accepting and donating sites, such as water. Water is well known to form hydrogen-bonded networks with both high enthalpies and constants of association, being stabilized with hydrogen bond donor sites. Nevertheless, the existence of the liquid–liquid phase equilibria of mixtures involving “hydrophobic” ILs is an indication that the solubility of imidazolium-based ILs depends on several factors such as the anion and cation structure and on the cation alkyl side chain length. For specific phase split systems, the interactions ion–ion and water–water are stronger than water–ion interactions observed in these mixtures.

It has recently been reported in molecular simulation studies [5–7] and experimental studies [8] that imidazolium-based ionic liquids exhibit medium range ordering, meaning that there is microphase segregation between polar and non-polar domains. Therefore, the solute–solvent interactions can be described in terms of the solute affinity to the different domains, according to its polarity. For example, in the case of water solubility in $[\text{C}_4\text{mim}][\text{PF}_6]$, the solute is concentrated in the charged domains and the interactions solute–ion are dominated by hydrogen bonding.

To our knowledge, few contributions dealing with liquid–liquid phase equilibrium of ILs and water have been reported [9–26] and systematic studies of the cation and the anion influ-

ence in the equilibria as well as the temperature dependence are, at this moment, very scarce and in need. This work is an overview of the mutual solubilities of water and imidazolium-based family cation ILs, where a systematic study of the anions tetrafluoroborate, 2-(2-methoxyethoxy)-ethylsulfate, tricyanomethane, hexafluorophosphate and bis(trifluoromethylsulfonyl)imide are available. The main goal of this contribution is to determine/understand the impact of the anion identity, the IL cation alkyl side chain length and of the group substitutions number in the imidazolium ring in the mutual solubilities with water.

Besides the design of ILs solvents for extraction and other industrial applications, the aqueous solubility of ionic liquids is also relevant regarding their environmental impact. Although it is well known that ILs reduce the air pollution risk due to their negligible vapour pressures, their release to aquatic environments could cause water contamination because of their potential toxicity and limited biodegradability. The water–IL mutual solubility measurements can be a method to predict the ILs toxicity at the cellular level, which seems to be mainly controlled by their hydrophobic character [27].

2. Ionic liquids and water mutual solubilities

The mutual solubilities of water and imidazolium-based family cation ionic liquids analysed in this work were taken from literature [16,20,25,26] and include 1-butyl-3-methylimidazolium tetrafluoroborate, $[\text{C}_4\text{mim}][\text{BF}_4]$, 1-butyl-3-methylimidazolium tricyanomethane, $[\text{C}_4\text{mim}][\text{C}(\text{CN})_3]$, 1-butyl-3-methylimidazolium 2-(2-methoxyethoxy)-ethylsulfate, $[\text{C}_4\text{mim}][\text{CH}_3(\text{C}_2\text{H}_4\text{O})_2\text{SO}_4]$, 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, $[\text{C}_n\text{mim}][\text{N}(\text{SO}_2\text{CF}_3)_2]$ with $n=2-8$, 1-alkyl-3-methylimidazolium hexafluorophosphate, $[\text{C}_n\text{mim}][\text{PF}_6]$ with $n=4, 6$ and 8 , and 1-butyl-2,3-dimethylimidazolium hexafluorophosphate, $[\text{C}_4\text{C}_1\text{mim}][\text{PF}_6]$, with a third substitution at the C2 position in the imidazolium ring.

Water visual solubility tests for $[\text{C}_n\text{mim}][\text{BF}_4]$ -based ILs performed at 298 K showed that they are completely miscible for alkyl groups smaller than pentyl and partially miscible for longer alkyl chain lengths [28]. Liquid–liquid complete phase equilibria is also available in the literature for the water– $[\text{C}_4\text{mim}][\text{BF}_4]$ system [16]. However, $[\text{BF}_4]^-$ - and $[\text{PF}_6]^-$ -based ILs are known to be moisture sensitive and to undergo hydrolysis in the presence of water, producing hydrogen fluoride and other hydrolysis products [29,30]. Detailed mass spectrometry studies performed in both equilibrium phases of water and $[\text{C}_8\text{mim}][\text{BF}_4]$ showed the presence of hydrolysis products in the order of 15% in mass in the water rich phase for samples kept at equilibrium for 24 h at 318 K [31]. For the $[\text{C}_n\text{mim}][\text{PF}_6]$ and $[\text{C}_4\text{C}_1\text{mim}][\text{PF}_6]$ ILs studied here, the mass spectrometry analysis showed just a small hydrolysis extent with a maximum of 0.35% of hydrolysis products in the water-rich phase for 2 years old samples which have been submitted to temperatures up to 318 K [26,31].

The typical liquid–liquid behaviour of increasing miscibility between both phases with the temperature increase was found for all the ILs analysed in this work. This information can

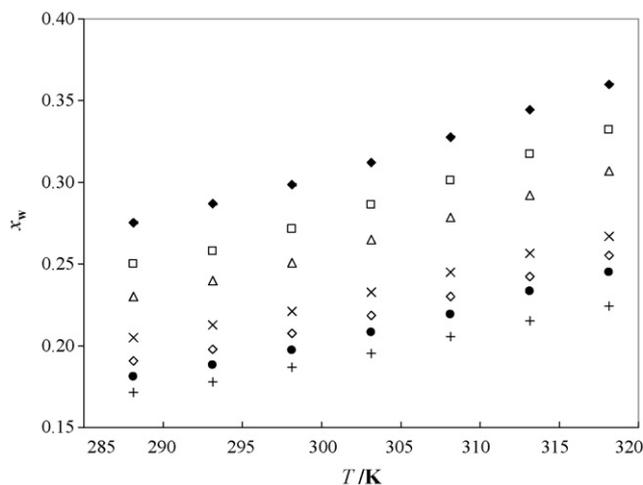


Fig. 1. Mole fraction solubility of water (x_w) as a function of temperature in the ILs: (◆) [C₂mim][N(SO₂CF₃)₂]; (□) [C₃mim][N(SO₂CF₃)₂]; (Δ) [C₄mim][N(SO₂CF₃)₂]; (×) [C₅mim][N(SO₂CF₃)₂]; (◇) [C₆mim][N(SO₂CF₃)₂]; (●) [C₇mim][N(SO₂CF₃)₂]; (+) [C₈mim][N(SO₂CF₃)₂].

be of useful significance because it points out that the cross-contamination of water–ILs systems will be larger at higher temperatures.

2.1. Solubility of water in ILs

The solubility of water in all the ILs analysed is well above of what can be considered infinite dilution, and besides the fact that they are considered hydrophobic ILs because they tend to form a second liquid phase with water, they are highly hygroscopic. The mole fractions solubilities of water in the ILs studied range from 0.19 to the complete miscibility at room temperature and depend on both the cation and the anion identity, being this last one the most important.

2.1.1. Cation influence

The influence of the cation alkyl chain length in the mutual solubilities of imidazolium-based ionic liquids is depicted in Fig. 1 for the [N(SO₂CF₃)₂][−] and in Fig. 2 for the [PF₆][−]-based imidazolium ILs. Both sets of data show that there is a hydrophobic tendency increase with the cation alkyl chain length, meaning that the ILs polarities decrease with the alkyl chain length increase of the cation. This is consistent with pure ILs polarity determined by spectroscopic studies, where it was verified that the polarities of the ILs are dependent on the cation, regardless of the anion identity [24,32].

It is interesting to note that this trend is the opposite of that observed for ILs–alcohols binary systems, where the ILs–alcohols mutual solubilities increase with the cation alkyl chain length. This behaviour is due to an increase in extension of the van der Waals interactions between the alkyl chains of both alcohols and ILs [33].

In Fig. 2, the results for [C₄C₁mim][PF₆], where the most acid hydrogen at the C2 position in the imidazolium cation ring is replaced by a methyl group, are also shown. This replacement greatly diminishes the ability of the cation to hydrogen

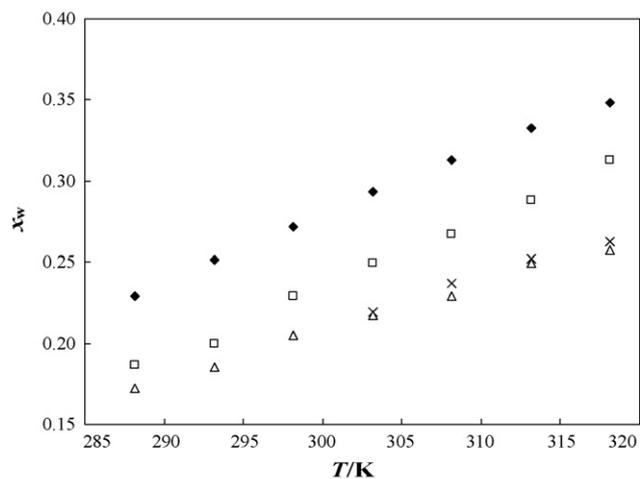


Fig. 2. Mole fraction solubility of water (x_w) as a function of temperature in the ILs: (◆) [C₄mim][PF₆]; (□) [C₆mim][PF₆]; (Δ) [C₈mim][PF₆]; (×) [C₄C₁mim][PF₆].

bond with water, resulting in a solubility value that is similar to the one found for [C₈mim][PF₆]. Clearly, hydrogen bonding of water with the acidic hydrogen of the imidazolium cation has a large influence in the liquid–liquid phase behaviour between imidazolium-based ILs and water.

These results are in agreement with the recent studies [25,34] of the relative cation–anion interaction strength between the imidazolium cation and the [BF₄][−] and [PF₆][−] anions using electrospray ionization mass spectrometry (ESI-MS) and tandem spectrometry (ESI-MS–MS). The authors found that for both anions, independently of the anion identity, the relative order of the total interaction strength increases in the order: [C₄C₁mim]⁺ < [C₈mim]⁺ < [C₆mim]⁺ < [C₄mim]⁺. These results corroborate the experimental water solubilities data, since the higher the relative strength between the cation and anion, the higher the strength of hydrogen bonding between water and the cation [35]. This point outs that, for a fixed anion, the solubility of water in the imidazolium-based ILs studied is strongly defined by the hydrogen bonding capability between the cation and the water oxygen. These results also support the observations obtained for [C₄C₁mim][PF₆], which presents a solubility in water close to that of [C₈mim][PF₆], following the order of the relative cation–anion bonding strength.

2.1.2. Anion influence

The anion influence can be analysed in Fig. 3, where the solubility of water in [C₄mim][BF₄], [C₄mim][CH₃(C₂H₄O)₂SO₄], [C₄mim][C(CN)₃], [C₄mim][PF₆] and [C₄mim][N(SO₂CF₃)₂] is depicted. The solubility of water decreases, and thus the ILs hydrophobicity increases, according to the following order: [BF₄][−] < [CH₃(C₂H₄O)₂SO₄][−] < [C(CN)₃][−] < [PF₆][−] < [N(SO₂CF₃)₂][−]. Bini et al. [36] reported the relative interaction strength for several cations classes based ILs in combination with different anions studied by electrospray ionization mass spectrometry. The authors conclude that the relative total cation–anion interaction strength due to the anion increases in the order: [N(SO₂CF₃)₂][−] << [PF₆][−] < [BF₄][−]. In fact, as veri-

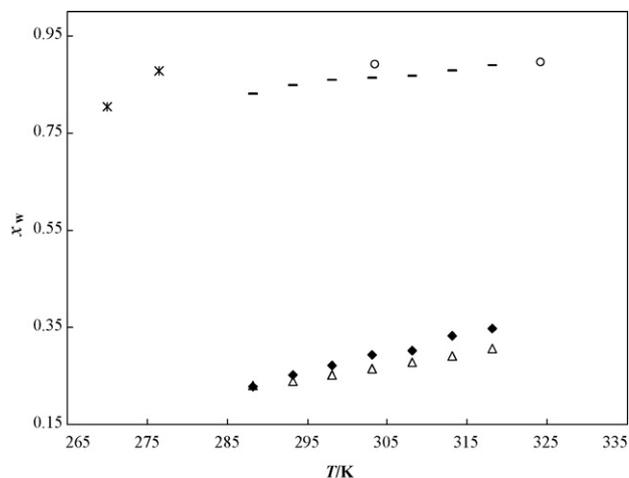


Fig. 3. Mole fraction solubility of water (x_w) as a function of temperature in the ILs: (✕) $[C_4mim][BF_4]$; (○) $[C_4mim][CH_3(C_2H_4O)_2SO_4]$; (-) $[C_4mim][C(CN)_3]$; (◆) $[C_4mim][PF_6]$; (△) $[C_4mim][N(SO_2CF_3)_2]$.

fied for the cation influence, the higher the relative cation–anion strength, the higher the mutual solubilities between ILs and water, due to the hydrogen bond strength that the anion can establish with water. As experimentally observed, the $[N(SO_2CF_3)_2]^-$ -based ILs present solubilities of water smaller than the $[PF_6]^-$ -based ILs, while $[C_4mim][BF_4]$ is totally miscible with water at room temperature. Although there is a large difference in the cation–anion interaction strength between $[N(SO_2CF_3)_2]^-$ and $[PF_6]^-$, this is not reflected in the solubility results. It should be noted that the relative ordering obtained by ESI-MS–MS is the result of the total interaction between the cation and the anion and not just the hydrogen bonding strength, which in this case defines the solubility of water.

It can be postulated that the solubility of water in imidazolium-based ILs is dependent on both the cation and anion hydrophobicity, that is, on the anion and cation hydrogen bonding ability.

2.2. Solubility of ILs in water

The solubilities of ILs in water cover a wide range of mole fractions when compared with the ILs rich-side of the equilibrium. The mole fraction solubility of the studied ILs in water ranges from 3.4×10^{-5} , for the $[C_8mim][Tf_2N]$, to complete miscibility at room temperature, as is the case of $[C_4mim][BF_4]$. Again, the solubility of ILs in water also depends on both the cation alkyl side chain length and on the anion identity. Also, the solubilities of ILs in water are more strongly dependent on the anion identity than on the cation chain length size. However, the effect of the cation size is more pronounced in the water-rich side solubility, where differences of one order of magnitude appear when comparing the solubility of $[C_4mim][PF_6]$ with $[C_8mim][PF_6]$ and even of two orders of magnitude comparing $[C_2mim][N(SO_2CF_3)_2]$ with $[C_8mim][N(SO_2CF_3)_2]$ in water at 318 K.

Due to the very low solubility of the studied imidazolium-based ILs in water, they may be considered to be at infinite

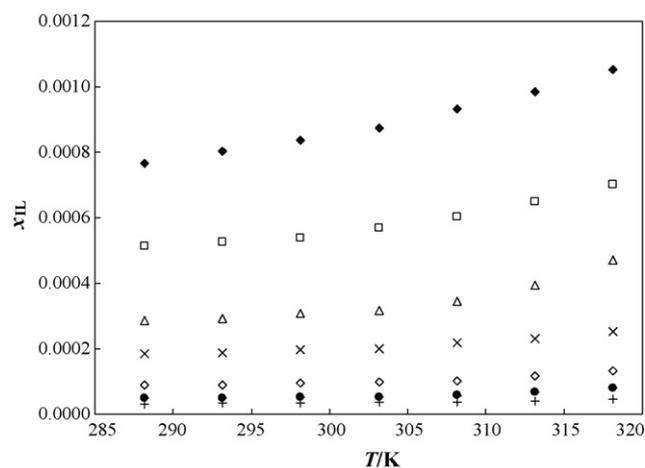


Fig. 4. Mole fraction solubility of ILs (x_{IL}) in water as a function of temperature for the ILs: (◆) $[C_2mim][N(SO_2CF_3)_2]$; (□) $[C_3mim][N(SO_2CF_3)_2]$; (△) $[C_4mim][N(SO_2CF_3)_2]$; (✕) $[C_5mim][N(SO_2CF_3)_2]$; (◇) $[C_6mim][N(SO_2CF_3)_2]$; (●) $[C_7mim][N(SO_2CF_3)_2]$; (+) $[C_8mim][N(SO_2CF_3)_2]$.

dilution and completely dissociated in the aqueous solution. In contrast, the IL rich-phase is far from what could be considered as a pure IL due to the high solubility of water.

2.2.1. Cation influence

Figs. 4 and 5 show the results for the $[N(SO_2CF_3)_2]^-$ -based ILs and for the $[PF_6]^-$ -based ILs, respectively. The cation influence is well pronounced and differences of one and two orders of magnitude are found in both the solubilities of the $[PF_6]^-$ - and $[N(SO_2CF_3)_2]^-$ -based ILs, respectively, with the alkyl side chain length increase. The same behaviour of decreasing solubilities with the alkyl chain length increase can be observed, in coherence with the ILs rich-phase behaviour.

From the molecular point of view the standard molar enthalpies of solvation are the result of three contributions: dissociation enthalpy of the ion aggregates in the theoretical gas phase, enthalpy of cavity formation in the solvent and enthalpy of

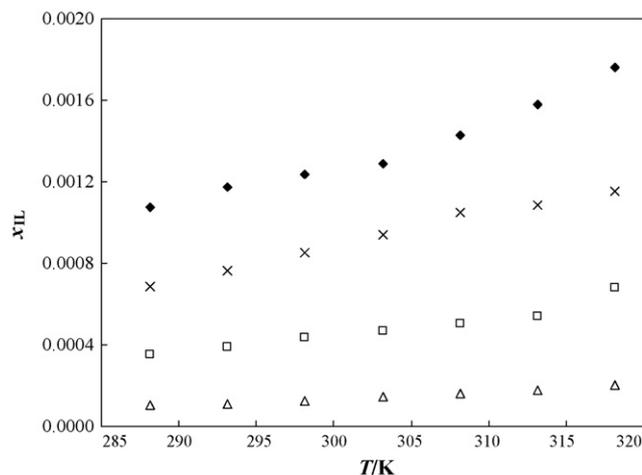


Fig. 5. Mole fraction solubility of ILs (x_{IL}) in water as a function of temperature for the ILs: (◆) $[C_4mim][PF_6]$; (□) $[C_6mim][PF_6]$; (△) $[C_8mim][PF_6]$; (✕) $[C_4C_1mim][PF_6]$.

solute–solvent interactions. The enthalpy of cavity formation is similar for all the ILs since we are considering the solubilities of ILs in the same solvent. The enthalpy of solute–solvent interactions, when the solvent is water, can be evaluated through surface tension studies since this property is a measure of the liquid surface cohesive energy and it is thus related to the strength of the interactions that are established between the anions and cations in an ionic liquid. Surface tension measurements [37] corroborate the mutual solubilities trend as well as the ESI-MS–MS results.

Enthalpically, in the ILs dissolution in water process there is a balance between the enthalpy of vaporization of ILs and the enthalpy of solvation of the ILs in water. The enthalpies of solution of the ILs in water are endothermic and small, as result of the high ILs enthalpies of vaporization [8], which further reflect the high stability of the ILs liquid phase, and a relatively high enthalpy of solvation of the anion and cation of the ILs in water. However, the experimental entropies of ILs in water display a small decrease in the entropic effect of approximately $-5 \text{ J K}^{-1} \text{ mol}^{-1}$ per methylene group addition to the $[\text{C}_n\text{mim}]^+$ cation [25]. The decrease of the ILs solubility is therefore driven by the decrease of the entropy of dissolution with the increase of the alkyl side chain. Clearly, the phase behaviour between ILs and water is the result of the interplay of several contributions with different relative weights depending on the system under study.

Exploring the hydrogen C2 substitution by a methyl group in the imidazolium ring, it can be seen that the $[\text{C}_4\text{C}_1\text{mim}][\text{PF}_6]$ presents a different behaviour of what was observed in the IL-rich phase. The solubility of this IL in water lays now between the $[\text{C}_4\text{mim}][\text{PF}_6]$ and $[\text{C}_6\text{mim}][\text{PF}_6]$, indicating that the hydrogen bonding on this side of the equilibrium is not one of the dominant factors in the solubility. ILs size and hydrophobicity seems to primarily define their solubility in water. From experimental pure ILs surface tensions values, the introduction of a methyl group on the $[\text{C}_4\text{mim}][\text{PF}_6]$ IL leads to an increase in the surface tension values [37]. Also, Hunt [38] reported the same odd behaviour for melting points and viscosity and hypothesized that the effects due to the loss in hydrogen bonding are less significant than those due to the loss of entropy. The loss of entropy enhances the alkyl chain association by lowering the amount of disorder in the system, eliminating the ion-pair conformers and increasing the rotational barrier of the alkyl chain. Thus, the reduction in the entropy leads to a greater ordering within the liquid and therefore to a slight increase in the surface tension values [37]. The introduction of the methyl group replacing the most acidic hydrogen has clearly some different impacts depending on the property under study and also on the fluid-rich phase predominance. Therefore, the phase behavior between ILs and water is the result of several competing interactions in solution and further studies concerning the cation structural variations are of main importance.

2.2.2. Anion influence

Fig. 6 presents the mole fraction solubilities of the studied imidazolium-based ILs in water when changing the anion while maintaining the cation. The same behaviour

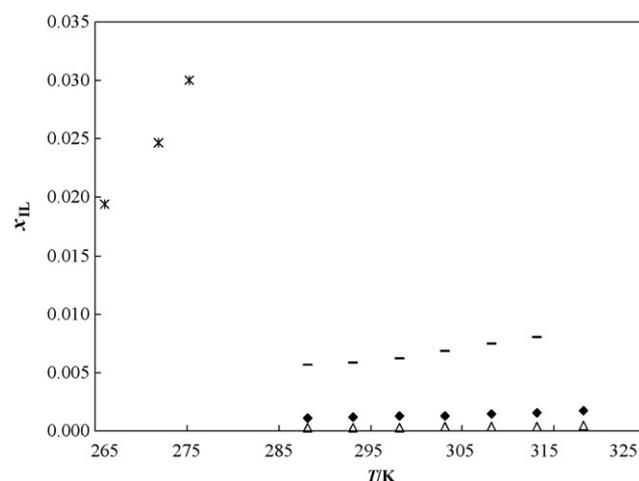


Fig. 6. Mole fraction solubility of ILs (x_{IL}) in water as a function of temperature for the ILs: (X) $[\text{C}_4\text{mim}][\text{BF}_4]$; (-) $[\text{C}_4\text{mim}][\text{C}(\text{CN})_3]$; (◆) $[\text{C}_4\text{mim}][\text{PF}_6]$; (Δ) $[\text{C}_4\text{mim}][\text{N}(\text{SO}_2\text{CF}_3)_2]$.

of the ILs-rich side of the equilibrium was found, with a decrease in solubilities values following the anion order: $[\text{BF}_4]^- > [\text{C}(\text{CN})_3]^- > [\text{PF}_6]^- > [\text{N}(\text{SO}_2\text{CF}_3)_2]^-$. Again and as stated before the ILs solubility increase follows the relative cation–anion strength increase between the imidazolium cation and the anion, when the anions $[\text{BF}_4]^-$, $[\text{PF}_6]^-$ and $[\text{N}(\text{SO}_2\text{CF}_3)_2]^-$ are considered [36].

3. Conclusions

The importance of the understanding of the mutual solubilities between water and imidazolium-based ILs is well illustrated in this work. It was showed that the detailed knowledge of the ILs structural variations impact in these mutual solubilities is of great significance for the ILs fine-tune with water and to manage their ecotoxicity impact. Both the cation and anion can affect the mutual solubilities between water and ILs, but the anion plays the major role on their phase behaviour. Also, the cation alkyl side chain length and the number of hydrogen substitutions in the imidazolium cation have some impact in the mutual solubilities, with the ILs hydrophobicity increasing with the alkyl chain length increase. Moreover, the water in IL solubility showed to be more dependent on the cation hydrogen bonding ability with water than the IL in water solubility.

Although most of the studied ILs are considered hydrophobic, they present a large solubility of water and are hygroscopic with mole fractions solubilities of water in the order of 10^{-1} for all the studied ILs. The water-rich phase showed to be more dependent on the ILs structural modifications where differences of two orders of magnitude in mole fraction units were verified for the studied ILs.

Acknowledgments

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References

- [1] K.N. Marsh, J.A. Boxall, R. Lichtenthaler, *Fluid Phase Equilib.* 219 (2004) 93–98.
- [2] M.J. Earle, K.R. Seddon, *Pure Appl. Chem.* 72 (2000) 1391–1398.
- [3] R.L. Gardas, M.G. Freire, P.J. Carvalho, I.M. Marrucho, I.M.A. Fonseca, A.G.M. Ferreira, J.A.P. Coutinho, *J. Chem. Eng. Data* 52 (2007) 80–88.
- [4] R.L. Gardas, M.G. Freire, P.J. Carvalho, I.M. Marrucho, I.M.A. Fonseca, A.G.M. Ferreira, J.A.P. Coutinho, *J. Chem. Eng. Data* 52 (2007) 1881–1888.
- [5] J.N.A. Canongia Lopes, A.A.H. Pádua, *J. Phys. Chem. B* 110 (2006) 3330–3335.
- [6] S.M. Urahata, M.C.C. Ribeiro, *J. Chem. Phys.* 120 (2004) 1855–1863.
- [7] Y. Wang, G.A. Voth, *J. Am. Chem. Soc.* 127 (2005) 12192–12193.
- [8] L.M.N.B.F. Santos, J.N. Canongia Lopes, J.A.P. Coutinho, J.M.S.S. Esperança, L.R. Gomes, I.M. Marrucho, L.P.N. Rebelo, *J. Am. Chem. Soc.* 129 (2007) 284–285.
- [9] J. McFarlane, W.B. Ridenour, H. Luo, R.D. Hunt, D.W. DePaoli, R.X. Ren, *Sep. Sci. Technol.* 40 (2005) 1245–1265.
- [10] J.G. Huddleston, A.E. Visser, W.M. Reichert, H.D. Willauer, G.A. Broker, R.D. Rogers, *Green Chem.* 3 (2001) 156–164.
- [11] V. Najdanovic-Visak, L.P.N. Rebelo, M.N. Ponte, *Green Chem.* 7 (2005) 443–450.
- [12] C.G. Hanke, R.M. Lynden-Bell, *J. Phys. Chem. B* 107 (2003) 10873–10878.
- [13] J.L. Anthony, E.J. Maginn, J.F. Brennecke, *J. Phys. Chem. B* 105 (2001) 10942–10949.
- [14] D.S.H. Wong, J.P. Chen, J.M. Chang, C.H. Chou, *Fluid Phase Equilib.* 194–197 (2002) 1089–1095.
- [15] J.M. Crosthwaite, S.N.V.K. Aki, E.J. Maginn, J.F. Brennecke, *J. Phys. Chem. B* 108 (2004) 5113–5119.
- [16] L.P.N. Rebelo, V. Najdanovic-Visak, Z.P. Visak, M.N. Ponte, J. Szydlowski, C.A. Cerdeirina, J. Troncoso, L. Romani, J.M.S.S. Esperança, H.J.R. Guedes, H.C. Sousa, *Green Chem.* 6 (2004) 369–381.
- [17] V. Najdanovic-Visak, J.M.S.S. Esperança, L.P.N. Rebelo, M.N. Ponte, H.J.R. Guedes, K.R. Seddon, J. Szydlowski, *Phys. Chem. Chem. Phys.* 4 (2002) 1701–1703.
- [18] Z.B. Alfassi, R.E. Huie, B.L. Milman, P. Neta, *Anal. Bioanal. Chem.* 377 (2003) 159–164.
- [19] N.V. Shvedene, S.V. Borovskaya, V.V. Sviridov, E.R. Ismailova, I.V. Pletnev, *Anal. Bioanal. Chem.* 381 (2005) 427–430.
- [20] U. Domańska, A. Marciniak, *Green Chem.* 9 (2007) 262–266.
- [21] U. Domańska, I. Bakala, J. Pernak, *J. Chem. Eng. Data* 52 (2007) 309–314.
- [22] P. Bonhôte, A.P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Gratzel, *Inorg. Chem.* 35 (1996) 1168–1178.
- [23] S.L.I. Toh, J. McFarlane, C. Tsouris, D.W. DePaoli, H. Luo, S. Dai, *Solvent Extraction Ion Exchange* 24 (2006) 33–56.
- [24] N. Papaiconomou, N. Yakelis, J. Salminen, R. Bergman, J.M. Prausnitz, *J. Chem. Eng. Data* 51 (2006) 1389–1393.
- [25] M.G. Freire, P.J. Carvalho, R.L. Gardas, I.M. Marrucho, L.M.N.B.F. Santos, J.A.P. Coutinho, *Phys. Chem. Chem. Phys.* (2007) submitted for publication.
- [26] M.G. Freire, C.M.S.S. Neves, P.J. Carvalho, R.L. Gardas, A.M. Fernandes, I.M. Marrucho, L.M.N.B.F. Santos, J.A.P. Coutinho, *J. Phys. Chem. B* (2007) submitted for publication.
- [27] J. Ranke, S. Stolte, J. Arning, M. Matzke, A. Bösch, U. Bottin-Weber, B. Jastorff, *Book of Abstracts BATIL Meeting*, Berlin, Germany, 2007.
- [28] A. Arce, M.J. Earle, S.P. Katdare, H. Rodríguez, K.R. Seddon, *Chem. Commun.* (2006) 2548–2550.
- [29] D.G. Archer, J.A. Widegren, D.R. Kirklin, J.W. Magee, *J. Chem. Eng. Data* 50 (2005) 1484–1491.
- [30] R.P. Swatloski, J.D. Holbrey, R.D. Rogers, *Green Chem.* 5 (2003) 361–363.
- [31] A.M. Fernandes, Not published private results.
- [32] S.N.V.K. Aki, J.F. Brennecke, A. Samanta, *Chem. Commun.* (2001) 413–414.
- [33] M.G. Freire, L.M.N.B.F. Santos, I.M. Marrucho, J.A.P. Coutinho, *Fluid Phase Equilib.* 255 (2007) 167–178.
- [34] R. Lopes da Silva, I.M. Marrucho, J.A.P. Coutinho, A.M. Fernandes, *Euchem Conference on Molten Salts and Ionic Liquids*, Wiley Book of Proceedings, submitted for publication.
- [35] L. Cammarata, S.G. Kazarian, P.A. Salter, T. Welton, *Phys. Chem. Chem. Phys.* 3 (2001) 5192–5200.
- [36] R. Bini, O. Bortolini, C. Chiappe, D. Pieraccini, T. Siciliano, *J. Phys. Chem. A* 111 (2007) 598–604.
- [37] M.G. Freire, P.J. Carvalho, I.M. Marrucho, A.M. Fernandes, A.J. Queimada, J.A.P. Coutinho, *J. Colloid Interface Sci.* 314 (2007) 621–630.
- [38] P.A. Hunt, *J. Phys. Chem. B* 111 (2007) 4844–4853.