Analysis of the isomerism effect on the mutual solubilities of bis(trifluoromethylsulfonyl)imide-based ionic liquids with water

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**ABSTRACT**

The knowledge of the liquid–liquid equilibria (LLE) between ionic liquids (ILs) and water is of utmost importance for environmental monitoring, process design and optimization. Therefore, in this work, the mutual solubilities with water, for the ILs combining the 1-methylimidazolium, [\text{C}_1\text{im}]\textsuperscript{+}; 1-ethylimidazolium, [\text{C}_2\text{im}]\textsuperscript{+}; 1-ethyl-3-propylimidazolium, [\text{C}_2\text{C}_3\text{im}]\textsuperscript{+}; and 1-butyl-2,3-dimethylimidazolium, [\text{C}_1\text{C}_2\text{C}_3\text{im}]\textsuperscript{+} cations with the bis(trifluoromethylsulfonyl)imide anion, were determined and compared with the isomers of the symmetric 1,3-dialkylimidazolium bis(trifluoromethylsulfonyl)imide ([\text{C}_n\text{C}_1\text{im}]\textsuperscript{+})\text{[NTf}_2\text{]}\textsuperscript{−}, with \(n = 1–3\) and of the asymmetric 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([\text{C}_n\text{C}_1\text{im}]\text{[NTf}_2\text{]}\textsuperscript{−}, with \(n = 2–5\) series of ILs. The results obtained provide a broad picture of the impact of the IL cation structural isomerism, including the number of alkyl side chains at the cation, on the water-IL mutual solubilities. Despite the hydrophobic behaviour associated to the [\text{NTf}_2]\textsuperscript{−} anion, the results show a significant solubility of water in the IL-rich phase, while the solubility of ILs in the water-rich phase is much lower. The thermodynamic properties of solution indicate that the solubility of ILs in water is entropically driven and highly influenced by the cation size. Using the results obtained here in addition to literature data, a correlation between the solubility of [\text{NTf}_2]\textsuperscript{−}-based ILs in water and their molar volume, for a large range of cations, is proposed. The CONductor like Screening MOdel for Real Solvents (COSMO-RS) was also used to estimate the LLE of the investigated systems and proved to be a useful predictive tool for the \textit{a priori} screening of ILs aiming at finding suitable candidates before extensive experimental measurements.

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**1. Introduction**

Ionic liquids (ILs), a novel and remarkable class of compounds, have received enormous attention during the past decade and their study has grown almost exponentially during this period of time [1]. The reason for their increased interest is related to their unique chemical and physical properties which makes ILs applicable as solvents for reactions and materials processing, as extraction media and as working fluids in mechanical and electrochemistry applications [2,3]. Most ionic liquids have high ionic conductivity, non-volatility, and flame resistance, and due to these unique physicochemical characteristics, ILs are often considered green solvents with a potential to replace conventional volatile solvents that are believed to contribute for the global warming [4,5]. Chemically, ILs are composed of bulky organic cations coupled with organic or inorganic anions. The combination of ions can lead to a large number of ionic liquids that provide considerable flexibility in the selection of the most suitable pairs for a specific chemical application and, consequently, to significant changes in their thermophysical properties. Therefore, they have been categorized as “designer solvents” owing to the quasi-infinite numbers of possible cations and anions combinations that can be envisioned [5].

Thermodynamic data such as liquid–liquid equilibrium (LLE) are of crucial importance in the design of industrial processes and evaluation of their environmental impact. Together with thermophysical properties, they can be used to develop thermodynamic

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http://dx.doi.org/10.1016/j.fluid.2014.08.007
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models [6] and can lead to a better understanding of the ILS nature, their benefits and limitations at an industrial scale [4]. On the other hand, the presence of water in ILS affects their properties, e.g. viscosity, a factor that makes the knowledge of the mutual solubilities between ILS and water very important together with the information that it provides on their environmental impact, toxicity and bioaccumulation [3]. Albeit non-volatile, even strongly hydrophobic ILS, such as the bis(trifluoromethylsulfonyl)imide-based fluids, present a non-negligible solubility in water [7] and thus may create environmental problems in case of their accidental release into the environment.

This work is an extension of our investigation into water--ILs miscibility for ILS containing the bis(trifluoromethylsulfonyl)imide anion [8–12]. The systems studied so far showed a very low solubility of ILS in the water-rich phase, considerable water mole fraction solubility in the IL-rich phase, and an upper critical solution behaviour. In the previous works where the imidazolium-based ILS were studied [8,9,11,13], it was verified that an increase in the IL cation alkyl side chain length results in a small increase in the upper critical solution temperature.

As part of our ongoing work on the LLE between [NTf2]-based ILS and water, we present here new data for ILS that have been hitherto poorly investigated. This work is focused on the structural variations of the cation, namely the number of alkyl side chains and their structural isomerism. The mutual solubilities measurements between ILS and water were carried out in the temperature range (288.15–318.15) K and compared with the predictions of COSMO-RS (Conductor like Screening MOdel for Real Solvents) [14–16], which proved to be a promising approach to model the phase equilibrium behaviour of systems involving ionic liquids [7,17].

Combining the systematic experimental measurements carried out here and the molecular modelling of the LLE, it is possible to rationalize the impact of the alkyl side chain length and number of aliphatic moieties on the mutual solubilities of ILS and water, contributing for the study of the isomerization effect, which is an important contribution for the design of ionic liquids with specific properties. Finally, a close correlation for the [NTf2]-based ILS solubilities in water with their molar volume is also proposed.

2. Experimental

2.1. Materials

The ILS studied in this work are displayed in Table 1 and their chemical structure are presented in Fig. 1.

In order to reduce the water and volatile compounds content to insignificant values, individual samples of ILS were dried under vacuum at 1 Pa and constant stirring at 353 K, for a minimum of 48 h. After, the purity of each ionic liquid was further checked by 1H, 13C, and 19F NMR spectra. A Metrohm 831 Karl Fischer coulometer using the analyte Hydranal®—Coulomat AG, from Riedel-de Haén, was used to determine the water content of the dried ionic liquids, and was found to be below 100 ppm for all samples. The water used in the measurements was double distilled, passed by a reverse osmosis system and further treated with a MilliQ plus 185 water purification apparatus, presenting a resistivity of 18.2 MΩ cm, a TOC smaller than 5 μg dm−3 and free of particles larger than 0.22 μm (M (H2O) = 18.01 g mol−1).

2.2. Solubility measurements

The mutual solubility measurements between water and ionic liquids were carried out at temperatures from 288.15 to 318.15 K, and at atmospheric pressure, using an experimental procedure previously described in detail [8–10]. Initially, the ILS and water phases were vigorously agitated and allowed to reach the saturation equilibrium for at least 48 h. This time period proved to be the minimum time required to guarantee a complete separation of the two phases and their saturation [6,8]. The flasks containing the phases in equilibrium were put inside an aluminium block specially designed for this purpose [13]. The temperature control was achieved with a PID temperature controller driven by a calibrated Pt100 (class 1/10) temperature sensor inserted in the aluminium block. A Julabo (model F25-HD) refrigerated bath was used as the cooling source. The temperature accuracy was ±0.01 K.

At each temperature, both phases were collected from the equilibrium vials using glass syringes kept at the same temperature of the measurements. The solubility of each ionic liquid in water was determined by UV–vis spectroscopy, by calibration curves previously established, and using a SHIMADZU UV–1700 PharmaSpec Spectrometer (λ = 209 nm for [C1im][NTf2] and [C2im][NTf2]; and λ = 211 nm for [C2C3im][NTf2] and [C4C1C1im][NTf2]), whereas the solubility of water in the IL was determined by KF titration. For the IL–rich phase, approximately 0.1 g were taken and directly injected in the KF coulometric titrator, whereas for the water-rich phase, ca. 0.5 g of each sample were taken and diluted in ultrapure water. Solubility results, at each temperature, are the average of at least five measurements of individual samples collected from the same equilibrium phase. In case of observing large standard deviations, new equilibrium phases were produced and new measured values added.

2.3. COSMO-RS

COSMO-RS (Conductor-like Screening MOdel for Real Solvents) is a predictive method, based on unimolecular quantum calculations [15], able to calculate the thermodynamic equilibria of pure fluids and mixtures. The details of this method can be found elsewhere [15,18]. In our earlier work, we have demonstrated the capability of COSMO-RS to predict the liquid–liquid equilibria of ILS with water [6,7,9,19], where a satisfactory qualitative agreement with experimental data was found, and confirming its high capability as a predictive tool. Therefore, in this work, we also utilized COSMO-RS to predict the liquid–liquid equilibria of water and the studied isomeric ILS.

The standard procedure of COSMO-RS calculations employed in this work consist of two steps. In the first step, quantum chemical COSMO calculations for the molecular species involved, performed with the TURBOMOLE 6.1 program package on the density functional theory, utilizing the BP functional B88-P86 with a triple-ζ valence polarized basis set (TZVP) [20]. In the second stage, the LLE of water and ILS were carried out by the COSMOTHERM program [21] using the parameter file BP,TZVP,C21_0110. Detailed calculations are explained in our previous work [6]. In all calculations,
the ILS (cation and anion) were always treated as isolated species at the quantum chemical level. It should be pointed out that in a previous work [19], the lowest energy conformations, or with the global minimum for both cation and anion, showed the best predictions of the experimental data. Therefore, in this work, the lowest energy conformations of all the species involved were used in the COSMO-RS calculations.

3. Results and discussion

3.1. Mutual solubilities

The experimental data for the mutual solubility between water and the studied ILS, along with the respective standard deviations, are given in Tables 2 and 3. The analysis of Table 2 reveals a significant mole fraction solubility of water in the IL-rich phase, and above 0.5 for the [C2 im][NTf2] and [C3 im][NTf2] ILS. Thus, in spite of the hydrophobic character usually associated to the bis(trifluoromethylsulfonyl)imide anion, it is shown here that monosubstituted ILS dissolve large amounts of water. The change on the nature and acidity of the imidazolium cation by an "extra" –N–H acidic site leads to a saturation limit above 1:1 for the pair water-IL. The water solubility in [C2C1 im][NTf2] and [C4C1C1 im][NTf2] is of the same order observed previously in the [C3C1 im][NTf2] and [C2C1 im][NTf2] series [8,13]. On the opposite side of the phase diagram, the mole fraction solubility of ILS in the water-rich phase is much lower, in the order of 10−3 to 10−4, which may be considered as an almost pure phase with the IL close to infinite dilution. In general, an when comparing the data obtained for [C1 im][NTf2] and [C2 im][NTf2], the mutual solubilities with water decrease with the increase on the alkyl side chain length of the cation due to an increase in the IL hydrophobic character. For all the studied ILS, the mutual solubilities increase with temperature, displaying an upper critical solution temperature behaviour. This is the expectable behaviour, and also observed with other imidazolium-based ILS combined with the [BF4]− or [PF6]− anions [9,22,23]. Watanabe and Katsuta [24] reported the solubility of [C2C1C1 im][NTf2] in water at 298.15 K. The relative deviation to the experimental value measured in this work is only 5%.

Aiming at studying the impact of the structural variation of ILS towards their mutual solubility with water, Fig. 2 depicts the phase diagrams of the studied ILS along with the corresponding isomers previously reported [8,13]. The ionic liquids studied in this work and the symmetric and asymmetric series with the same number of methylene groups in the alkyl side chains are compared, enabling us to investigate the impact of structural isomers towards their mutual solubilities with water. As depicted in Fig. 2a, the mole fraction solubility of water in the ionic liquid [C2C1 im][NTf2] is similar to that of [C2 im][NTf2]. Considering now the IL [C2C1C1 im][NTf2] with the respective structural isomers, [C3C1 im][NTf2] and [C3 im][NTf2], the trialkyl-substituted IL presents a lower solubility of water whereas the disubstituted ILS present similar solubility values. The introduction of a third aliphatic moiety substituting the most acidic hydrogen clearly reduces the hydrogen-bonding ability between the imidazolium cation and water with an impact on the water solubility. However, smaller differences are observed for the pair, [C2C1C1 im][NTf2] and [C3C1 im][NTf2] that contain the same number of aliphatic tails. Moreover, it is interesting to notice the significant differentiation of the solubility of water in [C2 im][NTf2] and in [C3 im][NTf2], also structural isomers. The change in the chemical nature of the cation and the presence of a N–H group increases the water solubility in the IL to a mole fraction higher than 0.5 (above 1:1, water:IL) that is an indication of a strong affinity and hydrogen-bonding between N–H and H2O.

The mole fraction solubility of the different ionic liquids in water is presented in Fig. 2b. Also here, as noted in the IL-rich phase, the mole fraction solubility of water in the ionic liquid [C2C1 im][NTf2] is similar to that of [C2C1C1 im][NTf2]. In the case of the trialkyl-substituted IL, [C2C1C1 im][NTf2], and their structural isomers [C2C1 im][NTf2] and [C3C1 im][NTf2], the solubility in water of the [C4C1 im][NTf2] is slightly larger than the respective isomers, contrary to what happens in the IL-rich phase. The solubility of the disubstituted isomers [C2C1 im][NTf2] and [C3C1 im][NTf2] is similar as they contain the same number of aliphatic tails. Finally, concerning the solubility in water of [C1 im][NTf2] and [C2 im][NTf2], and similarly to what observed is the IL-rich phase a large significant difference can be observed. Once again the strong affinity and hydrogen-bonding between N–H and H2O increases the ionic liquid solubility in water. In order to thoroughly understand the impact of the structural variations of ionic liquids on their mutual solubilities with water, the solubility variations are summarized in Fig. 3. The ionic liquids investigated in this work, together with the symmetric
([C₉C₃im][NTf₂], with n = 1–3) and asymmetric ([C₉C₁im][NTf₂], with n = 2–5) series are analysed in order to evaluate the variations in the mutual solubilities when adding a methyl group.

As observed in Fig. 3, in both phases, whenever a methyl group is introduced, the solubility decreases. In the IL-rich phase, this reduction is within the range 5–16%, if the introduction of the methyl group takes place in the aliphatic chains, and 26–52%, if directly attached to the aromatic ring. Concerning the water-rich phase, the reduction is more pronounced but less distinct; 36–44% for an addition of a methyl to the aliphatic chains, and 32–66% if to the aromatic ring. When the methyl group is added to the aromatic ring, the highest percent decrease correspond to the pair [C₂im][NTf₂]/[C₅C₁im][NTf₂] and the lowest to [C₃C₁im][NTf₂]/[C₄C₁C₁im][NTf₂], i.e., the introduction of a third aliphatic moiety has a less impact that the elimination of the “N–H” bond.

Concerning the IL-rich phase, when adding a methyl group to [C₁im][NTf₂] in the aliphatic chain the variation is 6%, but, if this addition causes the elimination of the “N–H” bond, the variation is 47%. In the same way, the variation in the solubility to obtain [C₂C₁im][NTf₂] from a monosubstituted IL ([C₁im][NTf₂]) is much larger than from a dissubstituted IL ([C₁C₁im][NTf₂]). The addition of methyl groups to obtain the symmetric and asymmetric series causes a more or less constant variation in the solubility (5–14%), being [C₃C₁im][NTf₂]/[C₄C₁im][NTf₂] the pair where the greatest variation occurs. Lastly the [C₄C₁im][NTf₂], where the introduction of a third aliphatic moiety to obtain [C₄C₁C₁im][NTf₂], reduce the hydrogen-bonding ability and, consequently, causes a significant decrease in the solubility.

On the other hand, in the water-rich phase although the changes are larger than in the IL-rich phase, these seem more similar the different isomers. For instance, when adding a methyl group to the monosubstituted IL [C₁im][NTf₂] the variations are 44% for the addition to the aliphatic chain and 66% if the addition takes place directly in the aromatic ring. To obtain [C₂C₁im][NTf₂] the addition of a methyl group to [C₂im][NTf₂] cause a variation of 66% while the addition to [C₁C₁im][NTf₂] causes a variation of only 44%. Again, the additions of methyl groups to obtain the

![Figure 2](image-url)
symmetric and asymmetric series, causes approximately constant variations in the solubility (36–43%). Concerning the trialkyl-substituted IL, [C₄C₁im][NTf₂], the addition of a methyl group to [C₄C₁im][NTf₂] causes merely a reduction of 32% in the IL solubility. Moreover, it is interesting to note that the variation on the solubility between the pairs [C₃C₂im][NTf₂] and [C₂C₂im][NTf₂]/[C₂C₁im][NTf₂] is almost the same in each phase, and four times higher in the water-rich phase.

3.1.1. Thermodynamic functions of solution

Aiming at determining the thermodynamic functions of solution, the temperature dependence of the mole fraction solubility was correlated using Eqs. (1) and (2) [8,10]. For the solubility of water in the IL-rich phase, it can be assumed that the process occurs at constant molar enthalpy of solution, and thus,

\[ \ln x_w = A + \frac{B}{T(K)} \]

where \( T \) is the absolute temperature, and \( A \) and \( B \) are empirical constants.

For the solubility of the ILs in water, there is a significant dependence on temperature for the enthalpy of solution, and therefore,

\[ \ln x_w = C + \frac{D}{T(K)} + E \ln(T(K)) \]

where \( C, D, \) and \( E \) are empirical constants.

The fitted parameters as well as their standard deviations are listed in Table 4. The maximum relative deviation to the experimental data is 2%, for both the water-rich and the ionic liquid-rich phases.

Solubility is a quantitative measure of the equilibrium composition of a saturated solution. When this equilibrium is established between two liquids, the standard molar thermodynamics functions, such as the Gibbs energy (\( \Delta_{sol} G_m^o \)), enthalpy (\( \Delta_{sol} H_m^o \)) and entropy of solution (\( \Delta_{sol} S_m^o \)) can be derived from the temperature dependence of the experimental solubility data [9]. These properties were calculated using Eqs. (3)–(5) [8,10,25] for the water-rich phase, where the solute could be considered at infinite dilution. In the IL-rich phase, the solubility of water is higher and the associated thermodynamic molar functions cannot be determined.

\[ \Delta_{sol} G_m^o = -RT \ln(x_w)_p \]

\[ \frac{\Delta_{sol} H_m^o}{RT^2} = \left( \frac{\partial \ln x_w}{\partial T} \right)_p \]

\[ \Delta_{sol} S_m^o = \left( \frac{\partial (T \ln x_w)}{\partial T} \right)_p \]

where \( p \) and \( m \) indicates isobaric condition during the process and a molar quantity, respectively.

The molar thermodynamic functions for the IL solution in water were estimated at 298.15 K and are reported in Table 5.

At 298.15 K, the \( \Delta_{sol} H_m^o \) of the studied ILs in water, remains approximately constant with the increase of the aliphatic moiety, because when the ionic liquid is in aqueous solution the interactions occur mainly with the charged head and are much less dependent on the alkyl chain. The experimental enthalpies of solution also show that the solubilization of ILs in water is an endothermic process, leading to an upper critical solution temperature behaviour type phase diagram. On the other hand, the standard Gibbs energy of solution increases with the alkyl chain length leading to a lower solubility of the heavier ILs in water. The molar entropies of solution are shown to be negative and dependent on the cation structure, decreasing with increasing the alkyl chain length (approximately \(-5.1 \text{K}^{-1} \text{mol}^{-1} \) per methylene addition to the cation and as shown previously [8–11]). Therefore, the solubility of the ILs in water is driven by the entropy of solution; the higher (less negative) the entropic change, the higher the solubility of the ILs in water.

The significant increase of solubility of the [C₁im][NTf₂] and [C₂im][NTf₂] in water is also entropically driven and is a results of the quite significant increase of the entropy of solution of \(-\text{(+25 K}^{-1} \text{mol}^{-1}) \) when compared with their isomers [8,13] and other members of the [NTf₂]-series of ILs as well as combined with
other anions. The significant increase in the entropy of solution is also related with the expected cation to water interaction via the N–H group that leads to a better solvation interaction with water and to a decrease of the cavitation entropy penalty (more hydrophilic).

3.1.2. COSMO-RS

The predicted phase diagrams of the binary mixtures composed of water and the studied ILs using COSMO-RS are presented in Fig. 2. The same increase on the hydrophobic character is observed for the experimental data and COSMO predictions. COSMO-RS is

![Graph](image-url)

**Fig. 4.** Calculated versus experimental solubility of bis(trifluoromethylsulfonyl)imide-based ionic liquids at 298.15 K in (a) IL-rich phase and (b) water-rich phase.
thus able to qualitatively predict the trend on the ILs affinity for water. The only exception found was for the prediction of the solubility change with the temperature for the ionic liquid containing the cation [C4C1im]+ in water. In opposition to the experimental information, COSMO-RS predicts a solubility decrease with rising temperature. This irregularity can be related to the fact that simple empirical interaction potentials are used in COSMO-RS to describe the weaker interactions of the ILs with water, which is expected to poorly describe their effective complexity.

Fig. 4 plots the calculated versus experimental solubility for several [NTf2]-based ILs, at both rich phases, and at 298.15 K. From the close correlations depicted in Fig. 4 it can be concluded that COSMO-RS can predict the mutual solubilities between the studied ILs and water.

It should be pointed out here that the latest COSMO file parameterization, BP_TZVＰ_C30_1401, was also used to predict the LLE of the binary systems investigated in this work, cf. Fig. 1S of Supporting Information, presenting a global relative deviations of 35.3 and 2.8% for the solubility of water in ILs and ILs in water, respectively. However, this COSMO-RS parameterization is also unable to correctly describe the solubility change with the temperature for the ILs [C4C1im][NTf2] and [C2C3im][NTf2] in water. With the file parameterization, BP_TZVＰ_C21_0110 the global relative deviations obtained were 16.8 and 1.2%. Since the latest version of COSMO-RS predicts the phase diagrams with a larger deviation from the experimental results and wrong trends, the oldest version is preferred and was used here. Despite some regular deviations, COSMO-RS shows to be a useful tool in the prediction of the binary systems behaviour, and able to correctly display the alkyl chain length and IL cation isomeric effect, and as previously observed [6–9].

3.1.3. Correlation for the solubility of bis(trifluoromethylsulfonyl)imide-based ionic liquids in water

The solubility of hydrophobic solutes in water, near infinite dilution, is controlled and strongly correlated to their molar volume [7,10,11]. For isomeric ILs, the molar volume is identical and, consequently, the solubilities are essentially the same. In this context, in our previous work [13] we have start to investigate the relevance of the solutes molar volume on the solubility of the [NTf2]-based ionic liquids in water, at 298.15 K, and a correlation was proposed. Here, new points were plotted together with the correlation obtained [13], in order to verify if it can be also used for more diverse systems, as shown in Fig. 5. The molar volumes were calculated based on density data taken from literature [12,26,27] and the aqueous solubility data used were those obtained in this work along with data previously published [8,10,11,13]. Data relative to other cations (pyridinium-, pyrrolidinium- and piperidinium-based [10,11,26,27]) combined with the same anion where also included in order to verify the robustness of the correlation proposed.

Despite the different cations families, the correlation [13] is able to correctly describe the solubility of [NTf2]-based ILs in water. However, it is observed that cations with different cores, i.e. with a more different chemical nature (like pyridinium-, pyrrolidinium- and piperidinium-based) and the monosubstituted imidazolium IL, deviate more from the proposed correlation that was constructed with imidazolium-based fluids only. On Fig. 5, the isomerism effect can also be analysed and, as can be seen, ionic liquids with the same molar volume present similar solubility in water. Exceptions are only the pair [C2im][NTf2]/[C2C3im][NTf2], which is understood due to the elimination of a ‘N−H’ bond in the imidazolium ring like explored before, and for ILs with a different core than imidazolium, namely, [C2C1pip][NTf2] and [C2py][NTf2].

4. Conclusions

In this work, the mutual solubilities of water and ILs composed by the [C1im]+, [C2im]+, [C2C3im]+ and [C2C1im]+ cations combined with the bis(trifluoromethylsulfonyl)imide anion, and their dependence with temperature, were evaluated and compared with the corresponding isomers. Despite the hydrophobic label attributed to the [NTf2]− anion, it was found that they can dissolved significant amounts of water. In particular, solubilities in the order of 0.5 (in mole fraction) were found for the monosubstituted ILs. The solubilities of the ionic liquids and water, in both phases follow the order: [C1im]|+ > [C2im]|+ ≫ [C2C3im]|+ ≫ [C2C1im]|+. The impact of the structural variation of the ILs cations towards their mutual solubilities with water were analysed and showed that the introduction of a methyl group always decrease the solubility. This decrement is more pronounced when the addition of the methyl group is carried to an “N−H” bond. Moreover, the solubilities of ILs in water with the same total number of carbons in the alkyl side chain are comparable, as they have similar molar volumes, and a useful correlation between the solubility of [NTf2]-based ILs and their molar volume was evaluated. Finally, the predictive results obtained with COSMO-RS for the LLE of the systems here studied are in good agreement with the experimental...
data supporting the applicability of this model to predict the solubility of other ionic liquids and water not experimentally available.

Acknowledgements

The authors thank financial support from Fundação para a Ciência e a Tecnologia (FCT, Portugal), European Union, QREN, FEDER and COMPETE for funding the CICECO (project PEST-C/CTM/LA0011/2013), and LSRE/LCM (project PEST-C/EQB/LA0020/2013). Thanks are also due to FCT for financial support for the Ph.D. and postdoctoral grants SFRH/BD/87084/2012, SFRH/BD/70641/2010, SFRH/BPD/88101/2012 for M.A.R.M., C.M.S.S.N., and K.A.K., respectively. S.P.P. also thanks FAPESB (APR0035/2014) for funding.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.fluid.2014.08.007.

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