

## Mutual Solubilities of Water and the [C<sub>n</sub>mim][Tf<sub>2</sub>N] Hydrophobic Ionic Liquids

Mara G. Freire,<sup>†</sup> Pedro J. Carvalho,<sup>†</sup> Ramesh L. Gardas,<sup>†</sup> Isabel M. Marrucho,<sup>†</sup>  
Luís M. N. B. F. Santos,<sup>‡</sup> and João A. P. Coutinho<sup>\*,†</sup>

CICECO, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal, and CIQ,  
Departamento de Química, Faculdade de Ciências da Universidade do Porto, R. Campo Alegre 687,  
4169-007 Porto, Portugal

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Ionic liquids (ILs) have recently garnered increased attention because of their potential environmental benefits as “green” replacements over conventional volatile organic solvents. While ILs cannot significantly volatilize and contribute to air pollution, even the most hydrophobic ones present some miscibility with water posing environmental risks to the aquatic ecosystems. Thus, the knowledge of ILs toxicity and their water solubility must be assessed before an accurate judgment of their environmental benefits and prior to their industrial applications. In this work, the mutual solubilities for [C<sub>2</sub>–C<sub>8</sub>mim][Tf<sub>2</sub>N] (*n*-alkyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide) and water between 288.15 and 318.15 K at atmospheric pressure were measured. Although these are among the most hydrophobic ionic liquids known, the solubility of water in these compounds is surprisingly large, ranging from 0.17 to 0.36 in mole fraction, while the solubility of these ILs in water is much lower ranging from  $3.2 \times 10^{-5}$  to  $1.1 \times 10^{-3}$  in mole fraction, in the temperature and pressure conditions studied. From the experimental data, the molar thermodynamic functions of solution and solvation such as Gibbs energy, enthalpy, and entropy at infinite dilution were estimated, showing that the solubility of these ILs in water is entropically driven. The predictive capability of COSMO-RS, a model based on unimolecular quantum chemistry calculations, was evaluated for the description of the binary systems investigated providing an acceptable agreement between the model predictions and the experimental data both with the temperature dependence and with the ILs structural variations.

### Introduction

Ionic liquids (ILs) are a class of molten salts and commonly consist on the assembly of large organic cations and inorganic or organic anions of smaller size and more asymmetrical shape. These factors tend to reduce the lattice energy of the 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, the ionic nature of these liquids results in a unique combination of properties for most ILs, namely, their high thermal stability, large liquidus range, high ionic conductivity, negligible vapor pressure, nonflammability, and a high solvating capacity for organic, inorganic, and organometallic compounds, which determined their high potential to be exploited as “green solvents” in the past several years.<sup>1,2</sup> Besides, the huge number of possible combinations between cations and anions allows the possibility of tuning ILs, that can be designed for a particular application or to present a specific set of intrinsic properties.

The unique properties of ionic liquids allow their use in several applications in the chemical industry such as solvents in organic synthesis, as homogeneous and biphasic transfer catalysts and in electrochemistry. ILs present also potential to be used in separation processes and extraction media where, among others, they have shown promising results in the liquid–liquid extraction of organics from water.<sup>3–5</sup> In particular, it has

been shown that they may play an important role in the recovery of butanol from fermentation broths and in the removal of organic contaminants from aqueous waste streams.<sup>4,5</sup> For the extraction of organic products from aqueous media, ILs with low water solubility are required. Therefore, the knowledge of the mutual solubilities of water and ILs prior to their industrial applications is of primary importance.

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 vapor pressures, their release to aquatic environments could cause water contamination because of their potential toxicity and limited biodegradability. The essential reason for considering ILs as “green” solvents arises from their nonvolatility which makes them ideal “green” substitutes for conventional organic solvents. Nevertheless, the ecotoxicity is an important factor that defines the applicability of ILs and should be strictly assessed. The ILs toxicity seems to be directly related and mainly controlled by their lipophilicity.<sup>6</sup> Several studies changing the anion in pyridinium and imidazolium-based ILs have already demonstrated that the ILs toxicity is primordial determined by the cation nature and it is essentially driven by the cation alkyl side chain length.<sup>6–10</sup> An increase in the ILs cation alkyl chain length increases their lipophilic character and leads to an increase in their ecotoxicity. Therefore, the ILs bioaccumulation is directly proportional to their hydrophobicity, and thus, the knowledge of their water solubility can be a way of predicting the toxicity and bioaccumulation impact of an ionic liquid in the ecosystem.<sup>6–10</sup>

Another factor that makes the knowledge of mutual solubility with water of importance is the way how the presence of water

\* Corresponding author. Phone: +351-234-370200. Fax: +351-234-370084. E-mail: jcoutinho@ua.pt.

<sup>†</sup> Universidade de Aveiro.

<sup>‡</sup> Universidade do Porto.

**TABLE 1: Experimental Mole Fraction Solubility of Water in [Tf<sub>2</sub>N]-Based ILs as a Function of Temperature**

	[C <sub>2</sub> mim][Tf <sub>2</sub> N]	[C <sub>3</sub> mim][Tf <sub>2</sub> N]	[C <sub>4</sub> mim][Tf <sub>2</sub> N]	[C <sub>5</sub> mim][Tf <sub>2</sub> N]	[C <sub>6</sub> mim][Tf <sub>2</sub> N]	[C <sub>7</sub> mim][Tf <sub>2</sub> N]	[C <sub>8</sub> mim][Tf <sub>2</sub> N]
T/K	( <i>x<sub>w</sub></i> ± <i>σ<sup>d</sup></i> )	( <i>x<sub>w</sub></i> ± <i>σ<sup>d</sup></i> )	( <i>x<sub>w</sub></i> ± <i>σ<sup>d</sup></i> )	( <i>x<sub>w</sub></i> ± <i>σ<sup>d</sup></i> )	( <i>x<sub>w</sub></i> ± <i>σ<sup>d</sup></i> )	( <i>x<sub>w</sub></i> ± <i>σ<sup>d</sup></i> )	( <i>x<sub>w</sub></i> ± <i>σ<sup>d</sup></i> )
288.15	0.2755 ± 0.0005	0.2502 ± 0.0004	0.2307 ± 0.0003	0.2052 ± 0.0005	0.1906 ± 0.0006	0.1806 ± 0.0009	0.1715 ± 0.0006
293.15	0.2869 ± 0.0008	0.2581 ± 0.0004	0.2443 ± 0.0006	0.2127 ± 0.0004	0.1978 ± 0.0006	0.1879 ± 0.0006	0.1781 ± 0.0003
298.15	0.2982 ± 0.0009	0.2715 ± 0.0007	0.2568 ± 0.0006	0.2211 ± 0.0005	0.2076 ± 0.0006	0.1971 ± 0.0004	0.1868 ± 0.0003
303.15	0.3119 ± 0.0007	0.2861 ± 0.0009	0.2715 ± 0.0007	0.2324 ± 0.0004	0.2187 ± 0.0005	0.2081 ± 0.0005	0.1949 ± 0.0005
308.15	0.3280 ± 0.0004	0.3013 ± 0.0007	0.2853 ± 0.0007	0.2449 ± 0.0001	0.2303 ± 0.0006	0.2190 ± 0.0006	0.2054 ± 0.0006
313.15	0.3446 ± 0.0002	0.3172 ± 0.0005	0.2989 ± 0.0004	0.2570 ± 0.0009	0.2424 ± 0.0006	0.2334 ± 0.0005	0.2149 ± 0.0004
318.15	0.3603 ± 0.0004	0.3324 ± 0.0007	0.3136 ± 0.0009	0.2669 ± 0.0007	0.2556 ± 0.0007	0.2447 ± 0.0009	0.2241 ± 0.0005

<sup>d</sup> Standard deviation.

in the ionic liquids can dramatically affect their physical properties such as viscosities, densities, and surface tensions.<sup>11–13</sup> Water may also act as a cosolvent increasing the mutual solubilities between alcohols and ILs<sup>11,14,15</sup> or as an antisolvent reducing the solubility of other compounds, for example, gases and nonpolar compounds, in ionic liquids.<sup>16,17</sup> Furthermore, the presence of water also affects the rates and selectivity of reactions involving or carried out in ILs.<sup>18</sup>

Some contributions dealing with experimental solubilities between ILs and water have already been reported.<sup>5,14,19–31</sup> However, careful and methodical studies of the cation effect in a common series and in a wide range of temperature, which thus allow the calculation of derived properties, are still scarce. In this work, a systematic study of the liquid–liquid equilibria between water and [C<sub>*n*</sub>mim], from [C<sub>2</sub>mim] to [C<sub>8</sub>mim], with the common anion [Tf<sub>2</sub>N], and from 288.15 to 318.15 K at atmospheric pressure, was performed. The bis(trifluoromethylsulfonyl)imide-based ILs could be one of the most interesting imidazolium-based ionic liquids for organics extraction from aqueous phases due to their high hydrophobicity, high thermal stability, relatively low viscosity, and water moisture stability,<sup>28</sup> and it is here shown that even this extremely “hydrophobic” ILs class presents important solubilities with water.

Traditional approaches to predict fluid properties or phase equilibria require a large data bank of vapor–liquid (VLE) and liquid–liquid (LLE) equilibrium experimental measurements. COSMO-RS<sup>32–36</sup> is a predictive method based on unimolecular quantum chemical calculations of the individual molecules, which has already proved to be a promising approach to model phase equilibria for ionic liquids. A number of works dealing with the application of COSMO-RS to the description of LLE systems of ILs and alcohols, hydrocarbons, ethers, ketones, or water systems can be found in the literature.<sup>37–43</sup> Surprisingly, just one application of COSMO-RS to IL–water LLE and VLE systems was previously attempted,<sup>43</sup> where this predictive method proved to be able to provide an adequate description of the solubility dependence with temperature and IL structural variations. The performance of this predictive method is analyzed here in the prediction of the water–IL binary systems which have also been experimentally measured. COSMO-RS proves to be, at least qualitatively, an a priori method of selection for predicting the water–IL binary systems phase behavior before extensive experimental measurements.

## Experimental Section

**Materials.** The ILs 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C<sub>*n*</sub>mim][Tf<sub>2</sub>N], with the alkyl side chain ranging between 2 and 8, were prepared accordingly to the methods reported in the literature.<sup>28</sup> The reagents [C<sub>*n*</sub>mim][Br] (*n* = 2 to 8) and [Li][Tf<sub>2</sub>N] were acquired at IoLiTec with purities of >99% and >98%, respectively. In order to reduce the water content and volatile compounds to negligible values,

the ILs individual samples were dried under constant agitation at vacuum (0.1 Pa) and at 353 K, for a minimum of 48 h. After that careful procedure, the ILs purities were checked by <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectroscopy being >99% for all ILs. The bromide content was quantified by ion chromatography and was inferior to 100 × 10<sup>−6</sup> in mass fraction for all samples. The water used was double distilled, passed by a reverse osmosis system, and further treated with a Milli-Q Plus 185 water purification apparatus. It has a resistivity of 18.2 MΩ·cm, a TOC smaller than 5 μg·L<sup>−1</sup>, and it is free of particles greater than 0.22 μm. The anolyte used for the coulometric Karl Fischer titration was Hydranal-Coulomat AG from Riedel-de Haën.

**Experimental Procedure.** The mutual solubilities measurements were performed at temperatures from 288.15 to 318.15 K and at atmospheric pressure. The two phases were initially put together in 22 mL glass vials, vigorously agitated, and allowed to reach equilibrium for a minimum of 48 h. This period was the minimum time period found for equilibration, where a complete separation of the two phases was achieved, and no further variations in mole fraction solubilities were observed, thus, assuring the complete saturation of both phases.

The vials were thermostated on an aluminum block immersed in an isolated air bath capable of maintaining the temperature within ±0.01 K by means of a PID temperature controller driven by a calibrated Pt100 (class 1/10) temperature sensor inserted in the aluminum block. In order to achieve temperatures below the room temperature, a Julabo circulator, model F25-HD, is coupled to the overall oven system allowing the passage of a thermostated fluid flux around the aluminum block.

The solubility of water in the IL-rich phase was determined with a Metrohm 831 Karl Fischer (KF) coulometer. IL-rich phase samples of ≈0.1 to 0.2 g were taken from the equilibrium vials using a glass syringe maintained in dry and warm conditions.

The solubility of ILs in the water-rich phase was determined by UV-spectroscopy using a SHIMADZU UV-1700, Pharma-Spec spectrometer, at a wavelength of 211 nm. This wavelength was found to be the maximum absorption length for all ILs under study and corresponds to the UV absorption of the imidazolium ring cation. Samples of ≈0.3 to 1.0 g were taken from the water-rich phase by means of a glass syringe and diluted by a factor ranging from 1:50 to 1:1000 (v:v) in pure water, depending on the IL solubility under study, in order to read values of absorbance in an adequate range. The mole fraction solubilities of ILs in water, as well as the mole fraction solubilities of water in ILs, were determined gravimetrically, weighing the samples of both rich phases. The dilutions of the water-rich phase samples avoid the phase split when measurements are carried out at temperatures different from room temperature.

The solubility results at each temperature were determined as the average of at least five independent measurements.

**TABLE 2: Experimental Mole Fraction Solubility of [Tf<sub>2</sub>N]-Based ILs in Water as a Function of Temperature**

	[C <sub>2</sub> mim][Tf <sub>2</sub> N]	[C <sub>3</sub> mim][Tf <sub>2</sub> N]	[C <sub>4</sub> mim][Tf <sub>2</sub> N]	[C <sub>5</sub> mim][Tf <sub>2</sub> N]	[C <sub>6</sub> mim][Tf <sub>2</sub> N]	[C <sub>7</sub> mim][Tf <sub>2</sub> N]	[C <sub>8</sub> mim][Tf <sub>2</sub> N]
<i>T</i> /K	10 <sup>4</sup> ( <i>x</i> <sub>IL</sub> ± σ <sup>a</sup> )	10 <sup>4</sup> ( <i>x</i> <sub>IL</sub> ± σ <sup>a</sup> )	10 <sup>4</sup> ( <i>x</i> <sub>IL</sub> ± σ <sup>a</sup> )	10 <sup>4</sup> ( <i>x</i> <sub>IL</sub> ± σ <sup>a</sup> )	10 <sup>5</sup> ( <i>x</i> <sub>IL</sub> ± σ <sup>a</sup> )	10 <sup>5</sup> ( <i>x</i> <sub>IL</sub> ± σ <sup>a</sup> )	10 <sup>5</sup> ( <i>x</i> <sub>IL</sub> ± σ <sup>a</sup> )
288.15	7.66 ± 0.01	5.15 ± 0.05	2.86 ± 0.01	1.84 ± 0.02	8.90 ± 0.03	4.85 ± 0.02	3.17 ± 0.01
293.15	8.03 ± 0.02	5.27 ± 0.01	2.92 ± 0.02	1.88 ± 0.03	8.96 ± 0.07	4.98 ± 0.04	3.23 ± 0.01
298.15	8.38 ± 0.05	5.40 ± 0.01	3.07 ± 0.01	1.96 ± 0.01	9.56 ± 0.02	5.09 ± 0.02	3.36 ± 0.01
303.15	8.75 ± 0.01	5.68 ± 0.01	3.18 ± 0.01	2.01 ± 0.01	9.73 ± 0.01	5.28 ± 0.09	3.55 ± 0.01
308.15	9.33 ± 0.08	6.04 ± 0.03	3.44 ± 0.02	2.18 ± 0.01	10.2 ± 0.1	5.81 ± 0.09	3.68 ± 0.02
313.15	9.85 ± 0.05	6.49 ± 0.05	3.94 ± 0.01	2.32 ± 0.04	11.7 ± 0.2	6.87 ± 0.01	3.94 ± 0.06
318.15	10.5 ± 0.1	7.01 ± 0.05	4.70 ± 0.01	2.53 ± 0.01	13.2 ± 0.2	7.93 ± 0.06	4.55 ± 0.07

<sup>a</sup> Standard deviation.**TABLE 3: Fitted Parameters for the Mole Fraction Solubility Correlations as a Function of Temperature**

IL	<i>A</i> ± σ <sup>a</sup>	( <i>B</i> ± σ <sup>a</sup> )/K	<i>C</i> ± σ <sup>a</sup>	( <i>D</i> ± σ <sup>a</sup> )/K	<i>E</i> ± σ <sup>a</sup>
[C <sub>2</sub> mim][Tf <sub>2</sub> N]	1.57 ± 0.09	−827 ± 26	−166 ± 22	6365 ± 1011	24 ± 3
[C <sub>3</sub> mim][Tf <sub>2</sub> N]	1.71 ± 0.10	−896 ± 31	−351 ± 20	14700 ± 899	52 ± 3
[C <sub>4</sub> mim][Tf <sub>2</sub> N]	1.78 ± 0.02	−936 ± 6	−873 ± 106	37782 ± 4807	130 ± 16
[C <sub>5</sub> mim][Tf <sub>2</sub> N]	1.29 ± 0.09	−831 ± 28	−375 ± 46	15725 ± 2095	55 ± 7
[C <sub>6</sub> mim][Tf <sub>2</sub> N]	1.48 ± 0.10	−909 ± 30	−670 ± 104	28778 ± 4739	99 ± 16
[C <sub>7</sub> mim][Tf <sub>2</sub> N]	1.57 ± 0.21	−948 ± 64	−917 ± 106	39641 ± 4814	136 ± 16
[C <sub>8</sub> mim][Tf <sub>2</sub> N]	1.12 ± 0.06	−833 ± 19	−518 ± 121	22032 ± 5471	76 ± 18

<sup>a</sup> Standard deviation.

### Thermodynamic Functions

When two partially miscible liquids are at thermodynamic equilibrium, the dissolution of one liquid into another is associated with changes in the thermodynamic functions, namely, standard molar Gibbs energy ( $\Delta_{sol}G_m^o$ ), standard molar enthalpy ( $\Delta_{sol}H_m^o$ ) and standard molar entropy ( $\Delta_{sol}S_m^o$ ) of solution, that can be determined from the temperature dependence of the experimental solubility data. These thermodynamic functions are associated with the changes that happen in the solute neighborhood, when the solute molecules are transferred to a hypothetical dilute ideal solution where the mole fraction of the solvent is equal to one and/or the solute is at infinite dilution and can be calculated according to the following equations:<sup>44</sup>

$$\Delta_{sol}G_m^o = -RT \ln(x_2)_p \quad (1)$$

$$\frac{\Delta_{sol}H_m^o}{RT^2} = \left( \frac{\partial \ln x_2}{\partial T} \right)_p \quad (2)$$

$$\Delta_{sol}S_m^o = R \left( \frac{\partial \ln x_2}{\partial \ln T} \right)_p \quad (3)$$

where  $x_2$  is the mole fraction solubility of the solute,  $R$  is the ideal gas constant,  $T$  is the temperature, the subscript  $p$  indicates that the process takes place at constant pressure, and the subscript  $m$  refers to the molar quantity.

Furthermore, dealing with liquid–liquid equilibrium, the standard molar enthalpy of solution,  $\Delta_{sol}H_m^o$ , is a sum of the standard molar enthalpy of solvation,  $\Delta_{svt}H_m^o$ , that reflects the solute–solvent interaction, and the standard molar enthalpy of vaporization of the solute to form an ideal gas,  $\Delta_l^s H_m^o$ ,

$$\Delta_{sol}H_m^o = \Delta_{svt}H_m^o + \Delta_l^s H_m^o \quad (4)$$

Thus, from the molar enthalpy of solution derived from experimental solubility data and using the molar enthalpy of vaporization of the solute, it is possible to estimate the molar

enthalpy of solvation of a given solute and thus infer about the solute–solvent interactions.

The standard molar Gibbs energy of solvation,  $\Delta_{svt}G_m^o$ , can be then derived using the hypothetical reference state for the solute, which considers the solute in the gas phase and at the standard pressure, as described below,

$$\Delta_{svt}G_m^o = \Delta_{sol}G_m^o + RT \ln \left( \frac{p(s_2, T)}{p^o} \right) \quad (5)$$

$$\Delta_{svt}S_m^o = \frac{\Delta_{svt}H_m^o - \Delta_{svt}G_m^o}{T} \quad (6)$$

where  $p(s_2, T)$  is the vapor pressure of the solute at the temperature  $T$  and  $p^o$  is the standard pressure of 10<sup>5</sup> Pa.

The thermodynamic functions presented above deal with solvation at a macroscopic level while the solvation is a molecular process, dependent upon local, rather than macroscopic, properties of the system. Another approach to define a standard state could be based on statistical mechanical methods as proposed by Ben-Naim.<sup>45</sup> The changes that occur in the solute neighborhood during the dissolution process due to the transfer of one solute molecule from a fixed position in an ideal gas phase into a fixed position in the solvent, at a constant temperature  $T$  and constant pressure  $p$ , with the composition of the system unchanged, are represented by the local molar Gibbs energy,  $\Delta_{svt}G_m^*$ , the local molar enthalpy,  $\Delta_{svt}H_m^*$ , and the local molar entropy,  $\Delta_{svt}S_m^*$ , of solvation.<sup>45–47</sup> It should be noted that these local molar solvation thermodynamic functions presented above have the advantage of being defined for the application in any concentration range including the study of the pure fluid. These local molar thermodynamic functions can be related to the conventional molar thermodynamic functions described in eqs 4 to 6 using the following eqs 7 to 9.

$$\Delta_{svt}G_m^* = \Delta_{svt}G_m^o - RT \ln \left( \frac{RT}{p^o V_{1,m}} \right) \quad (7)$$

$$\Delta_{svt}H_m^* = \Delta_{svt}H_m^o - RT(\alpha_1 - 1) \quad (8)$$

$$\Delta_{sur}S_m^* = \Delta_{sur}S_m^o + R \ln \left( \frac{RT}{p^o V_{1,m}} \right) - R(T\alpha_1 - 1) \quad (9)$$

where  $V_{1,m}$  is the molar volume of the solvent and  $\alpha_1$  is the isobaric thermal expansibility of the solvent, that can be derived from experimental density data.

## Results and Discussion

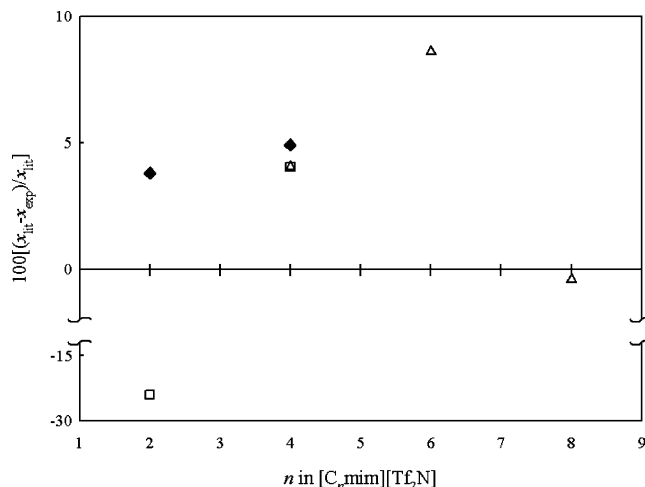
The mutual solubilities between the series  $[C_2mim][Tf_2N]$  to  $[C_8mim][Tf_2N]$  and water measured in the temperature range from 288.15 to 318.15 K and at atmospheric pressure are listed in Tables 1 and 2, as well as their respective standard deviations. The typical liquid–liquid equilibria behavior of increasing miscibility between both phases with the temperature was observed, and in spite of being considered “hydrophobic”, these ILs do present considerable solubilities for water, being substantially “hygroscopic”. This temperature dependence further indicates that the cross-contamination of water–IL systems will increase with the temperature increase.

The solubility of water in ILs, in mole fraction units, is several orders of magnitude higher than the solubility of ILs in water. These differences in the mutual solubilities were also predicted by molecular dynamics studies, where it was found that the IL ions are much less soluble in water than water is in the IL.<sup>48</sup> On the average, the authors stated that there is less than one single ion pair in the simulated bulk water slab, which means that the IL mole fraction solubility is less than  $10^{-3}$  for  $[C_2mim][Tf_2N]$ , what is in close agreement with the experimental results obtained in this work.

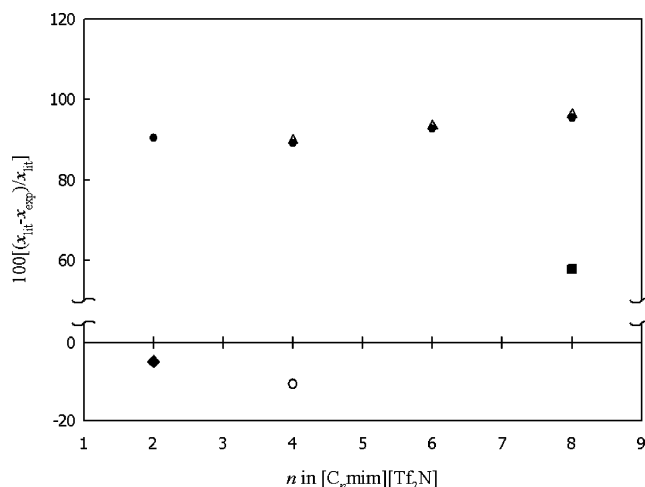
The experimental data obtained show that the decrease in the mutual solubilities between water and ILs is related to the increase in the hydrophobic character of the cation with the increase of the cation alkyl side chain length. The mole fraction solubilities of the studied ILs range from  $10^{-3}$  to  $10^{-5}$ , changing 2 orders of magnitude at the highest temperature studied. It is well-known that the anion plays the major effect in the mutual solubilities,<sup>14,31</sup> but it is here shown that the cation has also an important influence and can be used to tune the ILs mutual solubilities for the desired purposes.

Furthermore, the finding that the ILs solubility in water decreases with the alkyl chain length increase is in good agreement with toxicity studies.<sup>6–10</sup> Some contributions have already shown that the ILs toxicity increases with the alkyl chain length increase, which is a direct consequence of the ILs lipophilicity character increase.<sup>6–10</sup> It can be concluded that mutual solubility data constitute a valuable tool to predict and minimize the environmental impact of ionic liquids in aquatic systems prior to their applications.

An overall comparison of the experimental solubilities with the available literature data is shown in Figures 1 and 2. In Figure 1, the mole fraction solubility of water in ILs reported in literature, at two different temperatures, are compared against the results obtained in this work. In fact, there are large deviations between our data and some of the literature data, but this difference is also significant between different authors. In general, with the exception of Bonhôte et al.,<sup>28</sup> who shows an increase in water content with the alkyl chain length increase, the decreasing water solubility with alkyl chain length is generally observed. Figure 2 reports relative deviations between this work and literature data for the solubilities of  $[Tf_2N]$ -based ILs in water. The large deviations between different authors can be explained by the experimental difficulty in measuring the low ILs solubilities and also by the long equilibration time required to ensure that the equilibrium was reached. The results



**Figure 1.** Relative deviations between the experimental mole fraction solubility of water in ILs of this work ( $x_{exp}$ ) and those reported in the literature ( $x_{lit}$ ) at 293.15 K (empty symbols) and 298.15 K (full symbols) as a function of the carbon number,  $n$ , in  $[C_nmim][Tf_2N]$ :  $\Delta$ , McFarlane et al.;<sup>5</sup>  $\square$ , Bonhôte et al.;<sup>28</sup>  $\blacklozenge$ , Crosthwaite et al.<sup>21</sup>



**Figure 2.** Relative deviations between the experimental mole fraction solubility of ILs in water of this work ( $x_{exp}$ ) and those reported in the literature ( $x_{lit}$ ) at 293.15 K (empty symbols) and 298.15 K (full symbols) as a function of the carbon number,  $n$ , in  $[C_nmim][Tf_2N]$ :  $\blacktriangle$ , McFarlane et al.;<sup>5</sup>  $\circ$ , Shvedene et al.;<sup>25</sup>  $\blacklozenge$ , Crosthwaite et al.;<sup>21</sup>  $\bullet$ , Toh et al.;<sup>29</sup>  $\blacksquare$ , Papaiconomou et al.<sup>30</sup>

here obtained for  $[C_2mim][Tf_2N]$  at 298.15 K are in very close agreement with the results reported by Crosthwaite et al.<sup>21</sup> Furthermore, the results obtained for  $[C_4mim][Tf_2N]$  at 293.15 K are very close to the results of Shvedene et al.<sup>25</sup> who used an ion-selective electrode to perform these kind of measurements, showing the agreement between two different techniques for measuring solubilities of ILs in water.

**Temperature Dependence of Water in ILs Solubility.** The integration of eq 1, assuming that in the temperature range studied,  $\Delta_{sol}H_m^o$  can be considered temperature independent, leads to eq 10, that proved to accurately correlate the experimental solubility data of water in ILs,

$$\ln x_w = A + \frac{B}{(T/K)} \quad (10)$$

where  $x_w$  is the mole fraction solubility of the water in IL,  $T$  is the temperature, and  $A$  and  $B$  are correlation parameters.

The correlation constants obtained from the fitting of the experimental data are presented in Table 3. The proposed



**TABLE 4: Thermodynamic Standard Molar Properties of Solution of [Tf<sub>2</sub>N]-Based ILs in Water at 298.15 K**

IL	$(\Delta_{sol}H_m^0 \pm \sigma^a)/$ kJ·mol <sup>-1</sup>	$(\Delta_{sol}G_m^0 \pm \sigma^a)/$ kJ·mol <sup>-1</sup>	$(\Delta_{sol}S_m^0 \pm \sigma^a)/$ J·K <sup>-1</sup> ·mol <sup>-1</sup>
[C <sub>2</sub> mim][Tf <sub>2</sub> N]	7.1 ± 1.5	17.562 ± 0.016	-35.1 ± 5.1
[C <sub>3</sub> mim][Tf <sub>2</sub> N]	5.9 ± 1.5	18.652 ± 0.001	-42.6 ± 5.0
[C <sub>4</sub> mim][Tf <sub>2</sub> N]	7.1 ± 1.5	20.053 ± 0.008	-43.4 ± 5.1
[C <sub>5</sub> mim][Tf <sub>2</sub> N]	5.9 ± 1.5	21.169 ± 0.009	-51.0 ± 5.0
[C <sub>6</sub> mim][Tf <sub>2</sub> N]	6.0 ± 1.5	22.969 ± 0.004	-56.8 ± 5.1
[C <sub>7</sub> mim][Tf <sub>2</sub> N]	7.1 ± 1.5	24.504 ± 0.008	-58.4 ± 5.0
[C <sub>8</sub> mim][Tf <sub>2</sub> N]	5.6 ± 1.5	25.537 ± 0.002	-66.7 ± 5.1

<sup>a</sup> Standard deviation.

correlation shows a relative maximum deviation from experimental mole fraction data of 1%, which is observed for the lower temperature measured in this work and may be due to a decrease of the methodology accuracy at temperatures below the room temperature. Furthermore, the solubility of water in the studied series is large enough to not be considered at infinite dilution and thus the associated thermodynamic molar functions at 298.15 K for the equilibrium of water in the IL solution were not determined.

**Temperature Dependence of ILs in Water Solubility.** The correlation of experimental data for the solubility of ILs in water was carried out with eq 11 that proved to be able to describe the solubility of organics in water:

$$\ln x_{IL} = C + \frac{D}{(T/K)} + E \ln(T/K) \quad (11)$$

where  $x_{IL}$  is the mole fraction solubility of the IL in water,  $T$  is the temperature, and  $C$ ,  $D$ , and  $E$  are correlation parameters.

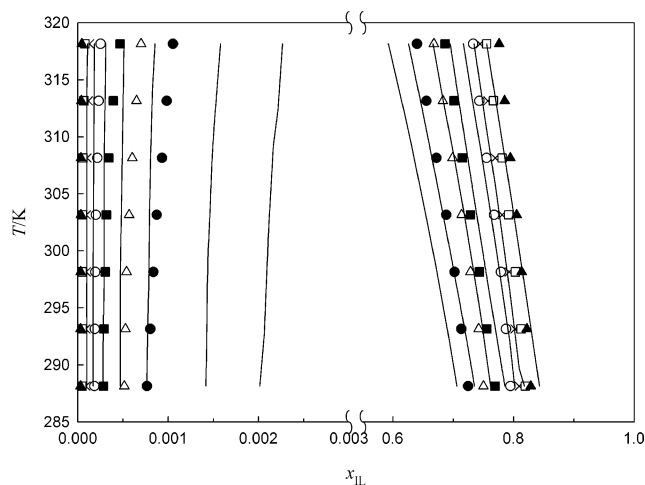
The correlation parameters for the various ionic liquids studied are reported in Table 3. The proposed correlation shows a relative maximum deviation from experimental mole fraction data of 3%, observed for the longer alkyl chain length ILs, which is probably associated with an increase of the experimental error due to the very small solubilities measured.

Because of the very low solubility of the ILs studied in water, the ILs in the water-rich phase may be considered to be at infinite dilution, and thus the associated standard thermodynamic molar functions of solution at 298.15 K were determined using eqs 1 to 3, derived from the mole fraction solubility dependence with temperature. The conventional standard molar enthalpy, Gibbs energy, and entropy of solution are reported in Table 4.

The enthalpy of solution derived for [C<sub>2</sub>mim][Tf<sub>2</sub>N] is very close to the value of 7.81 kJ·mol<sup>-1</sup> obtained by calorimetric measurements.<sup>49</sup> The enthalpies of solution of the ILs in water at 298.15 K are essentially independent of the alkyl chain length and reflect an endothermic process of dissolution. The enthalpy of dissolution of  $n$ -alkanes in water at 298.15 K displays also little dependency on the linear chain carbon number.<sup>50,51</sup> The ionic liquids, as the  $n$ -alkanes and other compounds which are poorly soluble in water, present, however, a significant increase in their solubility in water with the temperature increase.

The derived molar entropies of solution of ILs in water display a small decrease in the entropic effect of approximately  $-5 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  per methylene addition to the [C <sub>$n$</sub> mim] cation. The decrease of the ILs solubility in water with their alkyl chain length increase is therefore driven by the decrease in the entropy of dissolution. The same behavior is also observed for the  $n$ -alkanes dissolution in water, where the enthalpies of solution are also almost independent of the alkyl chain length and a remarkable entropic effect is observed.<sup>50,51</sup>

The conventional standard molar enthalpies of solvation,  $\Delta_{svt}H_m^o$ , were determined using the reported standard molar en-



**Figure 3.** Liquid-liquid phase diagram for water and ILs: ●, [C<sub>2</sub>mim][Tf<sub>2</sub>N]; △, [C<sub>3</sub>mim][Tf<sub>2</sub>N]; ■, [C<sub>4</sub>mim][Tf<sub>2</sub>N]; ○, [C<sub>5</sub>mim][Tf<sub>2</sub>N]; ×, [C<sub>6</sub>mim][Tf<sub>2</sub>N]; □, [C<sub>7</sub>mim][Tf<sub>2</sub>N]; ▲, [C<sub>8</sub>mim][Tf<sub>2</sub>N]. The symbols and the solid lines represent respectively the experimental data and COSMO-RS predictions. Prediction results follow the same trend as the experimental data.

thalpy of vaporization of each IL studied at 298.15 K,<sup>52</sup> and the conventional molar Gibbs energy of solvation using the ILs vapor pressures found in the open literature.<sup>53</sup> The reported vapor pressures of each IL were used to extrapolate them to 298.15 K using a linear fit of  $\ln[p(s, T)] = 1/T$  for the ILs available, while for the [C <sub>$n$</sub> mim][Tf<sub>2</sub>N] with  $n = 3, 5,$  and  $7$  from a linear representation of the  $p(s, T)$  as a function of  $n$  that proved to describe well the experimental data. The conventional solvation thermodynamic functions for the ILs studied are presented in Table 5. The local molar solvation properties of Ben-Naim were also determined and are presented in Table 5.<sup>51</sup>

The results obtained for all the ILs in water show a linear decrease of the molar enthalpies of solvation as a function of the alkyl chain length increase and represent an exothermic process of solvation, which reflects the favorable solute-solvent interactions. In fact, the results here obtained contribute to the understanding of the solubility mechanism of [Tf<sub>2</sub>N]-based ILs in water. At these very low concentrations, the ionic liquid solubility can be seen to occur hypothetically in a sequence of steps that could be summarized as (1) evaporation of a ion pair from the ionic liquid bulk; (2) dissociation of this ion pair; (3) formation of a cavity in the water to accommodate the ions; and (4) solvation of the ions in the water, since at these very low concentrations the ionic liquid is very extensively dissociated in the aqueous phase. There is an important increase in the heats of vaporization of the [C <sub>$n$</sub> mim][Tf<sub>2</sub>N] ionic liquids with increasing chain length as shown by Santos et al.<sup>52</sup> Keeping the same anion along the studied family, the energy required for cavity formation in step 3 will also increase with the cation volume. Although there is an increase in the energy of solvation with the cation size, as shown before, and a decrease in the interaction between cation and anion with increasing alkyl chain length as suggested by electrospray ionization mass spectrometry (ESI-MS) and tandem spectrometry (ESI-MS-MS)<sup>54</sup> studies, these changes will barely compensate the energy used in steps 1 and 3, and a constant standard heat of solution of approximately  $6.4 \pm 1.5 \text{ kJ}\cdot\text{mol}^{-1}$  is observed for this ionic liquid family. This leads to a situation, common to other hydrophobic compounds, where their solubility in water is driven by a decrease in the entropy of solution being the size of the molecules the controlling parameter on their solubility.

**TABLE 5: Thermodynamic Standard and Local Molar Properties of Solvation of [Tf<sub>2</sub>N]-Based ILs in Water at 298.15 K**

IL	( $\Delta_{solv}H_m^0 \pm \sigma^a$ )/ kJ·mol <sup>-1</sup>	( $\Delta_{solv}G_m^0 \pm \sigma^a$ )/ kJ·mol <sup>-1</sup>	( $\Delta_{solv}S_m^0 \pm \sigma^a$ )/ J·K <sup>-1</sup> ·mol <sup>-1</sup>	( $\Delta_{solv}H_m^* \pm \sigma^a$ )/ kJ·mol <sup>-1</sup>	( $\Delta_{solv}G_m^* \pm \sigma^a$ )/ kJ·mol <sup>-1</sup>	( $\Delta_{solv}S_m^* \pm \sigma^a$ )/ J·K <sup>-1</sup> ·mol <sup>-1</sup>
[C <sub>2</sub> mim][Tf <sub>2</sub> N]	-128.9 ± 6.2	-62.228 ± 0.016	-224 ± 21	-126.8 ± 6.2	-80.136 ± 0.016	-156 ± 21
[C <sub>3</sub> mim][Tf <sub>2</sub> N]	-141.1 ± 6.2	-61.423 ± 0.001	-267 ± 21	-138.9 ± 6.2	-79.331 ± 0.001	-200 ± 21
[C <sub>4</sub> mim][Tf <sub>2</sub> N]	-147.9 ± 6.2	-60.301 ± 0.008	-294 ± 21	-145.7 ± 6.2	-78.209 ± 0.008	-226 ± 21
[C <sub>5</sub> mim][Tf <sub>2</sub> N]	-156.1 ± 6.2	-59.975 ± 0.009	-322 ± 21	-153.9 ± 6.2	-77.883 ± 0.009	-255 ± 21
[C <sub>6</sub> mim][Tf <sub>2</sub> N]	-167.0 ± 6.2	-58.830 ± 0.004	-363 ± 21	-164.8 ± 6.2	-76.738 ± 0.004	-295 ± 21
[C <sub>7</sub> mim][Tf <sub>2</sub> N]	-172.9 ± 6.2	-58.561 ± 0.008	-383 ± 21	-170.7 ± 6.2	-76.469 ± 0.008	-316 ± 21
[C <sub>8</sub> mim][Tf <sub>2</sub> N]	-186.4 ± 6.2	-60.643 ± 0.002	-422 ± 21	-184.2 ± 6.2	-78.552 ± 0.002	-354 ± 21

<sup>a</sup> Standard deviation.

**Liquid–Liquid Equilibrium Prediction Using COSMO-RS.** COSMO-RS (conductor-like screening model for real solvents) is a novel method for the prediction of thermophysical properties of fluids based on unimolecular quantum calculations<sup>32–36</sup> and is an alternative to the structure-interpolating group-contribution methods (GCMs), equations of state (EoS) and correlations that require a large experimental database prior to their effective use. Furthermore, correlations are limited in scope and group contribution methods are not a suitable alternative at present due to the lack of IL group parameters. EoS are an interesting approach to the modeling of these systems but they require the ILs critical parameters that are not presently available.

The standard procedure of COSMO-RS calculations consists essentially of two steps: quantum chemical COSMO calculations for the molecular species involved, where the information about solvents and solutes is extracted, and COSMO-RS statistical calculations performed with the COSMOtherm program.<sup>55,56</sup>

Through the COSMO calculations, all molecules are supposed to act as solute molecules in a virtual conductor environment, where these molecules induce a polarization charge density  $\sigma$  on the interface between the molecule and the conductor, that is, on the molecular surface. These charges act back on the solute and generate a more polarized electron density than in vacuum. During the quantum chemical self-consistency cycle, the solute molecule is converged to its energetically optimal state in a conductor with respect to electron density, while the molecular geometry can be optimized using conventional methods for calculations in vacuum. Although time-consuming, one advantage of this procedure is that the quantum chemical calculations have to be performed just once for each ion or solvent of interest.

The COSMO-RS calculation procedure was performed using the COSMOtherm program<sup>55,56</sup> and describes all of the interactions between molecules as contact interactions of the molecular surfaces. These interactions can be related to the screening charge densities  $\sigma$  and  $\sigma'$  of the interacting surface pieces. For the statistical mechanical calculation, the molecular surface is split into small effective areas,  $a_{\text{eff}}$ , and the contact between each of these areas is considered to be independent. The application of statistical thermodynamics gives the chemical potential of each component, and from these, liquid–liquid equilibria (LLE), vapor–liquid equilibria (VLE), and other thermophysical properties of any mixture can be derived.

Within the COSMOtherm program, a particular pseudobinary approach was used to calculate the LLE of the ILs and water systems, with the cation and anion of the IL taken as separated compounds with the same mole fraction. The chemical potentials are calculated for the ternary system (anion + cation + water) with the chemical potential of the IL as the sum of the chemical potentials of both the cation and the anion. Finally, a numerical approach was used to find the two compositions having equal chemical potentials of the three components (in the pseudobinary

system) in the two phases at a particular temperature. The COSMO-RS calculations were carried at the BP/TZVP level (Turbomole,<sup>57,58</sup> DFT/COSMO calculation with the BP functional and TZVP<sup>59</sup> basis set using the optimized geometries at the same level of theory) and at the parameter file BP\_TZVP\_C21\_0105.

Figure 3 presents the liquid–liquid phase diagram between the [C<sub>2</sub>–C<sub>8</sub>mim][Tf<sub>2</sub>N] series and water and it should be noted the asymmetrical character of these binary systems behavior when adopting the mole fraction basis. The overall comparison between the experimental data and the predictive results is presented in Figure 3. The results obtained from COSMO-RS calculations show an acceptable agreement with the experimental data and follow the same hydrophobic tendency increase with the cation alkyl chain length increase for both rich phases, depicting the good qualitatively prediction capability of this model when dealing with the alkyl chain length impact in these mutual solubilities. Higher relative deviations were observed in the water-rich phase, probably due to the low solubility of the studied ILs in water. COSMO-RS can thus be very useful for the scanning of the growing number of known ILs to find suitable candidates, or to help in the design of new ILs, for specific applications before extensive experimental measurements are carried out.

## Conclusions

Novel data for the mutual solubilities between water and the [C<sub>2</sub>mim][Tf<sub>2</sub>N] to [C<sub>8</sub>mim][Tf<sub>2</sub>N] series of ILs in the temperature range between 288.15 and 318.15 K at atmospheric pressure were presented. It was observed that the ionic liquid hydrophobic character increases with the cation alkyl chain length increase and that the solubility of these ionic liquids in water is entropically driven. Moreover, the amphiphilic character of the imidazolium-based salts can be used to fine-tune the ILs mutual solubilities with water and to predict their ecotoxicity impact.

The standard molar enthalpies of solution of the ILs in water are significantly temperature dependent in the studied temperature range but showed to be essentially independent of the alkyl chain length at 298.15 K. The decrease of the ILs solubility is therefore driven by the entropy of dissolution decrease with the cation alkyl side chain increase. In fact, the dissolution behavior of ILs in water is qualitatively very similar to that observed for the *n*-alkanes and other organic compounds poorly soluble in water.

COSMO-RS showed to be capable to produce acceptable predictions for the liquid–liquid equilibria behavior of systems involving ILs and water, accordingly to both the ILs structural modifications and the temperature dependence. This model can be of considerable value for the design of ILs with tailored properties before taking extensive experimental measurements.

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