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# Effect of Water on the Viscosities and Densities of 1-Butyl-3-methylimidazolium Dicyanamide and 1-Butyl-3-methylimidazolium Tricyanomethane at Atmospheric Pressure<sup>†</sup>

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Despite the recent increase in the number of works addressing the effect of water on the thermophysical properties of ionic liquids (ILs), in particular densities and viscosities, the strong effect of the water content in the region of low water content on these properties requires further study for a deeper understanding of the phenomenon. Densities and viscosities of two imidazolium-based ionic liquids, 1-butyl-3-methylimidazolium dicyanamide [C<sub>4</sub>mim][N(CN)<sub>2</sub>] and 1-butyl-3-methylimidazolium tricyanomethane [C<sub>4</sub>mim][C(CN)<sub>3</sub>], and their binaries with water, for mole fractions up to 0.6, at atmospheric pressure and temperatures from (278.15 to 363.15) K were determined. The densities and viscosities of the pure ionic liquids and their binaries with water were described successfully by using several correlations. An extension to the Ye and Shreeve group contribution method shows a good agreement with the density data. An Orrick–Erbar-type approach and the Vogel–Tammann–Fulcher method were also applied to the experimental viscosity data, presenting a good agreement and allowing the estimation of new group contribution parameters, extending the applicability of these methods to new ILs. For mixtures, the one-constant Grunberg and Nissan equation was investigated for the correlation of the experimental viscosity binary mixture data of ILs + H<sub>2</sub>O, providing a good description of the experimental data using a single parameter for each ionic liquid studied.

## Introduction

Ionic liquids (ILs) are a class of *neoteric* solvents composed of large organic cations and organic or inorganic anions that at, or near, room temperature cannot form an ordered crystal and thus remain in the liquid state. ILs are becoming one of the fastest growing “green” media for chemists and engineers, bridging academic and industrial interests. Their tunable properties, through an endless combination of cations and anions, allow the design of solvents for the development of more efficient processes and products.<sup>1–9</sup>

During the last couple of years a number of studies have addressed the effect of water on the thermophysical and thermodynamic properties of ILs, in particular for densities and viscosities.<sup>1–3,5,8,10,11</sup> It is well-known that the phase equilibrium and thermophysical properties of ILs are greatly influenced by their water content.<sup>2–4,8,12–18</sup> Nonetheless, the strong effect of water content on the viscosities of ionic liquids is still of interest and an active area of study aimed at developing a deeper understanding of the phenomenon.

The study of the new classes of acidic or basic ILs is of great importance since the efficiency of many processes depends on the basicity of the media or can be controlled by it. In the wake of a previous work<sup>19</sup> where the basicity of the N(CN)<sub>2</sub> anion, as a means to enhance the absorption of sour gases, was investigated, the density and viscosity data for the pure and water

binary mixtures of 1-butyl-3-methylimidazolium dicyanamide [C<sub>4</sub>mim][N(CN)<sub>2</sub>] and 1-butyl-3-methylimidazolium tricyanomethane [C<sub>4</sub>mim][C(CN)<sub>3</sub>] were measured, at atmospheric pressure, for molar compositions up to 0.6 from (278.15 to 363.15) K.

A large number of methods developed to estimate the viscosity and density of pure compounds and their mixtures are available, standing as a key element on the development of more efficient processes and products, due to the lack of a wider selection of thermophysical properties. Thus, density<sup>20</sup> and viscosity<sup>8,21</sup> correlations previously proposed by us are here tested and extended for these new anions.

For mixtures, the one-constant Grunberg and Nissan<sup>22</sup> equation is here investigated for the correlation of the viscosity for binary mixtures of ILs + H<sub>2</sub>O, providing a good description of the experimental data.

## Experimental Section

**Materials and Procedure.** Two ILs based on the 1-butyl-3-methylimidazolium cation, 1-butyl-3-methylimidazolium dicyanamide, [C<sub>4</sub>mim][N(CN)<sub>2</sub>], and 1-butyl-3-methylimidazolium tricyanomethane, [C<sub>4</sub>mim][C(CN)<sub>3</sub>], were used in this study. The [C<sub>4</sub>mim][N(CN)<sub>2</sub>] was acquired at IoLiTec with mass fraction purities higher than 99 % and bromide impurity mass fraction lower than 10<sup>−4</sup>. The [C<sub>4</sub>mim][C(CN)<sub>3</sub>] was acquired at Merck with mass fraction purities higher than 98 % and halide mass fraction impurities lower than 10<sup>−4</sup>. The purities stated by the supplier, of each ionic liquid, were checked by <sup>1</sup>H NMR and <sup>13</sup>C NMR.

As discussed above, the viscosity of an ionic liquid is greatly influenced by its water content. Thus, to reduce to negligible

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values both water and volatile compounds, vacuum (0.1 Pa), stirring, and moderate temperature (353 K) for a period of at least 48 h were applied prior to the measurements. The final IL water content was determined with a Mettler Toledo DL32 Karl Fischer coulometer (using the Hydranal - Coulomat E from Riedel-de Haën as analyte), indicating a water mass fraction of  $16 \cdot 10^{-6}$  and  $28 \cdot 10^{-6}$  for  $[\text{C}_4\text{mim}][\text{C}(\text{CN})_3]$  and  $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$ , respectively.

The water used was double-distilled, passed through a reverse osmosis system, and further treated with a Milli-Q plus 185 water purification apparatus. It has a resistivity of  $18.2 \text{ M}\Omega \cdot \text{cm}$  and a total organic carbon (TOC) smaller than  $5 \mu\text{g} \cdot \text{L}^{-1}$ , and it is free of particles greater than  $0.22 \mu\text{m}$ .

**Experimental Measurements.** Measurements of viscosity and density were performed in the temperature range of (278 to 363) K at atmospheric pressure using an automated SVM 3000 Anton Paar rotational Stabinger viscometer–densimeter. The viscometer is based on a tube filled with the sample in which floats a hollow measuring rotor. Due to its low density, the rotor is centered in the heavier liquid by buoyancy forces. Consequently, a measuring gap is formed between the rotor and the tube. The rotor is forced to rotate by shear stresses in the liquid and is guided axially by a built-in permanent magnet, which interacts with a soft iron ring. The rotating magnetic field delivers the speed signal and induces eddy currents in the surrounding copper casing. These eddy currents are proportional to the speed of the rotor and exert a retarding torque on the rotor. Two different torques influence the speed of the measuring rotor, and at the equilibrium, the two torques are equal and the viscosity can be traced back to a single speed measurement. The SVM 3000 uses Peltier elements for fast and efficient thermostability. The temperature uncertainty is  $\pm 0.02 \text{ K}$  from (288.15 to 378.15) K. The relative uncertainty of the dynamic viscosity is  $\pm 0.35 \%$ , and the absolute uncertainty of the density is  $\pm 0.0005 \text{ g} \cdot \text{cm}^{-3}$ . Further details about the equipment and method can be found elsewhere.<sup>23</sup>

The binary systems ( $\text{H}_2\text{O} + \text{IL}$ ) were prepared by weighing both compounds using a high-precision analytical balance (Sartorius MC210P) with an uncertainty of  $\pm 1 \cdot 10^{-4} \text{ g}$  immediately before the measurements.

The IL purity was checked by NMR at the end of the study to confirm that no degradation due to the contact between the IL and water takes place during the measurements.

## Models

**Pure Liquid Viscosity Correlation.** A large number of methods developed to estimate the viscosity of pure compounds and mixtures are available.<sup>24–29</sup> The most common methods for the estimation of viscosity of pure and mixed liquids containing complex molecules, for which limited information is available, are based on group contribution (e.g., the Orrick–Erbar method,<sup>24</sup> the Sastry–Rao method,<sup>30</sup> and the UNIFAC–VISCO method<sup>31</sup>), the corresponding states concept (e.g., Przedziecki and Sridhar,<sup>32</sup> Teja and Rice,<sup>33,34</sup> and Queimada et al.<sup>35,36</sup>), or the corresponding-states group-contribution method (e.g., Yinghua et al.<sup>37</sup>).

In a previous work,<sup>8</sup> using an Orrick–Erbar-type approach<sup>24</sup> the viscosity of a large number of ionic liquids was estimated by fitting the parameters  $A$  and  $B$  of the following equation

$$\ln\left(\frac{\eta}{\rho M}\right) = A + \frac{B}{T/K} \quad (1)$$

where  $\eta$  and  $\rho$  are the viscosity in  $\text{mPa} \cdot \text{s}$  and density in  $\text{g} \cdot \text{cm}^{-3}$ , respectively.  $M$  is the molecular weight, and  $T$  is the absolute

temperature in K. The group contribution parameter table for  $A$  and  $B$  is here extended for the  $\text{N}(\text{CN})_2$  and  $\text{C}(\text{CN})_3$  anions.

To overcome the liquid density dependence of the previous approach, a correlation based on the Vogel–Tammann–Fulcher equation (eq 2) was also proposed<sup>21</sup>

$$\ln \eta/\text{Pa} \cdot \text{s} = A_\eta + \frac{B_\eta}{(T/K - T_{0\eta})} \quad (2)$$

where  $\eta$  is viscosity;  $T$  is temperature; and  $A_\eta$ ,  $B_\eta$ , and  $T_{0\eta}$  are adjustable parameters. The ratio of parameters  $B_\eta$  and  $T_{0\eta}$ ,  $B_\eta/T_{0\eta}$ , is also known as Angell strength parameter. As shown before,<sup>21</sup>  $T_{0\eta}$  is similar for all the ILs studied with an optimum and constant value of 165.06 K.  $A_\eta$  and  $B_\eta$  can be obtained by a group contribution method according to

$$A_\eta = \sum_{i=1}^k n_i a_{i,\eta} \quad (3)$$

$$B_\eta = \sum_{i=1}^k n_i b_{i,\eta} \quad (4)$$

where  $n_i$  is the number of groups of type  $i$ ;  $k$  is the total number of different groups in the molecule; and the parameters  $a_{i,\eta}$  and  $b_{i,\eta}$  are estimated parameters. The parameters  $a_{i,\eta}$  and  $b_{i,\eta}$  were reported for the studied ILs and here extended for the  $\text{N}(\text{CN})_2$  and  $\text{C}(\text{CN})_3$  anions.

**Liquid Mixture Viscosity Correlation.** The notion that liquid viscosities are very sensitive to the structure of the constituent molecules, at reduced temperatures below  $T_r \approx 0.7$ , also holds for liquid mixtures. Furthermore, even mild association effects between components can often significantly affect the viscosity. For a mixture of liquids, the shape of the curve of viscosity as a function of composition can be nearly linear for so-called “ideal” mixtures, but systems containing alcohols and/or water often exhibit a maximum or a minimum and sometimes both.<sup>38</sup>

Almost all methods to estimate or correlate liquid mixture viscosities rely on the knowledge of the pure components viscosities, making these methods interpolative. Nevertheless, there is no agreement on the best way to carry out the interpolation. Irving,<sup>38,39</sup> back in 1977, inspected more than 50 equations for binary liquid viscosities, classifying them by type and pointing out that only a few of them did not require some adjustable constant, determined from experimental mixture data. Moreover, the few that do not require such a parameter are only applicable to systems of similar components with comparable viscosities. Irving,<sup>38,39</sup> in a companion report from the National Engineering Laboratory, has also evaluated the 25 more promising equations with experimental data from the literature, recommending the one-constant Grunberg and Nissan<sup>22</sup> equation.

In this procedure, the low-temperature liquid viscosity for mixtures is given as

$$\ln \eta_m = \sum x_i \ln \eta_i + \frac{1}{2} \sum_{i=1}^n \sum_{j=1}^n x_i x_j G_{ij} \quad (5)$$

or for a binary system

$$\ln \eta_m = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12} \quad (6)$$

since  $G_{ii} = 0$ . The  $x$  is the liquid mole fraction of the  $i$ th component, and  $G_{ij}$  is an interaction parameter which is a function of the components  $i$  and  $j$  as well as the temperature. For mixtures of associating compounds,  $G_{ij}$  is a mild function of temperature<sup>40</sup> and can be determined as

$$G_{ij}(T) = 1 - [1 - G_{ij}(298 \text{ K})] \frac{573 - T/\text{K}}{275} \quad (7)$$

The  $G_{ij}$  parameter at 298 K, according to the Grunberg and Nissan method,<sup>22</sup> could be estimated by group contribution. To our knowledge, this approach has never been applied to ionic liquids, and therefore, due to the lack of a wider selection of IL cations and anions, only a generic  $G_{ij}$  parameter, for each IL, was estimated here.

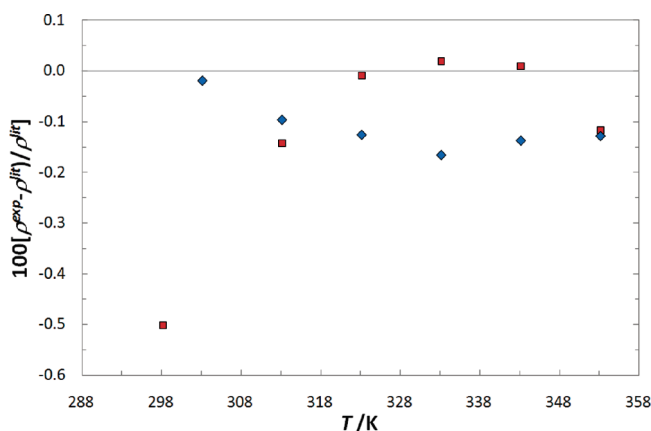
**Pure Liquid Density Correlation.** In a previous work,<sup>20</sup> the Ye and Shreeve<sup>41</sup> approach has been extended to the estimation of ionic liquid densities for a wide range of temperature, (273.15 to 393.15) K, and pressure, (0.10 to 100) MPa, according to the equation

$$\rho = \frac{M}{NV(a + bT + cp)} \quad (8)$$

where  $\rho$  is the density in  $\text{kg} \cdot \text{m}^{-3}$ ;  $M$  is the molecular weight in  $\text{kg} \cdot \text{mol}^{-1}$ ;  $N$  is the Avogadro constant;  $V$  is the molecular volume in  $\text{\AA}^3$ ,  $T$  is the temperature in K; and  $p$  is the pressure in MPa. This model will be tested here against the density data measured here.

## Results and Discussion

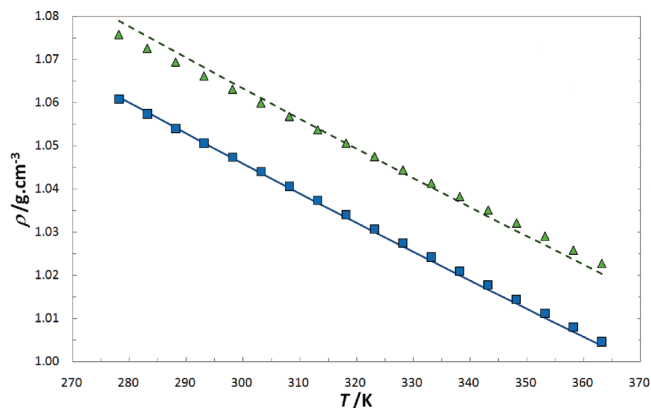
The viscosity and density measurements for the pure ILs and their mixtures with water were carried out in the temperature



**Figure 1.** Relative deviations between this work's experimental data and density data available in the literature as function of temperature.  $\blacklozenge$ ,  $[\text{C}_4\text{mim}][\text{C}(\text{CN})_3]$  from Gardas et al.;<sup>42</sup>  $\blacksquare$ ,  $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$  from Fredlake et al.<sup>6</sup>

**Table 1.** Experimental Viscosities,  $\eta$ , and Densities,  $\rho$ , for  $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$  and  $[\text{C}_4\text{mim}][\text{C}(\text{CN})_3]$

$T/\text{K}$	$[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$		$[\text{C}_4\text{mim}][\text{C}(\text{CN})_3]$	
	$\eta/\text{mPa} \cdot \text{s}$	$\rho/\text{g} \cdot \text{cm}^{-3}$	$\eta/\text{mPa} \cdot \text{s}$	$\rho/\text{g} \cdot \text{cm}^{-3}$
278.15	82.066	1.0758	76.637	1.0608
283.15	62.537	1.0726	56.944	1.0574
288.15	48.929	1.0694	43.550	1.0540
293.15	39.140	1.0662	34.129	1.0506
298.15	31.802	1.0631	27.318	1.0473
303.15	26.286	1.0599	22.263	1.0440
308.15	21.788	1.0568	18.449	1.0406
313.15	18.495	1.0537	15.512	1.0373
318.15	15.883	1.0506	13.210	1.0340
323.15	13.777	1.0475	11.381	1.0307
328.15	12.062	1.0444	9.9083	1.0275
333.15	10.653	1.0413	8.7048	1.0242
338.15	9.4752	1.0382	7.7117	1.0209
343.15	8.4846	1.0351	6.8811	1.0177
348.15	7.6425	1.0321	6.1810	1.0144
353.15	6.9228	1.0290	5.5892	1.0112
358.15	6.3043	1.0258	5.0804	1.0080
363.15	5.7700	1.0227	4.6415	1.0046



**Figure 2.** Density versus temperature for:  $\blacktriangle$ ,  $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$  and  $\blacksquare$ ,  $[\text{C}_4\text{mim}][\text{C}(\text{CN})_3]$ . The dashed and solid curves are calculated with the Gardas and Coutinho model<sup>20</sup> for  $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$  and  $[\text{C}_4\text{mim}][\text{C}(\text{CN})_3]$ , respectively.

range of (278 to 363) K at atmospheric pressure. The experimental viscosities and densities of the pure ILs studied here are reported in Table 1, and the viscosities and densities of the binary mixtures are reported in Tables 2 to 5. A comparison between the density data measured on this work and those previously reported by us<sup>42</sup> and by Fredlake et al.<sup>6</sup> (Figure 1) shows a good agreement with relative average deviation of  $-0.08\%$  and  $-0.12\%$ , respectively.

The extension of the Ye and Shreeve<sup>41</sup> group contribution method developed in our research group<sup>20</sup> was applied to estimate the pure component density data. The molecular volumes,  $V$ , of ions and groups, listed in Table 6, were either taken from the literature<sup>41</sup> or calculated following the Jenkin procedure.<sup>43</sup> The predicted densities are in good agreement with the experimental data as shown in Figure 2, with a relative average deviation of  $0.14\%$  and  $0.06\%$  for the  $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$  and  $[\text{C}_4\text{mim}][\text{C}(\text{CN})_3]$ , respectively.

The Gardas and Coutinho Orrick–Erbar approach<sup>8</sup> was applied to the correlation of the viscosity data measured in this work. The group contribution tables previously reported<sup>8</sup> are here further extended to the  $\text{N}(\text{CN})_2$  and  $\text{C}(\text{CN})_3$  anions with the parameters reported in Table 6. The Gardas and Coutinho viscosity correlation based on the Vogel–Tammann–Fulcher equation<sup>21</sup> was also applied. This model parameter table was also enhanced by the inclusion of two new  $a_{i,\eta}$  and  $b_{i,\eta}$  parameters for the  $\text{N}(\text{CN})_2$  and  $\text{C}(\text{CN})_3$  anions, thus extending the applicability of the model to new ILs.<sup>21</sup> The new parameters are reported in Table 6. As depicted in Figure 3, the Vogel–Tammann–Fulcher<sup>21</sup> model describes very well the experimental data in all the entire temperature ranges, presenting average relative deviations of  $1.27\%$  and  $1.44\%$  for the  $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$  and  $[\text{C}_4\text{mim}][\text{C}(\text{CN})_3]$ , respectively. By contrast, the Orrick–Erbar model fails to describe the viscosity at temperatures below 298 K and presents higher relative average deviations ( $5.90\%$  and  $6.72\%$  for the  $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$  and  $[\text{C}_4\text{mim}][\text{C}(\text{CN})_3]$ , respectively).

The excess volumes were calculated from the measurements according to the following equation<sup>44,45</sup> and depicted in Figure 4.

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \quad (9)$$

The excess thermodynamic properties, which depend on the composition, temperature, or both, are of great importance in understanding the nature of the molecular interactions present in the binary mixtures.

**Table 2.** Experimental Viscosities,  $\eta$ , for Binary Mixtures of  $\text{H}_2\text{O}$  (1) +  $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$  (2)

$x_1$	$T/\text{K}$								
	278.15	288.15	298.15	308.15	318.15	328.15	338.15	348.15	358.15
	$\eta/\text{mPa}\cdot\text{s}$								
0.0000	82.066	48.929	31.802	21.788	15.883	12.062	9.4752	7.6425	6.3043
0.0590	74.203	44.995	29.554	20.604	15.088	11.493	9.0473	7.3143	6.0482
0.1963	58.696	36.447	24.399	17.288	12.824	9.8847	7.8522	6.3968	5.3220
0.2736	48.940	30.873	20.945	14.996	11.216	8.7018	6.9498	5.6875	4.7483
0.3500	37.598	24.281	16.749	12.160	9.1985	7.2021	5.7983	4.7770	4.0073
0.3974	31.981	20.877	14.521	10.611	8.0724	6.3457	5.1257	4.2370	3.5773
0.4831	23.225	15.375	10.797	7.9511	6.0723	4.7921	3.8838	3.2227	2.7111

**Table 3.** Experimental Densities,  $\rho$ , for Binary Mixtures of  $\text{H}_2\text{O}$  (1) +  $[\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$  (2)

$x_1$	$T/\text{K}$								
	278.15	288.15	298.15	308.15	318.15	328.15	338.15	348.15	358.15
	$\rho/\text{g}\cdot\text{cm}^{-3}$								
0.0000	1.0758	1.0694	1.0631	1.0568	1.0506	1.0444	1.0382	1.0321	1.0258
0.0590	1.0753	1.0689	1.0625	1.0562	1.0501	1.0439	1.0377	1.0315	1.0253
0.1963	1.0743	1.0678	1.0614	1.0550	1.0487	1.0424	1.0362	1.0300	1.0238
0.2736	1.0728	1.0664	1.0599	1.0536	1.0473	1.0410	1.0347	1.0285	1.0223
0.3500	1.0711	1.0646	1.0591	1.0516	1.0452	1.0388	1.0324	1.0261	1.0198
0.3974	1.0694	1.0629	1.0563	1.0498	1.0433	1.0369	1.0305	1.0241	1.0177
0.4831	1.0662	1.0596	1.0529	1.0462	1.0396	1.0330	1.0264	1.0198	1.0132

**Table 4.** Experimental Viscosities,  $\eta$ , for Binary Mixtures of  $\text{H}_2\text{O}$  (1) +  $[\text{C}_4\text{mim}][\text{C}(\text{CN})_3]$  (2)

$x_1$	$T/\text{K}$								
	278.15	288.15	298.15	308.15	318.15	328.15	338.15	348.15	358.15
	$\eta/\text{mPa}\cdot\text{s}$								
0	76.637	43.550	27.318	18.449	13.210	9.9083	7.7117	6.181	5.0804
0.0458	67.845	39.303	25.053	17.190	12.476	9.463	7.433	6.006	4.966
0.1008	53.191	31.743	20.803	14.542	10.680	8.176	6.473	5.261	4.375
0.1750	47.795	28.846	19.027	13.375	9.889	7.615	6.056	4.944	4.125
0.2116	44.295	26.978	17.898	12.670	9.432	7.303	5.835	4.783	4.001
0.2885	37.679	23.277	15.616	11.153	8.361	6.514	5.232	4.309	3.618
0.4273	28.900	18.235	12.430	8.990	6.810	5.351	4.329	3.586	3.028
0.5034	25.052	15.990	10.999	8.013	6.106	4.820	3.916	3.273	2.748
0.5607	21.785	14.026	9.713	7.104	5.428	4.295	3.496	2.912	2.472

**Table 5.** Experimental Densities,  $\rho$ , for Binary Mixtures of  $\text{H}_2\text{O}$  (1) +  $[\text{C}_4\text{mim}][\text{C}(\text{CN})_3]$  (2)

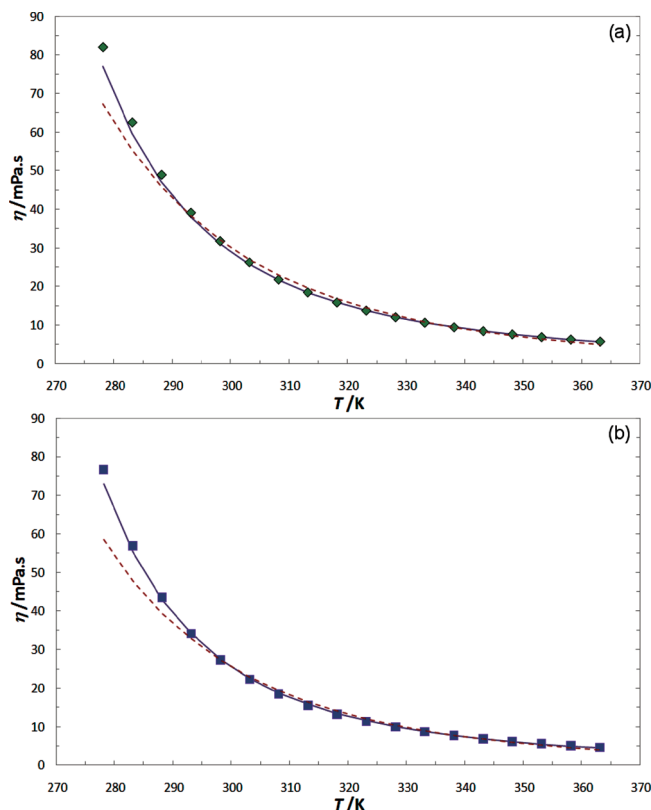
$x_1$	$T/\text{K}$								
	278.15	288.15	298.15	308.15	318.15	328.15	338.15	348.15	358.15
	$\rho/\text{g}\cdot\text{cm}^{-3}$								
0	1.0608	1.0540	1.0473	1.0406	1.0340	1.0275	1.0209	1.0144	1.0080
0.0458	1.0602	1.0532	1.0464	1.0395	1.0328	1.0261	1.0194	1.0129	1.0064
0.1008	1.0598	1.0528	1.0458	1.0390	1.0321	1.0254	1.0187	1.0121	1.0056
0.1750	1.0591	1.0521	1.0451	1.0380	1.0313	1.0245	1.0178	1.0112	1.0047
0.2116	1.0586	1.0515	1.0445	1.0376	1.0308	1.0240	1.0172	1.0106	1.0040
0.2885	1.0574	1.0504	1.0434	1.0364	1.0296	1.0228	1.0161	1.0094	1.0028
0.4273	1.0561	1.0489	1.0417	1.0347	1.0277	1.0208	1.0139	1.0071	1.0003
0.5034	1.0548	1.0476	1.0404	1.0332	1.0261	1.0190	1.0120	1.0051	0.9984
0.5607	1.0542	1.0469	1.0396	1.0324	1.0252	1.0180	1.0109	1.0039	0.9971

The excess molar volumes are positive over the whole range of compositions and temperatures, as depicted in Figure 4, and do not support or suggest a significant anion–water interaction. The decrease of the organization modes of the molecules within the mixtures is due to a disruption of the ordered molecular structure within the liquid and the weakening or breaking of strong like interactions. Due to the high relative permittivity of water, a decrease in the electrostatic force operating between ions is expected. Although we have not determined the excess volume in the entire concentration range, Figure 4 shows asymmetrical  $V^E(x)$  curves, presenting a maximum for water mole fraction higher than 0.5 for the  $\text{H}_2\text{O} + [\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$  system and around 0.3 for the  $\text{H}_2\text{O} + [\text{C}_4\text{mim}][\text{C}(\text{CN})_3]$ , suggesting that the breaking of strong interactions of the ILs is not so effective when there are few water molecules and that the ordered pure IL molecular structure is not destroyed.<sup>49,50</sup> As water concentration increases, the structure of the ionic liquid becomes weaker upon mixing, a fact that can be explained taking

into account the ordered structure of ILs, dominated by long-range forces (Coulombic), which are destroyed at low IL concentration.<sup>50</sup> This is in agreement with the atomistic simulations of Kelkar and Maginn<sup>10</sup> which suggest that this is because water preferentially solvates the anions and then begins to form clusters at higher concentrations. These authors<sup>10</sup> report that as the water concentration increases water–anion association probabilities remain high while water–cation associations decrease and water–water associations increase, indicating that water tends to cluster in ionic liquids.

Moreover, the increase of the  $V^E$  with temperature indicates that the mixture is more expansible than the pure compounds. Thus, the temperature increase leads to the loosening of aggregates in pure ionic liquids. In addition, hydrogen bonding is more temperature dependent (becoming negligible at high temperatures) than Coulombic interactions. As temperature increases, the negative contribution to  $V^E$  due to water–ion H-bonds decreases.





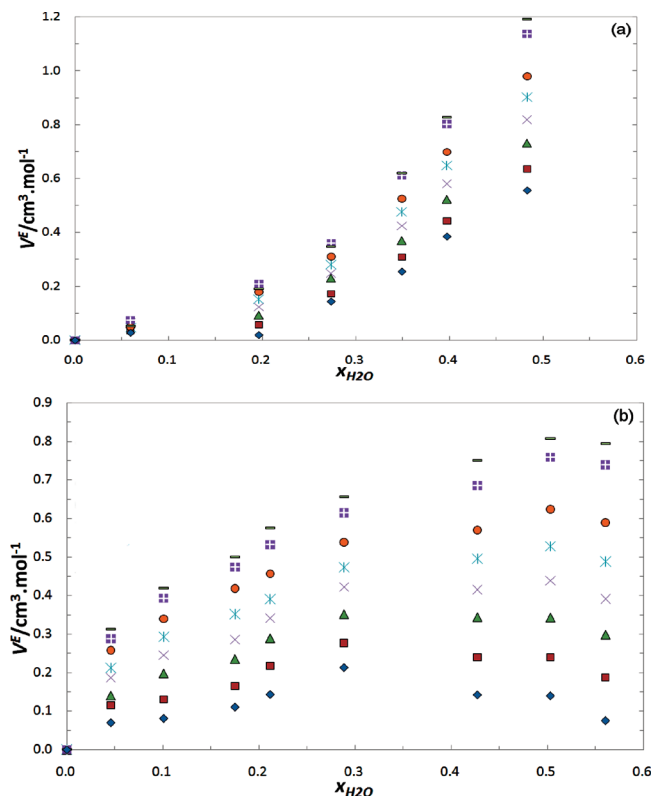
**Figure 3.** Viscosity versus temperature for the [C4mim][N(CN)2] (a) and [C4mim][C(CN)3] (b) ILs. The symbols represent experimental values; the solid curves are calculated with the Vogel–Tammann–Fulcher<sup>21</sup> model; and the dashed curves are calculated with the Orrick–Erbar<sup>24</sup> model.

**Table 6.** Group Contribution Parameters for the Orrick and Erbar<sup>24</sup> (Equation 1), Vogel–Tammann–Fulcher<sup>21</sup> (Equations 3 and 4), Grunberg and Nissan<sup>22</sup> (Equation 7), and Ye and Shreeve<sup>41</sup> Methods

Orrick and Erbar Method <sup>24</sup>		
cations/anions/groups	A	B/K
1,3-dimethylimidazolium (+)	6.56 <sup>a</sup>	1757.1 <sup>a</sup>
N(CN) <sub>2</sub> <sup>−</sup>	−19.22	510.0
C(CN) <sub>3</sub> <sup>−</sup>	−19.54	590.0
CH <sub>2</sub>	−0.63 <sup>a</sup>	250.4 <sup>a</sup>
CH <sub>3</sub>	−0.74 <sup>a</sup>	250.0 <sup>a</sup>
Vogel–Tammann–Fulcher Method <sup>21</sup>		
cations/anions/groups	$a_{i,\eta}$	$b_{i,\eta}/K$
1,3-dimethylimidazolium (+)	−7.271 <sup>a</sup>	510.51 <sup>a</sup>
N(CN) <sub>2</sub> <sup>−</sup>	−1.108	50.00
C(CN) <sub>3</sub> <sup>−</sup>	−1.602	99.54
CH <sub>2</sub>	−7.528 · 10 <sup>−2a</sup>	40.92 <sup>a</sup>
CH <sub>3</sub>	−1.450 · 10 <sup>−3a</sup>	8.02 <sup>a</sup>
Grunberg and Nissan Method <sup>22</sup>		
ionic liquids	$G_{12}$	
[C4mim][N(CN)2]	2.6546	
[C4mim][C(CN)3]	1.6317	
Ye and Shreeve's <sup>41</sup>		
cations/anions	$V/\text{\AA}^3$	
1-butyl-3-methylimidazolium (+)	238 <sup>a</sup>	
N(CN) <sub>2</sub> <sup>−</sup>	157	
C(CN) <sub>3</sub> <sup>−</sup>	126 <sup>a</sup>	

<sup>a</sup> Taken from ref 20.

Excess volumes of aqueous mixtures of ILs can be both positive and negative. Anouti et al.,<sup>46</sup> for aqueous solutions of

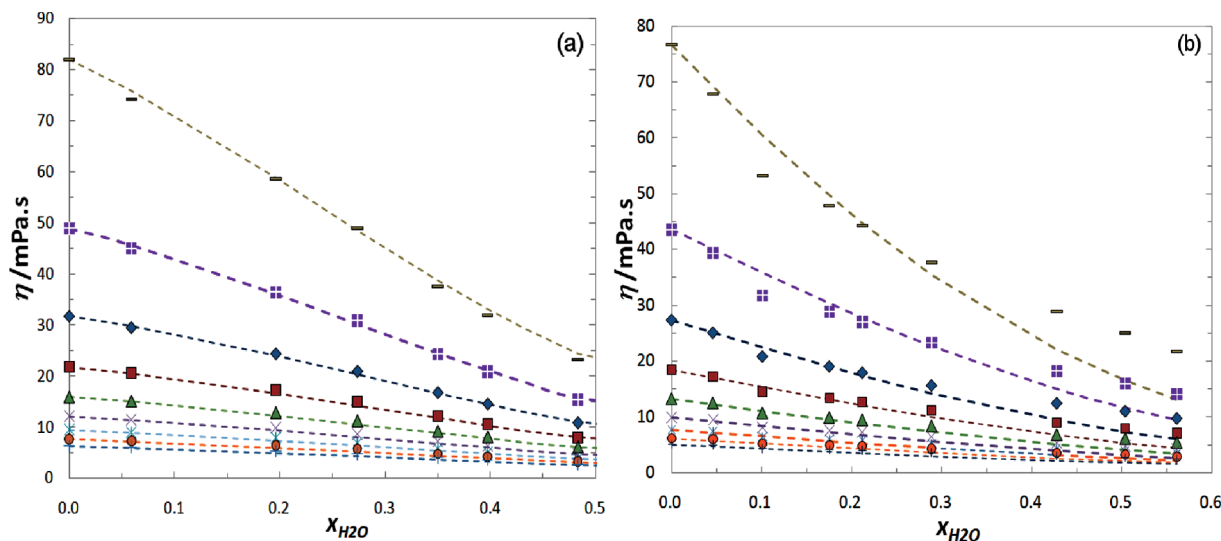


**Figure 4.** Excess molar volume,  $V^E$ , versus mole fraction of water for the binary systems H<sub>2</sub>O + [C4mim][N(CN)2] (a) and H<sub>2</sub>O + [C4mim][C(CN)3] (b): ◆, 278.15 K; ■, 288.15 K; ▲, 298.15 K; ×, 308.15 K; \*, 318.15 K; ●, 328.15 K; □, 348.15 K; and ○, 358.15 K.

pyrrolidinium nitrate [pyrr][NO<sub>3</sub>], Mokhtarani et al.,<sup>47</sup> for aqueous binary mixtures of [BuPy][BF<sub>4</sub>] and [OcPy][BF<sub>4</sub>], García-Miaja et al.,<sup>50</sup> for aqueous binary mixtures of [bpyr][BF<sub>4</sub>], and Rebelo et al.<sup>48</sup> and Zhou et al.,<sup>51</sup> for aqueous binary mixtures of [C4mim][BF<sub>4</sub>], among other authors<sup>49</sup> have already reported positive excess values. However, for the aqueous mixtures of [C4min][MeSO<sub>4</sub>], [C2mim][EtSO<sub>4</sub>], and [C6mim][Cl] negative values of the excess volumes have been reported.<sup>50,52–54</sup> For all these mixtures, excess volumes increase when temperature increases.

Comparing the excess volumes of the aqueous mixtures of ILs with the cation C4mim it can be concluded that the  $V^E$  values increase with the trend MeSO<sub>4</sub> < CF<sub>3</sub>SO<sub>3</sub> < C(CN)<sub>3</sub> < BF<sub>4</sub> < N(CN)<sub>2</sub>. The volumetric behavior of the aqueous mixtures of [C4min][C(CN)<sub>3</sub>] and [C4min][N(CN)<sub>2</sub>] is similar to that of [C4min][BF<sub>4</sub>]. García-Miaja et al.<sup>50</sup> have found that aqueous mixtures of [C4min][MeSO<sub>4</sub>] have negative values of the excess volumes and the excess enthalpies ( $H^E$ ), whereas for [C4min][BF<sub>4</sub>] and [C4min][CF<sub>3</sub>SO<sub>3</sub>]  $V^E$  and  $H^E$  values are positive for almost all mole fractions.<sup>48</sup> This behavior has been explained by the different capability of each anion to form hydrogen bonds with water molecules:<sup>50</sup> the sulfate functional group presents three clearly accessible, negatively charged oxygen atoms to form a hydrogen bond; the triflate anion, CF<sub>3</sub>SO<sub>3</sub>, presents two, with higher steric hindrance; and BF<sub>4</sub> has no oxygen atoms and has a symmetric distribution of the electric charge. Diacynamide N(CN)<sub>2</sub> and tricyanomethane C(CN)<sub>3</sub> have no oxygen atoms either and are symmetrical anions.

The one-constant Grunberg and Nissan<sup>22</sup> equation was used to correlate the experimental viscosity data for the binary systems H<sub>2</sub>O + [C4mim][N(CN)2] and H<sub>2</sub>O +



**Figure 5.** Viscosity versus mole fraction of water for the binary systems  $\text{H}_2\text{O} + [\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$  (a) and  $\text{H}_2\text{O} + [\text{C}_4\text{mim}][\text{C}(\text{CN})_3]$  (b). The symbols represent experimental values, and the solid curves are calculated with the Grunberg and Nissan<sup>38</sup> method. —, 278.15 K; □, 288.15 K; ◆, 298.15 K; ■, 308.15 K; ▲, 318.15 K; ×, 328.15 K; \*, 338.15 K; ●, 348.15 K; and +, 358.15 K.

$[\text{C}_4\text{mim}][\text{C}(\text{CN})_3]$ . This approach relies on the knowledge of the pure component viscosity, as a function of temperature, and in the determination of the parameter  $G_{ij}$  at 298 K. However, to our knowledge this approach has never been applied to ionic liquids making it impossible at this point to determine the parameter  $G_{ij}$  by group contribution. Thus, in this work only a  $G_{ij}$  parameter, for each ionic liquid, is determined. The optimum parameters determined for the studied ILs, reported in Table 6, allow a very good description of the experimental data of  $\text{H}_2\text{O} + [\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$ , for all the composition ranges, and a good description of the experimental data of  $\text{H}_2\text{O} + [\text{C}_4\text{mim}][\text{C}(\text{CN})_3]$  for low water concentrations, as depicted in Figure 5.

Viscosity is also dependent on the interaction forces. Nevertheless, there is not an agreement on how to account for the effect of interactions in the viscosity changes due to the fact that the concept of the ideal system is not established for viscosity. Viscosity deviation,  $\Delta\eta$ , departures from the Grunberg Nissan rule,  $\Delta\ln \eta$ , and excess activation energy are used in the literature for this aim. It was found that both  $\Delta\eta$  and  $\Delta\ln \eta$  values have an opposite sign to  $V^E$  and  $H^E$  values for a large number of molecular systems and some mixtures of ILs with molecular compounds.<sup>55–59</sup> In addition, larger excess activation energies (maximum around  $5000 \text{ J} \cdot \text{mol}^{-1}$  for water + alcohol) and larger and positive values of  $\Delta\eta$  and  $\Delta\ln \eta$  are attributed to associated mixtures.<sup>57,58</sup> Nevertheless, we have found that for  $\text{H}_2\text{O} + [\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$  and  $\text{H}_2\text{O} + [\text{C}_4\text{mim}][\text{C}(\text{CN})_3]$  the signs of  $\Delta\eta$  and  $\Delta\ln \eta$  are different for most of the concentrations,  $\Delta\eta$  being negative (opposite sign to the  $V^E$  values) and  $\Delta\ln \eta$  being positive (according with the positive values of  $G_{ij}$  in Table 6). For the excess activation energy at 308.15 K, we have obtained values around  $(4000 \text{ and } 3300) \text{ J} \cdot \text{mol}^{-1}$  for  $\text{H}_2\text{O} + [\text{C}_4\text{mim}][\text{C}(\text{CN})_3]$  and  $\text{H}_2\text{O} + [\text{C}_4\text{mim}][\text{N}(\text{CN})_2]$ , respectively. Taking into account the literature viscosity data<sup>51,52,60</sup> for other aqueous mixtures of ILs with the cation  $\text{C}_4\text{min}$ , we have found the following decreasing trend for the activation energies and for  $\Delta\ln \eta$   $\text{MeSO}_4 > \text{CF}_3\text{SO}_3 > \text{C}(\text{CN})_3 > \text{BF}_4 > \text{N}(\text{CN})_2$ . As expected, this trend is the opposite of that for excess volumes but not the same for  $\Delta\eta$ . Accordingly, the trend for the excess activation energy and  $\Delta\ln \eta$  can be explained<sup>50</sup> by the different capability of each anion to form hydrogen bonds with water molecules. Nevertheless, more experimental data are required for other ionic liquids and molecular compounds to confirm if this behavior is observed for other systems.

## Conclusions

Experimental data for the density and viscosity of pure and aqueous solutions of two ionic liquids, namely, 1-butyl-3-methylimidazolium dicyanamide and 1-butyl-3-methylimidazolium tricyanomethane, in the temperature range (278 to 363) K and at atmospheric pressure are presented.

The experimental data results show that the water content has a strong effect on the viscosity of the ILs, but the effect is only marginal on their densities.

Several methodologies were applied to the correlation of the experimental data here reported. An extension to the Ye and Shreeve<sup>41</sup> group contribution method shows a good agreement with the density data. The Gardas and Coutinho ionic liquid viscosity models based on the Orrick–Erbar approach<sup>8</sup> and the Vogel–Tammann–Fulcher method<sup>21</sup> were also applied to the experimental viscosity data, presenting a good agreement and allowing the estimation of new group contribution parameters, extending the applicability of these methods to new ILs.

For the binary systems of  $\text{H}_2\text{O} + \text{ILs}$  the one-constant Grunberg and Nissan<sup>22</sup> equation was fitted showing, once more, good agreement toward the experimental data and allowing the determination of a generic  $G_{12}$  parameter for each ionic liquid studied.

The excess volumes present asymmetrical  $V^E(x)$  curves for both the ILs, presenting at the water mole fraction region between 0.3 to 0.4 a trend change regime, suggesting a qualitative change in the water–IL interactions after the one water to two IL molar ratio.

For all the temperatures and for most of the compositions analyzed  $V^E$  is positive which indicates that the interactions among the IL and water molecules are weaker than those of the pure ILs and water.

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