Viscosity and Surface Tension of 1-Ethanol-3-methylimidazolium Tetrafluoroborate and 1-Methyl-3-octylimidazolium Tetrafluoroborate over a Wide Temperature Range

José Restolho,[†] **Ana P. Serro,**[†,‡] **José L. Mata,**[†,§] **and Benilde Saramago***[,†]

Centro de Química Estrutural, Instituto Superior Técnico, T U Lisbon, Av. Rovisco Pais, 1049-001 Lisboa, Portugal, Instituto Superior de Ciências da Saúde Egas Moniz, Quinta da Granja, Monte de Caparica, 2829-511 Caparica, Portugal, and Academia Militar, Paço da Rainha, 29, 1150-244 Lisbon, Portugal

Room-temperature ionic liquids based on the imidazolium cation are presently widely studied, but more data on important properties such as viscosity and surface tension are required. In this work, two imidazolium-based ionic liquids, 1-ethanol-3-methylimidazolium tetrafluoroborate [C_2OHMIM][BF_4] and 1-methyl-3-octylimidazolium tetrafluoroborate [OMIM][BF_4], were investigated. The former is a member of a new series that contains the alcohol $(CH_2)_2OH$ as a functional group. The latter, already studied by several authors, has a long side chain in the imidazolium ring that is responsible for its surfactant properties. The surface tension was determined using the pendant drop technique in a wide temperature range, (298 to 470) K, which has never been explored before with ILs. The viscosity was measured using a new technique (a quartz crystal microbalance) between (288 and 328) K. The surface tension and the viscosity of [C_2OHMIM][BF_4] are unexpectedly high when compared with those of [OMIM][BF_4]. The experimental values were interpreted in terms of the existing theories.

Introduction

Room-temperature ionic liquids (RTILs) based on the imidazolium cation have received considerable attention over recent years because of their unusual physicochemical properties, such as the ability to solubilize a great variety of organic and inorganic compounds, a large electrochemical window, and very low vapor pressure. These properties are responsible for their potential use as solvents in synthesis and catalysis and as electrolytes in electrochemical processes including electrodeposition, batteries, and solar cells.

Because ILs are adequate media for organic and inorganic reactions, efficient methods for extraction of the reaction products and recycling the solvent are necessary. To understand the processes that involve the transport of chemical species through interfaces, knowledge of the thermophysical properties is required. In particular, reliable data on surface tension and viscosity of ILs are important for the design of industrial processes.

One advantage of ionic liquids relative to the classical solvents is the possibility of tuning their properties through adequate choice of both anion and cation. Ionic liquids with the tetrafluoroborate ion are widely used because they behave as inert solvents in most reactions and provide a polar, weakly coordinating medium for the transition-metal catalysts.

For the present study, two ionic liquids of BF_4 anion and cations of *N*-alkylimidazolium of different sizes were selected: 1-ethanol-3-methylimidazolium tetrafluoroborate [C_2OHMIM]-[BF_4] and 1-methyl-3-octylimidazolium tetrafluoroborate [OMIM]-[BF_4]. [C_2OHMIM][BF_4] is a member of a new series of imidazolium-based RTIL [C_nO_mMIM][X] that contains the alcohol $(CH_2)_2OH$ as a functional group.[1] The introduction of this group to the imidazolium cation increases the solubility and enhances the partitioning of inorganic salts, which makes this RTIL appropriate as a recyclable media for organic transformations, including transition-metal catalysis. It is miscible with water and with ethanol but immiscible in diethyl ether. Furthermore, an unusual phase splitting was observed between [C_2OHMIM][BF_4] and dichloromethane, a very good solvent for ionic liquids.[2] To our knowledge, the surface tension of this ionic liquid was never measured, and the reported viscosity data were, apparently, obtained using samples with high water content.[1,3]

[OMIM][BF_4] belongs to the [C_nMIM][BF_4] series with $n = 8$. The increased length of the side chain is responsible for its surfactant properties as well as for a more hydrophobic character when compared with the members with lower n, and it also has increased viscosity. It can be used as a phase transfer catalyst (PTC) and has a low solubility in water at room temperature. Three sets of surface tension measurements are reported: two of them were obtained with a DuNouy tensiometer[4,5] and the other was obtained with the capillary rise method.[6] The viscosity data are rather inconsistent, varying between 473 mPa·s[7] and 135.0 mPa·s[1] at 293 K.

In the present work, the surface tension and the viscosity of [C_2OHMIM][BF_4] and [OMIM][BF_4] were determined as a function of the temperature. Particular attention was given to the manipulation of the samples and to the techniques used to keep the IL free of contamination. The surface tension was measured by the pendant drop method inside an environmental chamber (Ramé−Hart) modified with a temperature controller that allows precisely regulated temperatures between ambient and 573 K. This technique requires a small amount of reagent, which, in the case of ionic liquids, is a great advantage.

---

[*] Corresponding author. E-mail: b.saramago@ist.utl.pt.
[†] Instituto Superior Técnico.
[‡] Instituto Superior de Ciências da Saúde Egas Moniz.
[§] Academia Militar.

10.1021/je800727f CCC: $40.75

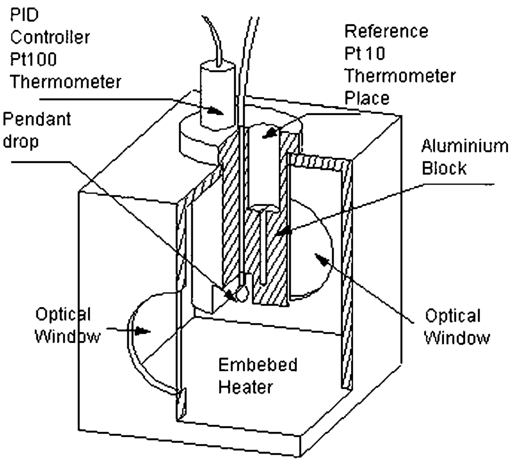

Figure 1

Figure 1. Temperature-controlled ambient chamber.

Furthermore, the closed environmental chamber yields the possibility of working under controlled atmosphere. In the case of highly hydrophilic ionic liquids, such as [C_2OHMIM][BF_4], filling the chamber with an inert gas is required, but for [OMIM][BF_4], it is sufficient to keep a low level of humidity with a desiccant.

For the viscosity measurements, a dissipative quartz crystal microbalance (QCM-D) was used in the temperature range (288 to 328) K. The use of the QCM-D technique in the measurement of the viscosity of moderately to highly viscous fluids has been discussed by several researchers.[8−13] Good agreement between the viscosity measurements obtained with this technique and values published in the literature for standard liquids has been reported.[12] This technique is particularly useful for ionic liquids because of the small volume needed for the measurements and the possibility of minimizing contact of the sample with ambient air. To our knowledge, this is the first time that a QCM-D was used to measure viscosity of RTILs.

Experimental Section

The ionic liquids were purchased from Solchemar and have a purity of > 98 %. The water mass fraction, checked by Karl Fischer, is $\sim 5 \cdot 10^{-3}$ for [C_2OHMIM][BF_4] and $\sim 3.4 \cdot 10^{-4}$ for [OMIM][BF_4]. [C_2OHMIM][BF_4] was vacuum dried at 353 K for at least 3 days, and the final water mass fraction was $\sim 8 \cdot 10^{-4}$. [OMIM][BF_4] was used as received. Both liquids were manipulated inside a glovebox filled with dried nitrogen.

The surface tension measurements were carried out by the pendant drop method using a video camera (jAi CV-A50) mounted on a Wild M3Z microscope to record the drop image. The video signal was transmitted to a frame grabber (Data Translation model DT3155), with the image acquisition and analysis performed on a computer running the ADSA-P software (Axisymetric Drop Shape Analysis, Applied Surface Thermodynamics Research Associates, Toronto, Canada).

The liquid drop was held between the parallel faces, 6 mm apart, of an aluminum block kept inside the ambient chamber Ramé-Hart model 100-07-00. (See Figure 1.) The block temperature was held constant, within ± 0.05 K, by means of a PID controller.

The temperature in the liquid drop location, monitored throughout the whole temperature range with a differential copper constantan thermocouple, is always lower than the temperature, T, in the aluminum block by an amount $\Delta T/\mathrm{K} = 0.0028\,T - 0.77$. The temperature of the liquid drop was corrected accordingly.

Table 1. Density, ρ, of [C_2OHMIM][BF_4] and [OMIM][BF_4] as a Function of Temperature, T[a,b]

	[C_2OHMIM][BF_4]	[OMIM][BF_4]
T/K	ρ/g·cm^{-3}	ρ/g·cm^{-3}
298.15	1.3080	1.1005
303.15	1.3047	
308.15	1.3014	1.0937
313.15	1.2961	
318.15	1.2947	1.0871
323.15	1.2915	
328.15	1.2883	1.0805

[a] Precision of the measurements obtained with Anton-Paar DMA 5000 is on the order of 10^{-5} g·cm^{-3}, and we expect the results to be accurate to 10^{-4} g·cm^{-3}. [b] Experimental values were adjusted to the linear equations $\rho/(\mathrm{g \cdot cm^{-3}}) = 1.3244 - 7.0 \cdot 10^{-4}\, T/(\mathrm{K})$ for [C_2OHMIM][BF_4] and $\rho/(\mathrm{g \cdot cm^{-3}}) = 1.1171 - 7.0 \cdot 10^{-4}\, T/(\mathrm{K})$ for [OMIM][BF_4], and the uncertainties are ± 0.0014 g·cm^{-3} and ± 0.0017 g·cm^{-3}, respectively.

The ambient chamber was dried with silica gel, and in the case of [C_2OHMIM][BF_4], the chamber was flushed with pure, dry nitrogen. Surface tension measurements were made in the temperature range of (298 to 470) K, allowing at least 0.5 h for thermal stabilization at each intermediate temperature.

A dissipative quartz crystal microbalance from KSV (QCM-Z500) was used as a viscometer. The viscosity was obtained through the immersion of a gold-coated quartz crystal (KSV) in the liquid using the KSV software based on the resistance-corrected Kanazawa equation.[14] The temperature range of the viscosity measurements, (288 to 328) K, was that allowed by the QCM temperature controller.

The QCM-D apparatus was first tested with two viscosity standards of moderately to high viscosity, respectively, diisodecylphthalate (Merck, purity 99.8 % by GC) and glycerol (Sigma-Aldrich, water mass fraction of $1 \cdot 10^{-3}$ by Karl Fischer titration). The results of the test, described in Appendix 1, indicate that the first harmonic of the fundamental frequency yields the best accuracy.

The density was measured using an Anton-Paar DMA 5000 vibrating-tube densimeter in the temperature range of (298 to 328) K and was linearly extrapolated to higher temperatures.

To test the effect of the presence of water in [C_2OHMIM][BF_4], several samples of different water content were prepared: a sample in equilibrium with the ambient air ($\sim 3 \cdot 10^{-2}$ of water mass fraction), as received ($\sim 5 \cdot 10^{-3}$ of water mass fraction), and vaccuum dried at 353 K for 1 day ($\sim 1.3 \cdot 10^{-3}$ of water mass fraction).

Results

The densities of both ionic liquids (dry samples), which are necessary for the experimental determination of the surface tension and the viscosity, linearly vary with the temperature. The fitting parameters are presented in Table 1. The densities obtained for [OMIM][BF_4] are in very good agreement with those of Gardas et al.,[15] whereas the values for [C_2OHMIM][BF_4] are slightly lower than those of Branco et al.[1] The density of the dry sample of [C_2OHMIM][BF_4] (given in Table 1) is similar to those of the samples with water mass fractions of $1.3 \cdot 10^{-3}$ and $5 \cdot 10^{-3}$, whereas the density of the sample with water mass fraction $\sim 3 \cdot 10^{-2}$ is 1.3 % lower in the whole temperature range.

The results of the measurements of the surface tension and the viscosity of [C_2OHMIM][BF_4] samples of different water content are presented in Figures 2 and 3, respectively.

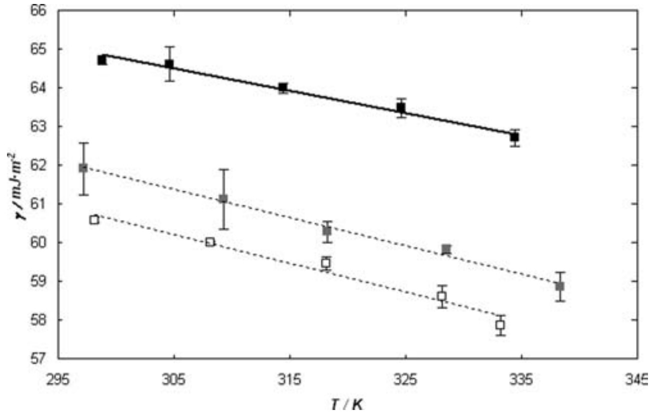

Figure 2. Comparison of the surface tension, γ, of [C_2OHMIM][BF_4] samples of different water mass fraction: ■, $8\cdot10^{-4}$; □, $5\cdot10^{-3}$; shaded square, $3\cdot10^{-2}$. The uncertainties are the standard deviations of the measurements corrected with the Student parameter (95 %). The lines are linear fits.

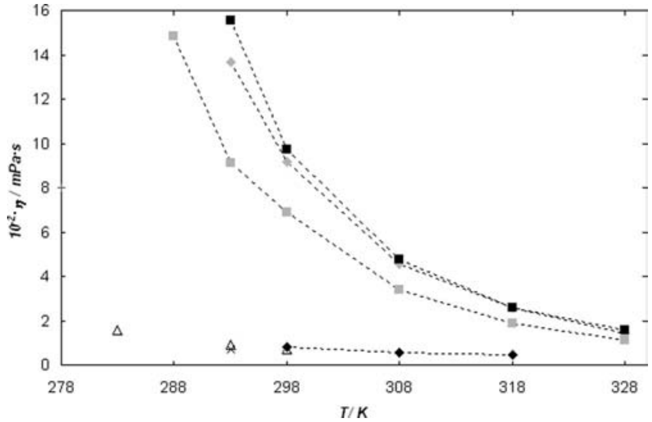

Figure 3. Comparison of the viscosity, η, of [C_2OHMIM][BF_4] samples of different water mass fraction: ■, our work $8\cdot10^{-4}$; shaded tilted square, our work $1.3\cdot10^{-3}$; shaded square, our work $5\cdot10^{-3}$; ◆, our work $3\cdot10^{-2}$; △, Branco et al.;[1] ×, Jain et al.[3]

Table 2. Experimental Values of the Surface Tension, γ, of [C_2OHMIM][BF_4] and [OMIM][BF_4] as a Function of the Temperature, T[a]

[C_2OHMIM][BF_4]		[OMIM][BF_4]	
T/K	γ/mJ·m^{-2}	T/K	γ/mJ·m^{-2}
298.85	64.7 ± 0.1	297.80	32.7 ± 0.1
304.63	64.6 ± 0.4	313.20	32.4 ± 0.2
314.40	64.0 ± 0.1	333.47	31.3 ± 0.2
324.66	63.5 ± 0.2	352.11	30.2 ± 0.2
334.43	62.7 ± 0.2	373.14	28.1 ± 0.1
353.36	61.7 ± 0.2	392.83	27.7 ± 0.1
372.20	59.9 ± 0.2	412.26	27.2 ± 0.2
392.33	59.1 ± 0.4	431.60	25.3 ± 0.2
411.27	57.5 ± 0.6	451.63	24.5 ± 0.1
430.80	56.4 ± 0.5	470.56	23.7 ± 0.1
452.13	55.4 ± 0.4		
470.56	53.6 ± 0.4		

[a] Uncertainties are the standard deviations of the measurements corrected with the Student parameter (95 %).

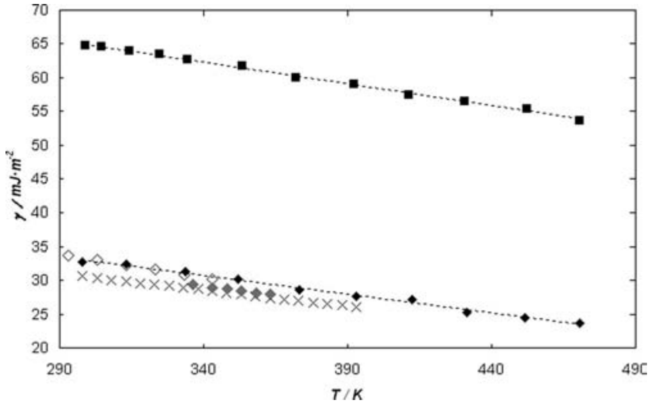

Figure 4. Temperature dependence of the surface tension, γ, of [C_2OHMIM][BF_4] (■) and [OMIM][BF_4]: ◆, our work; shaded tilted square, Law and Watson; ◇, Freire et al.;[5] ×, Ghatee and Zolghadr.[6] The lines are linear fits to eq 1.

Table 3. Surface Excess Entropy, S^S, and Surface Excess Energy, E^S, of [C_2OHMIM][BF_4] and [OMIM][BF_4] Calculated from the Linear Fitting, $\gamma = E^S - S^ST$, to our Data and Taken from the Literature[a]

	S^S	E^S
ionic liquid	mJ·m^{-2}·K^{-1}	mJ·m^{-2}
[C_2OHMIM][BF_4]	0.065 ± 0.001	84.3 ± 0.4
[OMIM][BF_4]	0.055 ± 0.002	49.3 ± 0.9
[OMIM][BF_4][b]	0.0551	47.9
[OMIM][BF_4][c]	0.0487	47.9
[OMIM][BF_4][d]	0.071	54.4

[a] Uncertainties are the standard deviations corrected with the Student parameter (95 %). [b] Ref 4. [c] Ref 5. [d] Ref 6.

Table 4. Experimental Values of the Viscosity, η, of [C_2OHMIM][BF_4] and [OMIM][BF_4] As a Function of the Temperature, T[a,b]

	[C_2OHMIM][BF_4]	[OMIM][BF_4]
T/K	η/mPa·s	η/mPa·s
293.15	1554 ± 115	413 ± 30
298.15	974 ± 72	325 ± 24
308.15	477 ± 35	205 ± 15
318.15	257 ± 19	129 ± 5
328.15	156 ± 6	86 ± 3

[a] Uncertainties result from calibration with DIDP for values lower than 171 mPa·s and with glycerol for the remaining values. (See Appendix 1.) [b] Results are averages of at least three experiments.

The values of the surface tension of [C_2OHMIM][BF_4] and [OMIM][BF_4] (dry samples) measured in the temperature range of (298 to 470) K are presented in Table 2 and plotted in Figure 4. They linearly decrease with increasing temperature according to the equation

$$\gamma = a - bT \tag{1}$$

where intercept, a, can be identified with the surface excess energy, E^S, and the slope, b, can be identified with the surface excess entropy, S^S, which is assumed to be temperature independent. The values of these parameters for both ionic liquids are listed in Table 3. In the case of [OMIM][BF_4], the comparison of our data with values of other authors shows that although in Figure 4 the results of Freire et al.[5] seem to yield the best agreement, the slope of the γ versus T dependence, S^S, coincides with that reported by Law and Watson[4] (Table 3).

The measurements of the viscosity of [C_2OHMIM][BF_4] and [OMIM][BF_4] as a function of temperature are given in Table 4. In Figure 5, our experimental values are compared with other values reported in the literature.

The most commonly used equation for describing the temperature dependence of viscosity is the Arrhenius equation

$$\eta = A\exp(\varepsilon/RT) \tag{2}$$

where ε is the activation energy for viscous flow. According to Seddon et al.,[16] the Arrhenius law can generally be applied to ionic liquids with cations of low symmetry, whereas for small, symmetric cations, the best fit is obtained with the Vogel–

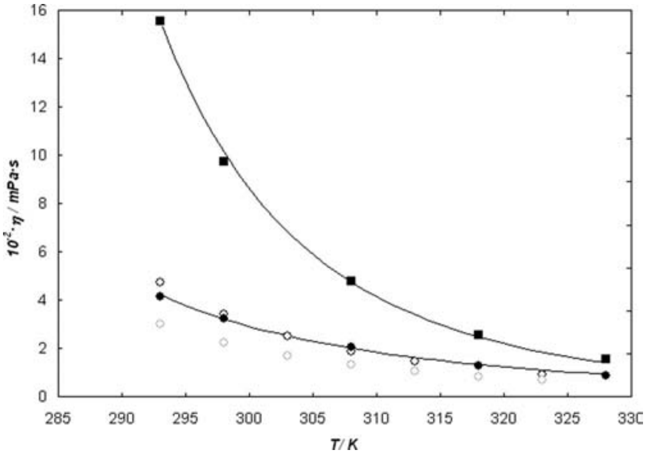

Figure 5. Temperature dependence of the viscosity, η, of $[C_2OHMIM][BF_4]$ (■) and $[OMIM][BF_4]$: ●, our work; ○, Harris et al.;[7] lightface open circle, Sanmamed et al.[26] The curves represent the fittings to eq 3 (VFT).

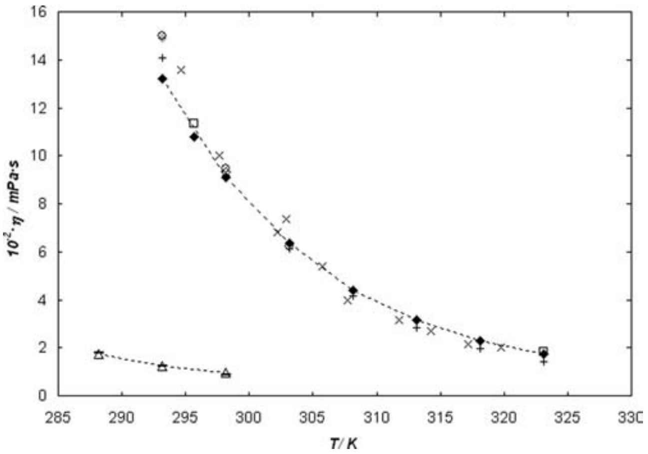

Figure 6. Temperature dependence of the viscosity, η, of glycerol: ◆, our work; ◇, Hammond et al.;[9] ×, Magazu et al.;[19] +, Dow;[33] ○, Sheely;[34] shaded tilted square, ref 35; □, Cook et al.;[36] and of DIDP: △, our work; −, Caetano et al.[32] The curves are trend lines.

Fulcher−Tamman (VFT) equation.[17−19] This is a three-parameter equation

$$\eta = \eta_0 \exp[B/(T - T_0)] = \eta_0 \exp[DT_0/(T - T_0)] \qquad (3)$$

where η_0, B, D, and T_0 are constants. D is inversely proportional to the fragility of the liquid, which refers to the rate at which the transport properties change with temperature near the glass transition. T_0 is the temperature at which the configurational entropy content of the supercooled liquid would vanish in a cooling process of infinite time scale. According to Angell et al.,[20] the glass-transition temperature, T_g, exceeds T_0 by an amount that depends on the D parameter. Although the VFT equation was first derived to describe the temperature dependence of transport properties in the vicinity of the glass-transition temperature, it leads to good fittings of the ionic liquid viscosities far from this temperature.[7] The adjustable parameters and the standard deviations taken from the fittings of the experimental results of the viscosity of $[C_2OHMIM][BF_4]$ and of $[OMIM][BF_4]$ to the above equations are presented in Table 5.

Discussion

A first comment on the uncertainty of the thermophysical data involving these ionic liquids is important. It is now well known that the presence of water and other impurities, even in small amounts, alters the properties of ionic liquids. In this work, we gave special attention to the effect of water because contamination with water vapor during experimental manipulation seems to be the main source of error. The studied liquids have different affinities for water. $[C_2OHMIM][BF_4]$ is highly hydrophilic; consequently, it is difficult to keep it free of water. In contrast, for $[OMIM][BF_4]$, this problem is much less acute because the water content of the liquid remains constant throughout the experiments. This is the reason why we decided to check the effect of water on only the viscosity and surface tension of $[C_2OHMIM][BF_4]$.

Table 5. Fitting parameters, A, and ε (Activation Energy for Viscous Flow) to Equation *2* (Arrhenius) and η_0, D (Constant that Is Inversely Proportional to the Fragility), and T_0 (Temperature at Which the Configurational Entropy Content of the Supercooled Liquid Would Vanish) to Equation *3* (VFT) and Corresponding Standard Deviations, σ

	$A \cdot 10^4$	ε	σ	η_0		T_0	σ
ionic liquid	mPa·s	$kJ \cdot mol^{-1}$	(Arrhenius)	mPa·s	D	K	(VFT)
$[C_2OHMIM][BF_4]$	0.0018	55.7	38	0.042	7.09	175	16
$[OMIM][BF_4]$	1.80	35.7	2	0.646	4.12	179	8

Several authors reported a weak dependence of the density of ILs on the amount of water,[15,18] which is in agreement with our findings. The 1.3 % decrease in the density of the $[C_2OHMIM][BF_4]$ sample equilibrated with ambient air is consistent with the results of Jacquemin et al.,[18] who found a (1 to 2) % decrease in the density of water-saturated ILs (mass fractions of water on the order of $3 \cdot 10^{-2}$) relative to the dry samples.

The dependence of the surface tension on the water content represented in Figure 2 for $[C_2OHMIM][BF_4]$ shows that the surface tension decreases by 6 % when the water content has a six-fold increase (from water mass fractions of $8 \cdot 10^{-4}$ to $5 \cdot 10^{-3}$), but it increases again by 1.6 % when the water content further increases to the mass fraction of $3 \cdot 10^{-2}$. A similar behavior was reported by Freire et al.[5] and attributed to the decrease in the electrostatic interactions between the hydrated ions for a small amount of water, followed by the appearance of water molecules not hydrogen bonded when more water is added.

Figure 3 shows four sets of viscosity measurements obtained with the samples containing $8 \cdot 10^{-4}$, $1.3 \cdot 10^{-3}$, $5 \cdot 10^{-3}$, and $3 \cdot 10^{-2}$ of water mass fraction. The good agreement obtained between our measurements for the $3 \cdot 10^{-2}$ sample and the values reported in the literature suggests that the ionic liquid samples studied by Branco et al.[1] and Jain et al.[3] were equilibrated with ambient air. In fact, the water content of the samples in Jain et al. was not reported, whereas in Branco et al., the ionic liquid was previously vaccuum dried but was then kept in contact with ambient air during the viscosity measurements.

In contrast with the surface tension, the viscosity of RTILs strongly depends on the water content, which is in agreement with the results of other authors.[18,21,22] The increase in the water content leads to a significant and consistent decrease in viscosity, which is not surprising considering the low viscosity of pure water (1 mPa·s at 293 K). In this case, the reduction of the cohesive energy concomitantly works with the presence of free water molecules on the reduction of the IL viscosity.

The surface tension of $[C_2OHMIM][BF_4]$ is considerably higher than that of $[OMIM][BF_4]$. (See Figure 4.) Langmuir's principle of independent surface action may help in the explanation of this difference. According to this principle, each part of a molecule that is actually present at the interface contributes with its own surface free energy to the surface tension of the liquid. It was successfully applied to the surface tension of liquid crystals[23] and, more recently, to that of ionic

Table 6. Surface Tension, γ, of Several Organic and Inorganic Compounds

compound	γ mJ·m^{-2} (T = 298 K)
imidazole[a]	43
water[b]	72.1
methanol (T = 293 K)[c]	22.5
octane[b]	21.0
symmetric inorganic halides[d]	15 to 24

[a] Extrapolated to 333 K.[37] [b] Ref 38. [c] Ref 4. [d] Extrapolated to 333 K.[4]

liquids.[4] In the latter case, the application of this principle demands the knowledge of the surface tensions of the separated ions. Although this is not possible, we may use extrapolated values to make a qualitative comparison. Table 6 shows the surface tensions of liquids whose molecules are similar to parts of the ionic liquid cation and anion. The comparison of these values with the surface tension of [C_2OHMIM][BF_4] suggests that the probability of accumulation of an imidazole ring on the surface with −OH group pointing to the vapor phase is rather high. For [OMIM][BF4], the situation is less clear. Both anion and cation should contribute to the surface structure, but the similarity of 32.7 mJ·m^{-2} with the average value of the surface tensions of octane (21 mJ·m^{-2}) and imidazole (43 mJ·m^{-2}) may indicate the predominance of the cation at the surface.

The analysis of the values of surface excess energy, E^S, and surface excess entropy, S^S, derived from the linear fittings of the temperature dependence of the surface tension and listed in Table 3 deserves the following comments. The comparison of our values of E^S and S^S for [OMIM][BF_4] and those reported in the literature shows that the best agreement was obtained with the results of Law and Watson.[4]The reason for this similarity certainly has to do with the fact that these authors, like us, used a preheated closed chamber for the surface tension measurements to avoid contact of the ionic liquid with ambient air.

The surface entropy of both ionic liquids is low compared with other organic compounds (e.g., 0.072 mJ·m^{-2}·K^{-1} for imidazole),[4] which indicates a high degree of surface ordering. The surface energy of [C_2OHMIM][BF_4] is much higher than that of [OMIM][BF_4] and is in the upper end of the usual range of surface energies of ionic liquids. Because [C_2OHMIM] is a small cation, implying low dispersive forces, hydrogen bonding should be responsible for this effect.

The temperature dependence of the surface tension may be also fitted to the empirical Guggenheim equation[24]

$$\gamma = \kappa(1 - T/T_C)^{11/9} \qquad (4)$$

where κ is a constant and T_C is the critical temperature. Fittings of our data from Table 2 lead to the following critical temperatures: T_C/K = 1507 ± 47 for [C_2OHMIM][BF_4] and T_C/K = 1015 ± 57 for [OMIM][BF_4]. The critical temperature of [OMIM][BF_4] is similar to the value T_C/K = 990 reported by Rebelo et al.[25] At this point we should stress that although the temperature range of our measurements is large it does not ensure a correct extrapolation to such high temperatures. However, we decided to present these estimates because as far as we know there is no other way to assess critical temperatures of ionic liquids experimentally.

Our viscosity data for [OMIM][BF_4] presented in Figure 5 are in good agreement with the values of Harris et al.,[7] at least above 298 K. Both sets of values were obtained with dried samples. In contrast, the values of Sanmamed et al.[26] are slightly lower, but they refer to a sample with a higher content in water (mass fraction of 1.768·10^{-3}). With respect to [C_2OHMIM][BF_4], the only values reported in the literature are, to our knowledge, those shown in Figure 3, which refer to samples that were not dried.

Fitting the data to the equations of Arrhenius and Vogel−Fulcher−Tamman (VFT) yields the parameters presented in Table 5. The standard deviation of the Arrhenius law is smaller for [OMIM], a cation of low symmetry, whereas the VFT equation works better for [C_2OHMIM], a small symmetric cation. Although in this case both equations may be applied, the VFT model has the advantage of yielding fitting parameters with physical meaning. The fragility of [OMIM][BF_4], which is inversely proportional to parameter D, is higher than that of [C_2OHMIM][BF_4], and this may be the reason why the viscosity of the former is much lower at room temperature. In fact, according to Angell et al.,[27] both the glass-transition temperature, T_g, and the fragility of ionic liquids are involved in determining the viscosity of a given ionic liquid at ambient temperature. Although the most fragile liquids are, in general, the cases with the highest T_g values, several exceptions to this rule have been found. In this case, both ionic liquids have similar values of T_g: 189 K[1] for [C_2OHMIM][BF_4] and 192 K[28] for [OMIM][BF_4]; therefore, the difference in fragility may be the determinant factor.

Although the high electrostatic interactions are responsible for the unusual physicochemical properties of the ionic liquids, the van der Waals (inductive) forces also play an important role. For example, the observed increase in the viscosity in a series of ionic liquids when the number of carbon atoms in the alkyl chain increases (keeping the same charge per mole of ions) led several authors [29,30] to claim that the cohesive energy is not determined by the Coulomb interactions. Recent molecular simulations of the cohesive energy of a series of [C_nMIM][NTf_2] (with $2 \leq n \leq 8$) compounds showed that as the length of the alkyl chain increases the contribution of the van der Waals forces increases, whereas the electrostatic interactions keep a constant value.[31] This behavior was attributed to the fact that when the alkyl side chains become longer the size of the nonpolar domains increases but the ionic network does not change. For $n = 8$, the van der Waals interactions contribute with 63 % to the total cohesive energy, whereas for $n = 2$, this contribution is 59 %.

Extrapolation of these conclusions to the ionic liquids studied here suggests that the viscosity of [OMIM][BF_4] should be mainly determined by inductive forces, whereas that of [C_2OHMIM][BF_4] results from inductive, electrostatic, and hydrogen-bonding interactions. As the temperature increases, the difference between the viscosities of both liquids significantly decreases. (See Figure 5). This corroborates the importance of the hydrogen-bonding contribution to the viscosity of [C_2OHMIM][BF_4] because these are the most temperature-dependent molecular interactions.

Conclusions

The density, surface tension, and viscosity of [OMIM] [BF_4] and [C_2OHMIM][BF_4], two ionic liquids with different functional groups in the imidazolium ring, were measured. The surface tension and the viscosity of [C_2OHMIM][BF_4] are significantly higher than those of [OMIM][BF_4], although the size of its cation is much smaller. [C_2OHMIM][BF_4] has one of the highest values of surface tension reported in the literature for RTILs. The viscosity of [C_2OHMIM][BF_4] sharply decreases with both temperature and water content, whereas density and surface tension show less dependence. The special features of this ionic liquid were attributed to the role of the hydrogen bonds.

Appendix 1

The values of the viscosity of diisodecylphthalate (DIDP)[32] and of glycerol[9,19,33−36] that are reported in the literature are compared with the values obtained with the QCM-D KSV software using the first and third harmonics of the fundamental frequency. Although the results of the third harmonic are usually taken to be the most reliable, in this case, the best agreement was found with the first harmonic. In Figure 6, the viscosity measurements obtained with the QCM and the values reported in the literature are plotted as a function of the temperature. The average deviation between our results and those of Caetano et al.[32] for DIDP is 3.9 %. For glycerol, excluding the values of Magazu et al.,[19] the average deviation is 7.4 % in the whole temperature range. Considering that glycerol is highly hygroscopic, it is difficult to keep constant water content during the experiments. As a consequence, the comparison of glycerol viscosity data from different sources is less meaningful than that of DIDP. These results validate the use of our QCM-D as a viscometer for viscous liquids.

Literature Cited

(1) Branco, L.; Rosa, J.; Ramos, J. J. M.; Afonso, C. A. M. Preparation and characterization of new room temperature ionic liquids. *Chem.—Eur. J.* **2002**, *8*, 3671–3677.

(2) Visak, V. N.; Rodriguez, A.; Visak, Z. P.; Rosa, J. N.; Afonso, C. A. M. M.; Ponte, N.; Rebelo, L. P. Co-solvent effects in LLE of 1-hydroxyethyl-3-methylimidazolium based ionic liquids + 2-propanol + dichloromethane or 1,2-dichloroethane. *Fluid Phase Equilib.* **2007**, *254*, 35–41.

(3) Jain, N.; Kumar, A.; Chauhan, S.; Chauhan, S. M. S. Chemical and biochemical transformations in ionic liquids. *Tetrahedron* **2005**, *61*, 1015–1060.

(4) Law, G.; R.; Watson, P. Surface tension measurements of *N*-alkylimidazolium ionic liquids. *Langmuir* **2001**, *17*, 6138–6141.

(5) Freire, M. G.; Carvalho, P. J.; Fernandes, A. M.; Marrucho, I. M.; Queimada, A. J.; Coutinho, J. A. P. Surface tensions of imidazolium based ionic liquids: anion, cation, temperature and water effect. *J. Colloid Interface Sci.* **2007**, *314*, 621–630.

(6) Ghatee, M. H.; Zolghadr, A. R. Surface tension measurements of imidazolium based ionic liquids at liquid−vapor equilibrium. *Fluid Phase Equilib.* **2008**, *263*, 168–175.

(7) Harris, K. R.; Kanakubo, M.; Woolf, L. A. Temperature and pressure dependence of the viscosity of the ionic liquids 1-methyl-3-octylimidazolium hexafluorophosphate and 1-methyl-3-octylimidazolium tetrafluoroborate. *J. Chem. Eng. Data* **2006**, *51*, 1161–1167.

(8) Martin, S. J.; Granstaff, V. E.; Frye, G. C. Characterization of a quartz crystal microbalance with simultaneous mass and liquid loading. *Anal. Chem.* **1991**, *63*, 2272–2289.

(9) Hammond, J. M.; Lec, R. M.; Zhang, X. J.; Libby, D. G.; Prager, L. A. An acoustic automotive engine oil quality sensor. *Proc. IEEE Int. Freq. Control Symp.* **1997**, *72*, 80.

(10) Saluja, A.; Kalonia, D. S. Measurement of fluid viscosity at microliter volumes using quartz impedance analysis. *AAPS Pharm. Sci. Tech.* **2004**, *5*, 1–14.

(11) Wang, D.; Mousavi, P.; Hauser, P. J.; Oxenham, W.; Grant, C. S. Quartz crystal microbalance in elevated temperature viscous liquids: temperature effect compensation and lubricant degradation monitoring. *Colloids Surf., A* **2005**, *268*, 30–39.

(12) Kankare, J.; Loikas, K.; Salomäki, M. Method for measuring the losses and loading of a quartz crystal microbalance. *Anal. Chem.* **2006**, *78*, 1875–1882.

(13) Cho, N.; D'Amour, J. N.; Stalgren, J.; Knoll, W.; Kanazawa, K.; Frank, C. W. Quartz resonator signatures under Newtonian liquid loading for initial instrument check. *J. Colloid Interface Sci.* **2007**, *315*, 248–254.

(14) Kanazawa, K.; Gordon, J. G. Frequency of a quartz microbalance in contact with liquid. *Anal. Chem.* **1985**, *57*, 1770–1771.

(15) Gardas, R. L.; Freire, M. G.; Carvalho, P. J.; Marrucho, I. M.; Fonseca, I. M. A.; Ferreira, A. G. M.; Coutinho, J. A. P. High-pressure densities and derived thermodynamic properties of imidazolium-based ionic liquids. *J. Chem. Eng. Data* **2007**, *52*, 80–88.

(16) Seddon, K. R.; Stark A. S.; Torres, M. J. Viscosity and Density of 1-Alkyl-3-methylimidazolium Ionic Liquids. In *Ionic Liquids III: Fundamentals, Progress, Challenges, and Opportunities*; Rogers, R. D., Sedon, K. R., Eds.; ACS Symposium Series 901; American Chemical Society: Washington, DC, 2004.

(17) Xu, W.; Cooper, E. I.; Angell, C. A. Ionic liquids: ion mobilities, glass temperatures, and fragilities. *J. Phys. Chem. B* **2003**, *107*, 6170–6178.

(18) Jacquemin, J.; Husson, P.; Padua, A. A. H.; Majer, V. Density and viscosity of several pure and water-saturated ionic liquids. *Green Chem.* **2006**, *8*, 172–180.

(19) Magazu, S.; Migliardo, F.; Malomuzh, N. P.; Blazhnov, I. V. Theoretical and experimental models on viscosity: I. Glycerol. *J. Phys. Chem. B* **2007**, *111*, 9563–9570.

(20) Angell, C. A.; Sare, E. J. Glass-forming composition regions and glass-transition temperatures for aqueous electrolyte solutions. *J. Chem. Phys.* **1970**, *52*, 1058–1068.

(21) Widegren, J. A.; Laesecke, A.; Magee, J. W. The effect of dissolved water on the viscosities of hydrophobic room temperature ionic liquids. *Chem. Commun.* **2005**, *1610*, 1612.

(22) Seddon, K. R.; Stark, A.; Torres, M. J. Influence of chloride, water, and organic solvents on the physical properties of ionic liquids. *Pure Appl. Chem.* **2000**, *72*, 2275–2287.

(23) Mach, P.; Huang, C. C.; Stoebe, T.; Wedell, E. D.; Nguyen, T.; Jeu, W. H.; Guittard, F.; Naciri, J.; Shashidhar, R.; Clark, N.; Jiang, I. M.; Kao, F. J.; Liu, H.; Nohira, H. Surface tension obtained from various smectic free-standing films: the molecular origin of surfacetension. *Langmuir* **1998**, *14*, 4330–434.

(24) Guggenheim, E. A. The principle of corresponding states. *J. Phys. Chem.* **1945**, *13*, 253–261.

(25) Rebelo, L. P. N.; Canongia Lopes, J. N.; Esperança, J. M. S. S.; Filipe, E. On the critical temperature, normal boiling point, and vapor pressure of ionic liquids. *J. Phys. Chem. B* **2005**, *109*, 6040–6043.

(26) Sanmamed, Y. A.; González-Salgado, D.; Troncoso, J.; Cerdeiriña, C. A.; Romaní, L. Viscosity-induced errors in the density determination of room temperature ionic liquids using vibrating tube densitometry. *Fluid Phase Equilib.* **2007**, *252*, 96–102.

(27) Angell, C. A.; Sare, E. J.; Bressel, R. D. Concentrated electrolyte solution transport theory: directly measured glass temperatures and vitreous ice. *J. Chem. Phys.* **1967**, *71*, 2759–2761.

(28) Crosthwaite, J. M.; Muldoon, M. J.; Dixon, J. K.; Anderson, J. L.; Brennecke, J. F. Phase transition and decomposition temperatures, heat capacities and viscosities of pyridinium ionic liquids. *J. Chem. Thermodyn.* **2005**, *37*, 559–568.

(29) Xu, W.; Wang, L.; Nieman, R. A.; Angell, C. A. Ionic liquids of chelated orthoborates as model ionic glassformers. *J. Phys. Chem. B* **2003**, *107*, 11749–11756.

(30) Tokuda, H.; Hayamizu, K.; Ishii, K.; Susan, M. A. B. H.; Watanabe, M. Physicochemical properties and structures of room temperature ionic liquids. 2. Variation of alkyl chain length in imidazolium cation. *J. Phys. Chem. B* **2005**, *109*, 6103–6110.

(31) Santos, L. M. N. B. F.; Lopes, J. N. C.; Coutinho, J. A. P.; Esperanca, J. M. S. S.; Gomes, L. R.; Marrucho, I. M.; Rebelo, L. P. N. Ionic liquids: first direct determination of their cohesive energy. *J. Am. Chem. Soc.* **2007**, *129*, 284–285.

(32) (a) Caetano, F. J. P.; Fareleira, J. M. N. A.; Oliveira, C. M. B. P.; Wakeham, W. A. New measurements of the viscosity of diisodecylphthalate using a vibrating wire technique. *J. Chem. Eng. Data* **2005**, *50*, 1875–1878. (b) Caetano, F. J. P.; Fareleira, J. M. N. A.; Fröba, A. P.; Harris, K. R.; Leipertz, A.; Oliveira, C. M. B. P.; Trusler, J. P. M.; Wakeham, W. A. An industrial reference fluid for moderately high viscosity. *J. Chem. Eng. Data* **2008**, *53*, 2003–2011.

(33) Dow. Viscosity of Aqueous Glycerine Solutions. http://www.dow.com/glycerine/resources/table18.htm (accessed July 2008).

(34) Sheely, M. L. Glycerol viscosity tables. *Ind. Eng. Chem* **1932**, *24*, 1060–1064.

(35) Faculty of Science at the University of Waterloo. The Liquid State. http://www.science.uwaterloo.ca/~cchieh/cact/c123/liquid.html (accessed July 2008).

(36) Cook, R. L., Jr.; Herbst, C. A.; Herschbach, D. R. Pressure and temperature dependent viscosity of two glass forming liquids: glycerol and dibutyl phthalate. *J. Chem. Phys.* **1994**, *100*, 5178–5189.

(37) Law, G.; Watson, P. R. Surface orientation in ionic liquids. *Chem. Phys. Lett.* **2001**, *345*, 1–4.

(38) Vazquez, R.; Nogueira, R.; Busquets, S.; Mata, J. L.; Saramago, B. Wetting films of polar and nonpolar liquids. *J. Colloid Interface Sci.* **2005**, *284*, 652–657.

Received for review October 2, 2008. Accepted January 4, 2009. This study was financially supported by the project PCDT/QUI/66211/2006. J.R. was awarded a research grant of the same project. A.P.S. acknowledges the Portuguese Foundation for Science for postdoctoral grant SF RH/BPD/5666/2001.

JE800727F