

Surface tensions of imidazolium based ionic liquids: Anion, cation, temperature and water effect

Mara G. Freire^a, Pedro J. Carvalho^a, Ana M. Fernandes^b, Isabel M. Marrucho^a,
António J. Queimada^c, João A.P. Coutinho^{a,*}

^a CICECO, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal

^b Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal

^c Laboratory of Separation and Reaction Engineering (LSRE), Faculdade de Engenharia, Universidade do Porto, Rua do Doutor Roberto Frias, 4200-465 Porto, Portugal

Received 30 April 2007; accepted 1 June 2007

Available online 8 June 2007

Abstract

This work addresses the experimental measurements of the surface tension of eight imidazolium based ionic liquids (ILs) and their dependence with the temperature (288–353 K) and water content. The set of selected ionic liquids was chosen to provide a comprehensive study of the influence of the cation alkyl chain length, the number of cation substitutions and the anion on the properties under study. The influence of water content in the surface tension was studied for several ILs as a function of the temperature as well as a function of water mole fraction, for the most hydrophobic IL investigated, [omim][PF₆], and one of the more hygroscopic IL, [bmim][PF₆]. The surface thermodynamic functions such as surface entropy and enthalpy were derived from the temperature dependence of the surface tension values.

© 2007 Elsevier Inc. All rights reserved.

Keywords: Surface tension; Ionic liquids; Imidazolium based ionic liquids; Temperature dependence; Water content; Effective ionic concentration; Molar conductivity; Critical temperature

1. Introduction

Room-temperature ionic liquids (RTILs) are a class of organic salts commonly composed of relatively large organic cations and inorganic or organic anions that cannot form an ordered crystal and thus remain liquid at or near room temperature. Unlike molecular liquids, the ionic nature of these liquids results in a unique combination of intrinsic physical properties such as high thermal stability, large liquidus range, high ionic conductivity, negligible vapor pressures, nonflammability and a highly solvating capacity, for both polar and nonpolar compounds [1–3]. These features simplify their manipulation and purification facilitating their use in multiple reaction and extraction cycles and lead to the recognition of a number of ionic liquids as environmentally friendly “green” solvents [4].

Among the several applications foreseeable for ionic liquids in the chemical industry such as solvents in organic synthesis, as homogeneous and biphasic transfer catalysts, and in electrochemistry, there has been considerable interest in the potential of ILs for separation processes as extraction media where, among others, ILs have shown promising in the liquid–liquid extraction of organics from water, alcohols or hydrocarbons [5,6].

The complete design of industrial processes and new products based on ILs are only achieved when their thermophysical properties, such as viscosity, density and interfacial tension, are adequately characterized. Unfortunately, adequate thermophysical characterization of ILs is still limited and therefore it is necessary to accumulate a sufficiently large data bank not only for process and product design but also for the development of correlations for these properties.

In this work the influence of temperature, anion, cation and water content on the surface tension of eight imidazolium based ionic liquids, viz. [bmim][BF₄], [omim][BF₄], [bmim][Tf₂N],

* Corresponding author.

E-mail address: jcoutinho@dq.ua.pt (J.A.P. Coutinho).

[bmim][PF₆], [omim][PF₆], [hmim][PF₆], [bmmim][PF₆] and [bmim][CF₃SO₃], were investigated.

An extensive study of the effect of the water content in the surface tension was carried. The presence of low water contents leads to a decrease on the surface tension to a minimum followed by an increase to a higher and constant value.

Using the quasi-linear surface tension variation with temperature observed for all the ILs the surface thermodynamic properties, such as surface entropy and surface enthalpy, were derived as well as the critical temperature, by means of the Eötvös [7] and Guggenheim [8] equations.

Since the thermophysical properties of the ionic liquids are related to their ionic nature, the surface tensions were correlated with the molar conductivity ratio, expressed as the effective ionic concentration [9].

2. Experimental

2.1. Materials

Surface tensions were measured for eight imidazolium based ILs, namely, 1-butyl-3-methyl-imidazolium tetrafluoroborate, [bmim][BF₄], 3-methyl-1-octyl-imidazolium tetrafluoroborate, [omim][BF₄], 1-butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide, [bmim][Tf₂N], 1-butyl-3-methyl-imidazolium hexafluorophosphate, [bmim][PF₆], 3-methyl-1-octyl-imidazolium hexafluorophosphate, [omim][PF₆], 1-hexyl-3-methyl-imidazolium hexafluorophosphate, [hmim][PF₆], 1-butyl-2,3-dimethyl-imidazolium hexafluorophosphate, [bmmim][PF₆], and 1-butyl-3-methyl-imidazolium trifluoromethanesulfonate [bmim][CF₃SO₃]. The [bmim][BF₄] was acquired at Solvent Innovation with a stated mass fraction purity state >98% and a mass fraction of chloride ion of <100 ppm. The [bmim][PF₆], [hmim][PF₆], [omim][BF₄] and [bmim][CF₃SO₃] were acquired at IoLiTec with mass fraction purities >99%. The bromide impurity mass fraction in the [bmim][PF₆] is 85 ppm, in the [hmim][PF₆] is <100 ppm, in the [omim][BF₄] is 64 ppm and the [bmim][CF₃SO₃] is halogen free since it was produced directly from butylimidazole and methyltriflate. The [omim][PF₆] and [bmmim][PF₆] were acquired at Solchemar with mass fraction purities >99%. The chloride mass fraction content in both ILs is <80 ppm. The [bmim][Tf₂N] was synthesized in our laboratory based on a metathesis anion exchange reaction of 1-butyl-3-methylimidazolium bromide, [bmim][Br], with 1.2 equivalent amount of [Li][Tf₂N] in water, followed by repeatedly washing, as described in literature [10,11]. The reagents [bmim][Br] and [Li][Tf₂N] were acquired at IoLiTec with purities of >99% and >98%, respectively. The mass fraction bromide impurity in the [bmim][Tf₂N], determined by ion chromatography, is 37 ppm. The purities of each ionic liquid were checked by ¹H NMR, ¹³C NMR and ¹⁹F NMR. 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⁻¹ and it is free of particles greater than 0.22 µm.

In order to reduce the water content and volatile compounds to negligible values, vacuum (0.1 Pa), steering and moderate temperature (353 K) for at least 48 h were applied to all the ILs samples prior to the measurements. After this proceeding, the water content in the ILs was determined with a Metrohm 831 Karl–Fischer coulometer indicating very low levels of water mass fraction content, as (485, 371, 181, 87, 18, 601, 121, 21) × 10⁻⁶ for [bmim][BF₄], [omim][BF₄], [bmim][CF₃SO₃], [bmmim][PF₆], [omim][PF₆], [bmim][PF₆], [bmim][Tf₂N] and [hmim][PF₆], respectively.

The influence of water content in the surface tensions was studied for both water saturated and atmospheric saturated ILs. With this purpose two highly hydrophobic, [omim][PF₆] and [bmim][Tf₂N], and two less hydrophobic and highly hygroscopic ILs, [omim][BF₄] and [bmim][PF₆] were studied. These compounds were saturated with ultra pure water, maintaining the two phases in equilibrium, at 293.15 K for at least 48 h, which was previously found to be the necessary time to achieve equilibrium [12]. Between each temperature measurements the ILs were kept in equilibrium with ultra pure water inside the measurement cell, being the water removed and the interface carefully cleaned, by aspiration, and the water content determined before each new measurement. At saturation, for the same temperature, the ILs present a water mass fraction content of (15259, 14492, 25621, 171789) × 10⁻⁶ for [bmim][Tf₂N], [omim][PF₆], [bmim][PF₆] and [omim][BF₄], respectively [12,13].

The atmospheric saturated ILs were dry and kept in contact with atmospheric air covered with a permeable membrane for several days, for each temperature measured. The water mass fraction content of [omim][PF₆], [bmim][Tf₂N], [omim][BF₄] and [bmim][PF₆] was (1340, 1252, 3530 and 3381) × 10⁻⁶, respectively, as determined by Karl Fisher coulometry.

To have a more complete picture of the effect of water concentration in the ionic liquid surface tension, the surface tension of [bmim][PF₆] and [omim][PF₆] for various water concentrations was also studied.

2.2. Experimental measurements

The surface tension of each IL was measured with a NIMA DST 9005 tensiometer from NIMA Technology, Ltd. with a Pt/Ir Du Noüy ring, based on force measurements, for which it has a precision balance able to measure down to 10⁻⁹ N. The sample surface was cleaned before each measurement by aspiration to remove the surface active impurities present at the interface and to allow the formation of a new interface. The measurements were carried in the temperature range from 293 to 353 K and at atmospheric pressure. The sample under measurement was kept thermostated in a double-jacketed glass cell by means of a water bath, using an HAAKE F6 circulator equipped with a Pt100 probe, immersed in the solution, and able to control the temperature within ±0.01 K.

For each sample at least five sets of three immersion/detachment cycles were measured, giving a minimum of at least 15 surface tension values, which allow the determination of an average surface tension value for each temperature as well

as the expanded associated uncertainty [14,15]. Further details about the equipment and method can be found elsewhere [16–18].

For mass spectrometry ionic liquids were used as acetonitrile solutions (1.5×10^{-4} M). Electrospray ionization mass spectrometry (ESI-MS) and tandem spectrometry (ESI-MS-MS) were acquired with Micromass Q-ToF 2 operating in the positive ion mode. Source and desolvation temperatures were 80 and 100 °C, respectively. Capillary voltage was 2600 V and cone voltage 25 V. ESI-MS-MS spectra were acquired by selecting the precursor ion with the quadrupole, performing collisions with argon at energies of 2–30 eV in the hexapole, followed by mass analysis of product ions by the TOF analyzer. N₂ was used as nebulization gas. The ionic liquid solutions were introduced at a $10 \mu\text{L min}^{-1}$ flow. The breakdown graphs were obtained by acquiring the ESI-MS-MS spectra of each ion investigated at increasing collision energies and plotting the relative abundance of precursor and fragment ions as a function of collision energy. The relative order of hydrogen bond strength between cation and anion in each ion-pair studied, was obtained by acquiring the ESI-MS-MS spectra, at 10 eV collision energy, of the cluster ions $[\text{C}_1 \dots \text{A} \dots \text{C}_2]^+$ and measuring the relative abundances of the two fragment ions observed.

3. Results and discussion

3.1. Surface tension measurements

Previous measurements have confirmed the ability of the equipment used to accurately measure interfacial tensions for hydrocarbons and fluorocarbon systems, validating the methodology and experimental procedure adopted in this work [16–19]. The liquid densities of the pure compounds necessary for the surface tension measurements using the Du Noüy ring were obtained from the literature [20–24].

The surface tension data of the dry ILs are reported in Table 1. The relative deviations between the experimental data

obtained in this work and those reported by other authors [20,25–31] are presented in Fig. 1. The data measured show average deviations of 4%, in respect with the available literature data. These deviations are larger than those previously observed for hydrocarbon and fluorocarbon compounds [16–19] using the same equipment, but it must also be stressed that large discrepancies were also observed among the data from different authors [20,25–31] as can be observed in Fig. 1. Not only the surface tension data available today for ionic liquids are rather scarce but also most of the measurements were carried either using compounds of low purity or without a careful attention towards the preparation of the sample, in particular drying, and often those measurements have been carried for purposes other than an accurate determination of the surface tensions.

The experimental values show that both the anion and cation have an influence on the surface tensions. Within the imidazolium family the increase in the cation alkyl chain length reduces the surface tension values. Both compounds with the octyl chain present surface tensions lower than the corresponding butyl homologue. Surprisingly the introduction of a methyl group on the [bmim][PF₆] IL, substituting the most acidic hydrogen at the C₂ position in the imidazolium ring [32], leads to an increase in the surface tension values of the [bmmim][PF₆], when compared with [bmim][PF₆]. Hunt [33] reported the same odd behavior for melting points and viscosity and hypothesized that the effects due to the loss in hydrogen bonding are less significant than those due to the loss of entropy. The loss of entropy enhances the alkyl chain interactions by lowering the amount of disorder in the system, eliminating the ion-pair conformers, and increasing the rotational barrier of the alkyl chain. Thus, the reduction in the entropy leads to a greater ordering within the liquid and consequently to the surface, leading to a slight increase in the surface tension.

Similarly, an increase in the size of the anion leads to a decrease on the surface tensions with their values following the sequence [BF₄] > [PF₆] > [CF₃SO₃] > [Tf₂N], which agrees with Deetlefs et al. [34] hypothesis that the increase of the an-

Table 1
Experimental surface tension (γ) of the dry ionic liquids studied

[bmim][BF ₄]		[bmim][PF ₆]		[bmim][Tf ₂ N]		[bmim][CF ₃ SO ₃]	
<i>T</i> (K)	$\gamma \pm \sigma^a$ (mN m ⁻¹)	<i>T</i> (K)	$\gamma \pm \sigma^a$ (mN m ⁻¹)	<i>T</i> (K)	$\gamma \pm \sigma^a$ (mN m ⁻¹)	<i>T</i> (K)	$\gamma \pm \sigma^a$ (mN m ⁻¹)
293.15	44.81 ± 0.02	293.15	44.10 ± 0.02	293.15	33.60 ± 0.01	293.20	35.52 ± 0.03
303.15	44.18 ± 0.02	303.15	43.52 ± 0.04	303.15	33.09 ± 0.02	303.20	35.05 ± 0.03
312.65	43.58 ± 0.02	313.15	42.90 ± 0.03	313.15	32.50 ± 0.01	313.20	34.62 ± 0.02
322.15	42.90 ± 0.02	323.15	42.21 ± 0.03	323.15	31.92 ± 0.01	323.20	34.19 ± 0.02
331.45	42.27 ± 0.03	333.15	41.53 ± 0.03	333.15	31.35 ± 0.02	333.20	33.71 ± 0.02
341.35	41.64 ± 0.02	343.15	41.07 ± 0.01	343.15	30.90 ± 0.02	343.20	33.30 ± 0.03
[omim][PF ₆]		[bmmim][PF ₆]		[omim][BF ₄]		[hmim][PF ₆]	
293.15	35.16 ± 0.01	303.15	44.80 ± 0.03	288.15	34.15 ± 0.03	293.15	39.02 ± 0.02
303.15	34.60 ± 0.02	313.15	44.07 ± 0.01	293.15	33.62 ± 0.02	303.15	38.35 ± 0.02
313.15	33.89 ± 0.02	323.15	43.52 ± 0.04	303.15	33.04 ± 0.02	313.15	37.71 ± 0.01
323.15	33.14 ± 0.02	333.15	42.68 ± 0.02	313.15	32.26 ± 0.01	323.15	37.09 ± 0.01
333.15	32.67 ± 0.01	343.15	42.02 ± 0.02	323.15	31.67 ± 0.01	333.15	36.47 ± 0.01
343.15	31.98 ± 0.01	353.15	41.37 ± 0.02	333.15	30.87 ± 0.02	343.15	35.91 ± 0.04
				343.15	30.20 ± 0.02	353.15	35.15 ± 0.02

^a Expanded uncertainty with an approximately 95% level of confidence.

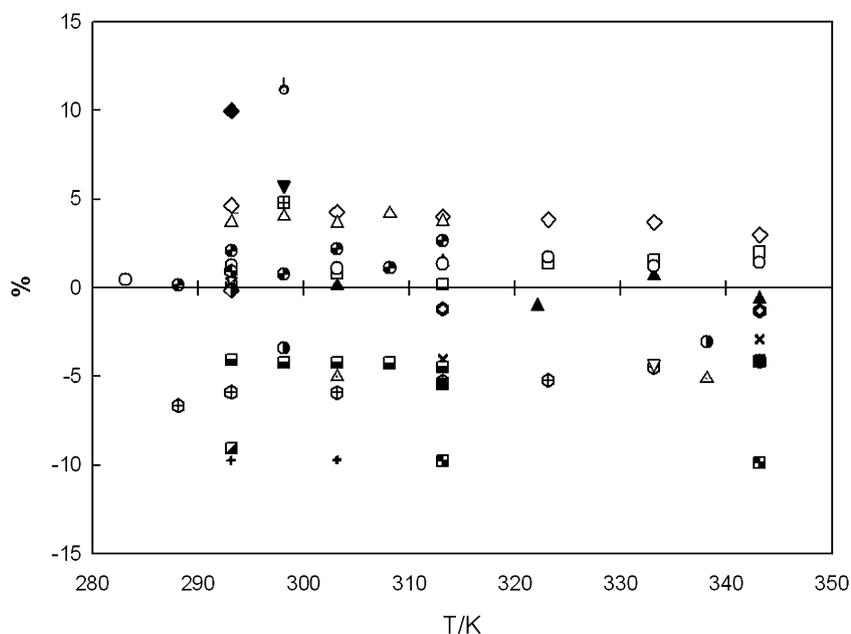


Fig. 1. Relative deviations between the experimental surface tension data of this work and those reported in the literature: (□) [bmim][BF₄] [20]; (+) [bmim][BF₄] [25]; (▼) [bmim][BF₄] [28]; (◼) [bmim][BF₄] [31]; (■) [bmim][BF₄] [26]; (◇) [bmim][PF₆] [25]; (◊) [bmim][PF₆] [28]; (–) [bmim][PF₆] [31]; (●) [bmim][PF₆] [30]; (◈) [bmim][PF₆] [27]; (▲) [bmim][PF₆] [29]; (×) [bmim][PF₆] [26]; (○) [omim][PF₆] [25]; (⊕) [omim][PF₆] [28]; (⊙) [omim][PF₆] [31]; (△) [omim][PF₆] [30]; (☆) [omim][PF₆] [27]; (⊗) [omim][PF₆] [26]; (⊕) [omim][BF₄] [25]; (▽) [omim][BF₄] [31]; (■) [omim][BF₄] [26]; (⊙) [bmim][Tf₂N] [28]; (△) [bmim][Tf₂N] [26]; (◆) [bmim][Tf₂N] [27]; (⊕) [hmim][PF₆] [30]; (⊙) [hmim][PF₆] [26].

ion size and the increasing of the diffuse nature of the anion negative charge lead to a more delocalized charge and therefore to a decrease on the ability to hydrogen bonding. This is an odd result as, usually, the surface tensions of organic compounds increase with the size of the molecules. However these changes are actually a result of the energetic rather than steric interactions, contrary to the suggestion of Law and Watson [25]. Since the surface tension is a measure of the surface cohesive energy, it is thus related to the strength of the interactions that are established between the anions and cations in an ionic liquid. The increase in surface tensions with size in most organic compounds results from an increase in the forces between the molecules with their size. Ionic liquids are complex molecules where coulombic forces, hydrogen bonds and Van der Waals forces all are present in the interaction between the molecules with the hydrogen bonds being probably the most important forces in ionic liquids [11,34,35]. Although the increase in size of the molecule leads to an increase of the Van der Waals forces it will also contribute to a dispersion of the ion charge and a reduction on the hydrogen bond strength.

The measured data presents surface tension values well above those of conventional organic solvents, such as methanol (22.07 mN m⁻¹) [36] and acetone (23.5 mN m⁻¹) [36], as well as those of *n*-alkanes [16–18], but still lower than those of water (71.98 mN m⁻¹) [36].

Complex molecules tend to minimize their surface energies by exposing to the vapor phase their parts with lower surface energy. An alcohol will have a surface tension close to an alkane and not to water as the alkyl chains will be facing upwards at surface to minimize the surface energy. Yet the surface tensions for the ionic liquids are close to those of imidazole extrapolated to the same temperatures [31]. According to the Langmuir's

principle of independent surface action [37] this is an indication of the presence of the imidazolium ring at the surface rather than the alkyl chain as usual in compounds with alkyl chains. That the surface may be made up of mainly of anions is also precluded by the surface tensions that the surface would present in this case. The [PF₆] should have a surface tension close to [SF₆] that has a value of circa 10 mN m⁻¹ at –50 °C [38], other fluorinated ions should also have very low surface tensions. The only explanation for these high surface tensions are the hydrogen bonds that exist between the cations, and the anions and cations, as discussed below, that increase the interactions between the ions leading to enhanced values of surface tension.

3.2. Mass spectrometry and hydrogen bonding

Mass spectrometry measurements have been carried out as described above to establish the relative strength of the hydrogen bonds in ionic liquids for the anions and cations studied here. A higher abundance of ion C₁⁺ in the ESI-MS-MS spectra of the heterodimer [C₁...A...C₂]⁺ will imply a stronger bond between the cation C₂⁺ and the anion A [39]. The analysis of the ESI-MS-MS spectra obtained for the binary mixtures of ionic liquids used to form the clusters, shows that the relative strength of the hydrogen bonds observed in [C₁...BF₄...C₂]⁺ and in [C₁...PF₆...C₂]⁺ is the following

$$[\text{bmmim}]^+ < [\text{omim}]^+ < [\text{hmim}]^+ < [\text{bmim}]^+,$$

while that observed in [A...bmim...A]⁻ is

$$[\text{BF}_4]^- > [\text{CF}_3\text{SO}_3]^- > [\text{PF}_6]^- > [\text{Tf}_2\text{N}]^-.$$

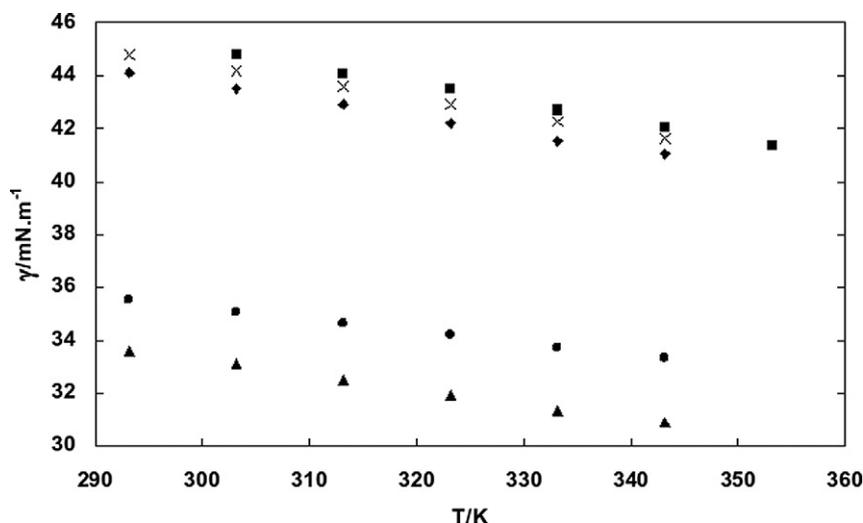


Fig. 2. Surface tension vs temperature of ILs with the common [bmim] cation: (▲) [bmim][Tf₂N]; (●) [bmim][CF₃SO₃]; (◆) [bmim][PF₆]; (×) [bmim][BF₄]; (■) [bmmim][PF₆].

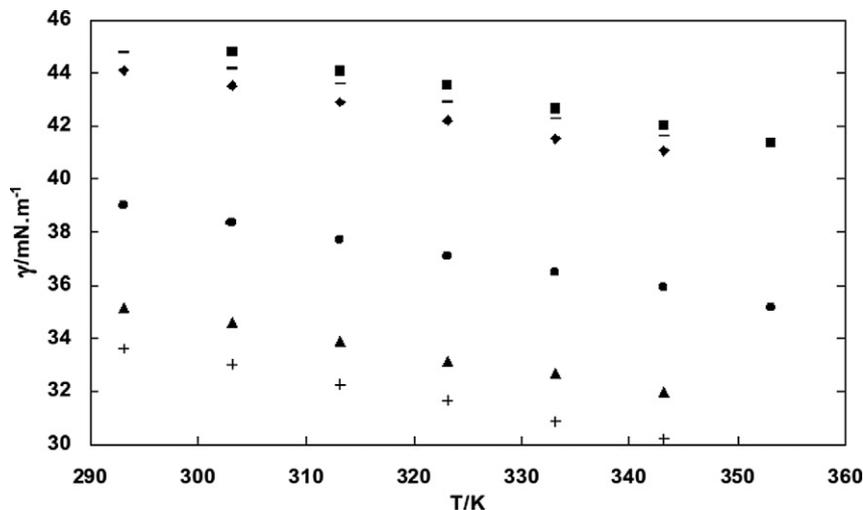


Fig. 3. Surface tension vs temperature of ILs with the common [PF₆] and [BF₄] anions: (■) [bmmim][PF₆]; (—) [bmim][BF₄]; (◆) [bmim][PF₆]; (●) [hmim][PF₆]; (▲) [omim][PF₆]; (+) [omim][BF₄].

The relative strength of the hydrogen bonds observed for the cations can be rationalized in terms of chain length increase on the N¹-alkyl group of the imidazolium, which reduces the H...F distance, and of the introduction of a second methyl group, which removes the most acidic hydrogen from carbon 2. Both factors contribute to a reduction in the interactions between cations and anions. For the anions, the relative position of [CF₃SO₃][−] will probably be explained by the larger negative charge on the oxygen atoms as compared with the fluorine atoms [40].

The relative strength of the hydrogen bonds observed is, with two exceptions, in agreement with the surface tensions measured showing that the surface tension data measured and reported in Table 1 and in Figs. 2, 3 and S1 (in Supporting information) are dependent on the strength of the interactions established between the anions and cations. A possible explanation for the increase in surface tensions of [bmmim][PF₆], contrary to what was expected based on relative hydrogen bond

strength, has already been discussed above. The second exception refers to the relative position of anions [PF₆][−] and [CF₃SO₃][−], which is reversed when compared with surface tension values of [bmim][PF₆] and [bmim][CF₃SO₃]. This may be due to entropic rather than energetic effects due to the shape and symmetry of the [PF₆][−] anion, which could lead to a greater ordering within the liquid.

3.3. Thermodynamic properties

Using the quasi-linear surface tension variation with temperature for all the ILs observed in the studied temperature range, the surface thermodynamic properties, surface entropy and surface enthalpy, were derived. The surface entropy, S^γ , can be obtained from [41,42]

$$S^\gamma = -\frac{d\gamma}{dT}, \quad (1)$$

Table 2
Surface thermodynamic functions for the ionic liquids studied

RTILs	Dry ILs		Saturated ILs	
	$(S^\gamma \pm \sigma) \times 10^{-5}$ (Jm ⁻² K ⁻¹)	$(H^\gamma \pm \sigma) \times 10^{-2}$ (Jm ⁻²)	$(S^\gamma \pm \sigma) \times 10^{-5}$ (Jm ⁻² K ⁻¹)	$(H^\gamma \pm \sigma) \times 10^{-2}$ (Jm ⁻²)
[bmim][PF ₆]	6.2 ± 0.1	6.23 ± 0.05	6.4 ± 0.4	6.3 ± 0.2
[hmim][PF ₆]	6.34 ± 0.08	5.76 ± 0.03		
[omim][PF ₆]	6.7 ± 0.1	5.49 ± 0.05	6.3 ± 0.2	5.30 ± 0.07
[bmmim][PF ₆]	6.9 ± 0.1	6.57 ± 0.05		
[bmim][BF ₄]	6.35 ± 0.07	6.34 ± 0.02		
[omim][BF ₄]	7.1 ± 0.1	5.44 ± 0.04	6.9 ± 0.4	5.4 ± 0.1
[bmim][Tf ₂ N]	5.5 ± 0.1	4.97 ± 0.03	5.4 ± 0.2	4.96 ± 0.06
[bmim][CF ₃ SO ₃]	4.45 ± 0.04	4.86 ± 0.01		

and the surface enthalpy, H^γ , can be obtained from the following expression [41,42]

$$H^\gamma = \gamma - T \left(\frac{d\gamma}{dT} \right), \quad (2)$$

where γ stands for the surface tension and T for the temperature.

The thermodynamic functions for all the ILs studied at 298.15 K and the respective expanded uncertainties, derived from the slope of the curve $\gamma = f(T)$ in combination with the law of propagation of uncertainty, are presented in Table 2 [43].

The most important indication from the surface thermodynamic properties is the low surface entropies. Compared to other organic compounds the surface entropies are remarkably low. Even the *n*-alkanes, which are an example of surface organization [44] have surface entropies that are 50 to 100% higher than the ionic liquids here studied. This is a clear indication of high surface organization in these fluids in agreement with the simulation results by Lynden-Bell [45] and the surface studies of Watson and Law [25,31,46] using direct recoil spectroscopy, Imori et al. [47] using sum frequency generation, Bowers et al. [48] using neutron reflectometry measurements, and Slouskin et al. [49] using X-ray reflectometry measurements. On a previous work [50], using a completely different approach, we have also shown that the surface of ionic liquids was highly organized. Using experimental and simulation values of heats of vaporization for imidazolium based ionic liquids with alkyl chain lengths ranging from ethyl to octyl, and with the [Tf₂N] anion, it was shown that a high degree of organization was present in the ionic liquids. Although that work put the emphasis on the bulk organization rather than the surface, the direct relation between the heats of vaporization and the surface tensions makes those results even more significant to the understanding of surface structure than the bulk and indicate that a great organization is present at surface as well. Although all these studies do not fully agree on the model of the surface structure, all of them indicate that a significant degree of surface ordering would be present and thus would be the cause for the reduced surface entropy observed. It is thus not surprising that the surface entropies increase with the size of the alkyl chain as can be seen in Table 2 for the [PF₆] and [BF₄] compounds. The surface cannot be made up just of cations, but both cations and anions should be present, and the surface entropies seem

to be more affected by the anion type than by the cation chain length. The surface enthalpy by its turn seems to decrease with the increasing chain length of the cation and also to suffer an important dependence on the anion. The change in the surface enthalpies seems to follow the decrease in strength of the hydrogen bonding observed for these ionic liquids with, again, the curious exception of the [bmmim][PF₆]. More good quality data for other ionic liquids, however, are required to make reliable generalizations of these observations.

3.4. Influence of the water content on the surface tension of ionic liquids

A major issue concerning ionic liquids thermophysical properties is the influence of the water content on their values. This is well established for densities [24,28], viscosities [11,28], melting points, glass transitions [28], and gas solubilities [51], among others. Although Huddleston et al. [28] show some results on the influence of water on the surface tensions, the surface tension data available do not allow any discussion on the effect of water on the surface tensions of ionic liquids. Also some references [52,53] seem to indicate that the water content has little or no influence on the surface tension values. In this work, besides a careful determination of the surface tensions of dry ionic liquids, the surface tensions of four water saturated ionic liquids ([bmim][Tf₂N], [omim][BF₄], [bmim][PF₆] and [omim][PF₆]) were measured along with the dependence on the water content for two ionic liquids ([bmim][PF₆] and [omim][PF₆]). These surface tension values are reported in Supporting information. The respective surface thermodynamic properties are reported in Table 2. Here it is possible to observe that both the surface entropies and the surface enthalpies are not significantly affected by the water content of the saturated ionic liquids.

The measured surface tension values of saturated ILs indicate that, for the more hydrophobic ILs, the surface tensions of the saturated ILs are very similar to those obtained for the dry ones. Nonetheless, in both cases it shows a decrease in the surface tension for low water content. The same behavior can be seen for [omim][BF₄] (as shown in Fig. S2 in Supporting information), [omim][PF₆] and [bmim][PF₆] as well as for the hydrophobic (yet somewhat hygroscopic) [bmim][Tf₂N] ionic liquid, with a decrease in the surface tension for low water contents.

For a more complete information on the effect of the water content in the surface tension, measurements have been carried for the [bmim][PF₆] and [omim][PF₆] as a function of the water content at 303 K as shown in Figs. 4a and 4b. Both ILs studied present a minimum in the surface tension for low water contents increasing for a higher and constant value. The effect of the water on the surface tensions seems to be more important for the more hydrophilic ionic liquids. In effect for [omim][PF₆] this variation is almost insignificant, while for [bmim][PF₆] this variation is quite considerable, 6%. It is well established that water accommodates in the ionic liquid structure by establishing hydrogen bonds with both the anion and the cation, leading to the decrease of the IL physical properties by means of the reduction of the electrostatic attractions between the ions and

therefore to a decrease on the overall cohesive energy. The presence of low water content forces the ionic liquid to rearrange into a new different internal order in which more water can be accommodated, till a point where further addition of water leads to a complete solvation of the ions and to the appearance of water molecules not hydrogen-bonded to the IL and thus to a new structural rearrangement leading to an increase in the physical properties [6,11,54].

This dependency of the surface tension on the water content of the ionic liquid may explain the discrepancies between some results of this work when compared to literature data. Most authors who measured ILs surface tensions neither report the ILs water content and impurity levels nor make reference to any drying methodology [25,27,31]. Only Huddleston et al. [28] seems to have dried the ILs used although for a short period of just 4 h, leading to a final water content higher than those achieved in this work and, as consequence, obtaining values of surface tensions lower than those obtained for dry ILs.

3.5. Estimated critical temperatures

Critical temperatures (T_c) of ionic liquids are one of the most relevant thermophysical properties since they can be used in many corresponding states correlations for equilibrium and transport properties of fluids [55]. Due to ILs intrinsic nature, with negligible vapor pressures and low decomposition temperatures, the determination of critical temperature can be at least challenging. Nonetheless several methods for critical temperature estimation based on surface tension data can be found in literature [7,8,55]. The estimation of the critical temperature of the used ionic liquids based on the temperature dependence of the surface tension and liquid density were carried by means of the Eötvös [7] and Guggenheim [8] empirical equations described below and are reported in Table 3.

$$\gamma \left(\frac{M}{\rho} \right)^{2/3} = K(T_c - T), \quad (3)$$

$$\gamma = K \left(1 - \frac{T}{T_c} \right)^{11/9}, \quad (4)$$

respectively, where γ is the surface tension, T_c the critical temperature, M the molecular weight and ρ the density of the ionic liquid. Both equations reflect the fact that γ becomes null at

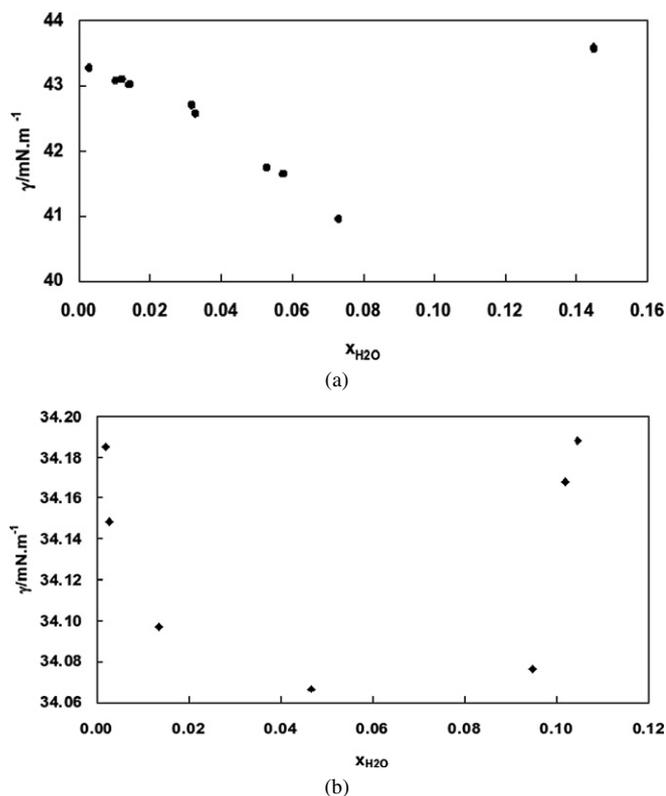


Fig. 4. (a) Surface tension dependency with [bmim][PF₆] water content, mole fraction at 303.15 K. (b) Surface tension dependency with [omim][PF₆] water content, mole fraction at 303.15 K.

Table 3

Estimated critical temperatures, T_c (K), using both Eötvös [7] (Eot) and Guggenheim [8] (Gug) equations, comparison and relative deviation from literature data

RTILs	This work data		Rebelo et al. [26]				Valderrama et al. [56]		
	(Eot)	(Gug)	(Eot)		(Gug)		(GCM)	(Eot)	(Gug)
	T_c (K)	T_c (K)	T_c (K)	RD (%)	T_c (K)	RD (%)	T_c (K)	RD (%)	RD (%)
[bmim][PF ₆]	977 ± 22	958 ± 17	1187	17.7	1102	13.1	544.0	-79.6	-76.1
[hmim][PF ₆]	1116 ± 15	1039 ± 10	1109	-0.6	1050	1.0	589.7	-89.2	-76.2
[omim][PF ₆]	977 ± 22	958 ± 17	997	2.0	972	1.4	625.5	-53.7	-50.7
[bmmim][PF ₆]	1159 ± 19	1091 ± 16							
[bmim][BF ₄]	1183 ± 12	1113 ± 8	1240	4.6	1158	3.9	632.3	-87.1	-76.0
[omim][BF ₄]	870 ± 16	873 ± 11	1027	15.3	990	11.8	726.1	-19.8	-20.2
[bmim][Tf ₂ N]	1110 ± 18	1032 ± 13	1077	-3.1	1012	-2.0	851.8	-30.3	-21.2
[bmim][CF ₃ SO ₃]	1628 ± 55	1264 ± 8					697.1	-133.5	-81.3

(GCM), Group Contribution Method.

very complex matter and exceptions to the rule of increasing surface tensions with increasing cation–anion interaction were observed notably with the [bmim] cation. The substitution of the most acidic hydrogen, on the carbon 2, by a methyl group, leads to a state of less entropy and therefore to an enhance of the alkyl chain interactions. Lowering the disorder in the surface leads to a increase on the surface tensions of this ionic liquid when compared with the homologous unsubstituted compound.

The influence of the water content on the surface tensions was also investigated. Low water contents contribute to a decrease on the surface tension of ionic liquids. This decrease is more prominent for the less hydrophobic ionic liquids being almost insignificant for the most hydrophobic ones. Nevertheless the decrease on the surface tension is followed by an increase to a higher and constant value, that for the more hydrophobic ionic liquids is similar to the surface tension values of the dry IL. The surface tension decrease is due to the water accommodation in the ionic liquid structure, by establishing hydrogen bonds with both the anion and cation, leading to a reduction of the electrostatic attractions between the ions and therefore to a decrease on the overall cohesive energy.

Being shown that the surface tensions depend on the strength of the interactions between anion and cation, and in particular that they could be related with the hydrogen bond strength as measured by mass spectrometry, it was attempted to develop a correlation for surface tensions with the cation–anion interactions. For that purpose, a correlation with the effective ionic concentration (C_{eff}) was developed showing that this could be a useful parameter for the estimation of the surface tension of ionic liquids.

Acknowledgments

This work was supported by Fundação para a Ciência e a Tecnologia (Project POCI/EQU/58152/2004). M.G. Freire acknowledges the financial support from Fundação para a Ciência e a Tecnologia through her Ph.D. (SFRH/BD/14134/2003) scholarship.

Supporting material

Supplementary material for this article may be found on Science Direct, in the online version.

Please visit DOI: [10.1016/j.jcis.2007.06.003](https://doi.org/10.1016/j.jcis.2007.06.003).

References

- [1] R.D. Rogers, K.R. Seddon, *Science* 302 (2003) 792.
- [2] C. Chiappe, D. Pieraccini, *J. Phys. Org. Chem.* 18 (2005) 275.
- [3] K.N. Marsh, J.A. Boxall, R. Lichtenthaler, *Fluid Phase Equilib.* 219 (2004) 93.
- [4] K.R. Seddon, *J. Chem. Technol. Biotechnol.* 68 (1997) 351.
- [5] J.G. Huddleston, H.D. Willauer, R.P. Swatloski, A.E. Visser, R.D. Rogers, *Chem. Commun.* 16 (1998) 1765.
- [6] L. Cammarata, S.G. Kazarian, P.A. Salter, T. Welton, *Phys. Chem. Chem. Phys.* 3 (2001) 5192.
- [7] J.L. Shereshfey, *J. Phys. Chem.* 35 (1931) 1712.
- [8] E.A. Guggenheim, *J. Chem. Phys.* 13 (1945) 253.
- [9] H. Tokuda, S. Tsuzuki, M. Susan, K. Hayamizu, M. Watanabe, *J. Phys. Chem. B* 110 (2006) 19593.
- [10] H. Tokuda, K. Hayamizu, K. Ishii, M. Susan, M. Watanabe, *J. Phys. Chem. B* 108 (2004) 16593.
- [11] K.R. Seddon, A. Stark, M. Torres, *Pure Appl. Chem.* 72 (12) (2000) 2275.
- [12] M.G. Freire, C.M.S.S. Neves, P.J. Carvalho, R.L. Gardas, A.M. Fernandes, I.M. Marrucho, L.M.N.B.F. Santos, J.A.P. Coutinho, *Green Chem.* (2007), submitted for publication.
- [13] M.G. Freire, P.J. Carvalho, R.L. Gardas, L.M.N.B.F. Santos, I.M. Marrucho, J.A.P. Coutinho, *Green Chem.* (2007), submitted for publication.
- [14] R.D. Chirico, M. Frenkel, V.V. Diky, K.N. Marsh, R.C. Wilhoit, *J. Chem. Eng. Data* 48 (2003) 1344.
- [15] The NIST Reference on Constants, Units, and Uncertainty, <http://www.physics.nist.gov/cuu/>.
- [16] L.I. Rolo, A.I. Caco, A.J. Queimada, I.M. Marrucho, J.A.P. Coutinho, *J. Chem. Eng. Data* 47 (2002) 1442.
- [17] A.J. Queimada, A.I. Caco, I.M. Marrucho, J.A.P. Coutinho, *J. Chem. Eng. Data* 50 (2005) 1043.
- [18] A.J. Queimada, F.A.E. Silva, A.I. Caco, I.M. Marrucho, J.A.P. Coutinho, *Fluid Phase Equilib.* 214 (2) (2003) 211.
- [19] M.G. Freire, P.J. Carvalho, A.J. Queimada, I.M. Marrucho, J.A.P. Coutinho, *J. Chem. Eng. Data* 51 (2006) 1820.
- [20] J. Yang, J. Gui, X. Lu, Q. Zhang, H. Li, *Acta Chim. Sinica* 63 (2005) 577.
- [21] R. Gomes De Azevedo, J.M.S.S. Esperanca, J. Szydowski, Z.P. Visak, P.F. Pires, H.J.R. Guedes, L.P.N. Rebelo, *J. Chem. Thermodyn.* 37 (2005) 888.
- [22] Z. Gu, J.F. Brennecke, *J. Chem. Eng. Data* 47 (2002) 339.
- [23] M. Krummen, P. Wasserscheid, J. Gmehling, *J. Chem. Eng. Data* 47 (2002) 1411.
- [24] R.L. Gardas, M.G. Freire, P.J. Carvalho, I.M. Marrucho, I.M.A. Fonseca, A.G.M. Ferreira, J.A.P. Coutinho, *J. Chem. Eng. Data* 52 (1) (2007) 80.
- [25] G. Law, P.R. Watson, *Langmuir* 17 (2001) 6138.
- [26] L.P.N. Rebelo, J.N. Canongia Lopes, J.M.S.S. Esperanca, E. Filipe, *J. Phys. Chem. B* 109 (2005) 6040.
- [27] S.V. Dzyuba, R.A. Bartsch, *Chem. Phys. Chem.* 3 (2002) 161.
- [28] J.G. Huddleston, A.E. Visser, W.M. Reichert, H.D. Willauer, G.A. Broker, R.D. Rogers, *Green Chem.* 3 (2001) 156.
- [29] V. Halka, R. Tsekov, W. Freyland, *Phys. Chem. Chem. Phys.* 9 (2005) 2038.
- [30] A. Pereiro, P. Verdía, E. Tojo, A. Rodriguez, *J. Chem. Eng. Data* 52 (2) (2007) 377.
- [31] G. Law, P.R. Watson, *Chem. Phys. Lett.* 345 (2001) 1.
- [32] L. Crowhurst, P.R. Mawdsley, J.M. Perez-Arlandis, P.A. Salter, T. Welton, *Phys. Chem. Chem. Phys.* 5 (2003) 2790.
- [33] P. Hunt, *J. Phys. Chem. B* 111 (18) (2007) 4844.
- [34] M. Deetlefs, C. Hardacre, M. Nieuwenhuysen, A. Padua, O. Sheppard, A. Soper, *J. Phys. Chem. B* 110 (2006) 12055.
- [35] K. Dong, S. Zhang, D. Wang, X. Yao, *J. Phys. Chem. A* 110 (2006) 9775.
- [36] The NIST Chemistry WebBook, <http://webbook.nist.gov/chemistry/>.
- [37] I. Langmuir, *Phenomena Atoms and Molecules*, Philosophical Library, New York, 1950.
- [38] DIPPR Design Institute for Physical Properties: DIPPR 801 Database, Brigham Young University, 1998.
- [39] R.G. Cooks, J.T. Koskinen, P.D. Thomas, *Int. J. Mass Spectrom.* 34 (1999) 85.
- [40] S. Tsuzuki, H. Tokuda, K. Hayamizu, M. Watanabe, *J. Phys. Chem. B* 109 (2005) 16474.
- [41] A.D. McNaught, A. Wilkinson, *Compendium of Chemical Terminology*, Iupac Recommendations, second ed., Blackwell Science, Cambridge, 1997.
- [42] A.W. Adamson, A.P. Gast, *Physical Chemistry of Surfaces*, sixth ed., Wiley, 1997.
- [43] J.C. Miller, J.N. Miller, *Statistics for Analytical Chemistry*, third ed., PTR Prentice–Hall, Chichester, 1993.
- [44] E. Sloutskin, C.D. Bain, B.M. Ocko, M. Deutsch, *Faraday Discuss.* 129 (2005) 339.
- [45] R.M. Lynden-Bell, *Mol. Phys.* 101 (2003) 2625.
- [46] G. Law, P.R. Watson, A.J. Carmichael, K.R. Seddon, *Phys. Chem. Chem. Phys.* 3 (2001) 2879.

- [47] T. Iimori, T. Iwahashi, H. Ishiib, K. Seki, Y. Ouchi, R. Ozawac, H. Hamaguchic, D. Kim, Chem. Phys. Lett. 389 (2004) 321.
- [48] J. Bowers, C.P. Butts, P.J. Martin, M.C. Vergara-Gutierrez, R.K. Heenan, Langmuir 20 (2004) 2191.
- [49] E. Slouskin, B. Ocko, L. Tamam, I. Kuzmenko, T. Gog, M. Deutsch, J. Am. Chem. Soc. 127 (2005) 7796.
- [50] L.M.N.B.F. Santos, J.N. Canongia Lopes, J.A.P. Coutinho, J.M.S.S. Esperanca, L.R. Gomes, I.M. Marrucho, L.P.N. Rebelo, J. Am. Chem. Soc. 128 (2006) 284.
- [51] D. Fu, X. Sun, J. Pu, S. Zhao, J. Chem. Eng. Data 51 (2006) 371.
- [52] I. Malham, P. Letellier, M. Turmine, J. Phys. Chem. B 110 (2006) 14212.
- [53] J. Sung, Y. Jeon, D. Kim, T. Iwahashi, T. Iimori, K. Seki, Y. Ouchi, Chem. Phys. Lett. 406 (2005) 495.
- [54] S. Rivera-Rubero, S. Baldelli, J. Am. Chem. Soc. 126 (2004) 11788.
- [55] B.E. Poling, J.M. Prausnitz, J.P. O'Connell, The Properties of Gases and Liquids, fifth ed., McGraw-Hill, 2000.
- [56] J. Valderrama, P. Robles, Ind. Eng. Chem. Res. 46 (2007) 1338.
- [57] A.L. Lydersen, Estimation of Critical Properties of Organic Compounds, Report 3, Engineering Experimental Station, Madison, WI, 1955.
- [58] K.K. Joback, R. Reid, Chem. Eng. Commun. 57 (1987) 233.
- [59] K.M. Klincewicz, R.C. Reid, AIChE J. 30 (1984) 137.
- [60] M.J. Earle, J.M.S.S. Esperanca, M.A. Gilea, J.N. Canongia Lopes, L.P.N. Rebelo, J.W. Magee, K.R. Seddon, J.A. Widegren, Nature 439 (2006) 831.
- [61] F.C. Gozzo, L.S. Santos, R. Augusti, C.S. Consorti, J. Dupont, M.N. Eberlin, Chem. Eur. J. 10 (2004) 6187.
- [62] H. Tokuda, K. Hayamizu, K. Ishii, M. Susan, M. Watanabe, J. Phys. Chem. B 109 (2005) 6103.
- [63] T. Umecky, M. Kanakubo, Y. Ikushima, J. Mol. Liq. 119 (2005) 77.