Influence of the anion on the surface tension of 1-ethyl-3-methylimidazolium-based ionic liquids

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ABSTRACT

The air–liquid interfacial tensions of eight ionic liquids, from (298 to 343) K, are presented in this work. The studied ionic liquids are formed by the fixed 1-ethyl-3-methylimidazolium cation combined with the anions acetate, dicyanamide, dimethylphosphate, methylphosphonate, methanesulfonate, thiocyanate, tosylate, and trifluoromethanesulfonate. The selected ionic liquids allowed a comprehensive study through the influence of the anion nature on the surface tension and on their surface ordering. A slight dependence of the surface tension with the ionic liquid molar volume was identified. The surface thermodynamic functions are mainly controlled by the anion which constitutes a given ionic liquid. The hypothetical critical temperatures of all ionic liquids were estimated by means of the Eötvos and Guggenheim correlations and are presented.

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1. Introduction

Ionic liquids (ILs), known as salts with a melting temperature below 100 °C, have been largely explored in the past few years and are at last reaching their place in the chemical industry. Ionic liquids are composed of ions, and as a result, there are a large number of potential fluids to be synthesized by simple structural rearrangements. In an ideal situation, the combination of different ions allocates the tailoring of their properties and characteristics, and allows them to be *quasi* specific fluids for particular applications. Moreover, the ionic nature of ionic liquids is the main characteristic responsible for their outstanding properties, namely a negligible vapor pressure, a high ionic conductivity, non-flammability, high thermal and chemical stabilities, and an enhanced solvation ability for a large array of compounds [1–6].

The burgeoning area of research involving ionic liquids ranges from their use as lubricants [7], in gas separation processes [8], as gas storage media [9], as solvents in multiphasic homogeneous catalytic reactions [5,10], as solvent media and catalysts in heterogeneous reactions [11], as extractive phases of biotechnological and analytical interest [12,13], as potential solvents in extractive distillation processes to separate water–ethanol mixtures [14], as enhanced candidates to dissolve and process biomass [15], among many other current and exploratory purposes. In general, most of

the applications concerning ionic liquids involve the presence of a second phase (liquid or gas phase) whereas the interface among the fluids plays a vital role. Therefore, the knowledge of the interface properties of ionic liquids, namely surface and interfacial tensions, and the relationship of these properties with the chemical structure of the compounds, are crucial requirements for choosing an improved ionic liquid for a specific purpose.

Besides the measurements of the thermophysical properties of ionic liquids aiming at achieving a complete database, it is highly important to understand the interactions that occur at the bulk and the interfacial phenomena with the surrounding media. In fact, the surface tension is closely related to the intermolecular interactions that occur at the bulk (cohesive energy) and the molecular orientation at the surface. Albeit several methods can be used to measure the surface tension of ionic liquids, this property has been lagged behind when compared with density and viscosity measurements. Reliable and accurate measurements of surface tensions of ionic liquids are non trivial. First of all, the presence of surface active impurities leads to large deviations in the surface tension values. Moreover, most of the ionic liquids are highly hygroscopic and the control of their water content at low values is not an easy task. A review regarding the surface tensions of ionic liquids and ionic liquid solutions was recently reported [16] and addresses these peculiar issues and sources of error in the determination of this property, and provides a complete compilation of the data published hitherto. The general trends on the surface tension values according to the ionic liquid chemical structure are also

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TABLE 1
Water content (weight fraction percentages) in the studied ionic liquids.

Ionic liquid	Water content/(wt%)
[C_2mim][CH_3CO_2]	0.046
[C_2mim][SCN]	0.039
[C_2mim][N(CN)$_2$]	0.037
[C_2mim][Tos]	0.056
[C_2mim][CF_3SO_3]	0.002
[C_2mim][CH_3OHPO_2]	0.017
[C_2mim][(OCH_3)$_2PO_2$]	0.014
[C_2mim][CH_3SO_3]	0.029
[C_4mim][PF_6]	0.019
[C_4mim][Ntf_2]	0.030
[C_4mim][CF_3SO_3]	0.001
[C_4mim][BF_4]	0.001

provided and discussed [16]. Although the effect of the alkyl chain length, cation core and group functionalization of ionic liquids have been widely explored, on the contrary, the effect of the anion is a scattered studied field [16].

Aiming at gathering a better understanding on the anion effect upon the surface tensions and surface ordering of ionic liquids, in this work, we present surface tension data for eight 1-ethyl-3-methylimidazolium-based ionic liquids. The relationship between the surface tensions of ionic liquids and their molar volume is also explored. Furthermore, the surface tensions were determined as a function of temperature allowing the determination of the related surface thermodynamic functions. The hypothetical critical temperatures of the ionic liquids investigated were also estimated by means of the Etövos [17] and Guggenheim [18] equations.

## 2. Experimental

2.1. Chemicals

Eight 1-ethyl-3-methylimidazolium-based ionic liquids combined with different anions were studied in this work, *viz.*, acetate ([C_2mim][CH_3CO_2]), thiocyanate ([C_2mim][SCN]), dicyanamide ([C_2mim][N(CN)$_2$]), tosylate ([C_2mim][Tos]), trifluoromethanesulfonate ([C_2mim][CF_3SO_3]), methylphosphonate ([C_2mim][CH_3OHPO_2]), dimethylphosphate ([C_2mim][(OCH_3)$_2PO_2$]), and methanesulfonate ([C_2mim][CH_3SO_3]). The ionic structures of the investi-

gated ionic liquids are depicted in figure 1. All the described ionic liquids were acquired at Iolitec, with the exception of 1-ethyl-3-methylimidazolium methylphosphonate which was purchased from Solvionic. Additionally, four other ionic liquids, namely 1-butyl-3-methylimidazolium tetrafluoroborate ([C_4mim][BF_4]), 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4mim][PF_6]),1-butyl-3-methylimidazolium trifluoromethanesulfonate ([C_4mim][CF_3SO_3]), and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C_4mim][Ntf_2]) were studied with the aim of comparing surface tension data on ionic liquids gathered with a different method (pendant drop and du Noüy ring methods). The 1-butyl-3-methylimidazolium-based ionic liquids were purchased from Iolitec.

To remove traces of water and volatile compounds, individual samples of each ionic liquid were dried at moderate temperature (≈ 323 K) and at high vacuum ($\approx 10^{-5}$ Pa), under constant stirring, and for a minimum period of 48 h. After this purification procedure, the purity of all ionic liquids samples was further checked by ^{1}H and ^{13}C NMR (and ^{19}F NMR for all the fluorinated ionic liquids) and showed to be $\geqslant$ 99 wt%. Moreover, the water content of each ionic liquid, after the drying step and immediately before the measurements of the surface tensions, was determined by Karl Fischer titration making use of a Metrohm 831 Karl Fischer coulometer. The reagent employed was Hydranal - Coulomat AG from Riedel-de Haën. The water content of each ionic liquid is presented in table 1.

2.2. Apparatus and procedure

The surface tension of each sample was determined through the analysis of the shape of the pendant drop and measured using a Dataphysics contact angle system OCA-20. Drop volumes of (15 ± 2) μL (depending on the ionic liquid) were obtained using a Hamilton DS 500/GT syringe connected to a Teflon coated needle placed inside an aluminium air chamber capable of maintaining the temperature within ±0.1 K. The temperature was attained by circulating water in the double jacketed aluminium cell by means of a Julabo F-25 water bath. The surface tensions measurements were performed in the temperature range from (298 to 343) K. The temperature inside the aluminium chamber, and at which the surface tensions were determined, was measured with a Pt100 within ±0.1 K which was placed at a distance of approximately
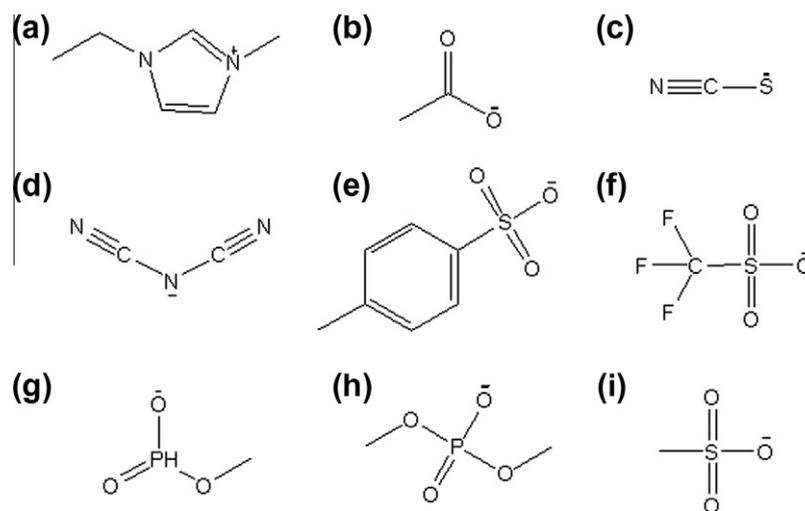
FIGURE 1. Ionic structures of (a) 1-ethyl-3-methylimidazolium ([C_2mim]$^+$); (b) acetate ([CH_3CO_2]$^-$); (c) thiocyanate ([SCN]$^-$); (d) dicyanamide ([N(CN)$_2$]$^-$); (e) tosylate ([Tos]$^-$); (f) trifluoromethanesulfonate or triflate ([CF_3SO_3]$^-$); (g) methylphosphonate ([CH_3OHPO_2]$^-$); (h) dimethylphosphate ([(OCH_3)$_2PO_2$]$^-$); (i) methanesulfonate ([CH_3SO_3]$^-$).

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2 cm to the liquid drop. After attaining a specific temperature, the measurements were carried out after 30 min to guarantee the thermal stabilization. Silica gel was kept inside the air chamber aiming at keeping a dry environment and to avoid the adsorption of moisture by the ionic liquids. For the surface tensions determination at each temperature, and for each ionic liquid, at least six drops were formed and measured. For each drop, an average of 130 images was additionally captured. The analysis of the drop shape was performed with the software modules SCA 20. The density values required for the calculation of the surface tensions from the drop image data were taken from literature [19].

In order to validate the equipment and methodology used, the surface tension of ultra-pure and deionised water, *n*-decane, and *n*-dodecane were determined from (298 to 343) K, and are in close agreement with literature values [20–22]. Also the surface tensions of $[C_4mim][PF_6]$, $[C_4mim][Ntf_2]$, $[C_4mim][CF_3SO_3]$, and $[C_4mim][BF_4]$ were determined in the temperature interval between (298 and 343) K, using the density values for the $[C_4mim]$-based ionic liquids taken from literature [23–25], and were compared with previous results published by us using the du Noüy ring method [26,27].

3. Results and discussion

3.1. Surface tension

Previous data reported by us [26], using a distinct equipment (based on the du Noüy ring method), were used to evaluate the ability of the method here employed to determine the surface tension of novel ionic liquids, as well as to compare the data gathered from two different equipments. The surface tension data measured in this work for $[C_4mim][PF_6]$, $[C_4mim][Ntf_2]$, $[C_4mim][CF_3SO_3]$, and $[C_4mim][BF_4]$ are presented in Supporting Information. The relative average deviation of the data gathered in this work and those of literature [26,27] is 0.79%, meaning that the deviations between two different techniques are usually lower than those observed amongst different authors – see discussion below.

The surface tension values for the $[C_2mim]$-based ionic liquids are presented in table 2 and depicted in figure 2. For $[C_2mim][Tos]$ and $[C_2mim][(OCH_3)_2PO_2]$ the measurements were carried out only above 303 K since both ionic liquids are solid at lower temperatures. The data previously published [27] for 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)amide ($[C_2mim][Ntf_2]$) are also depicted in figure 2 aiming at enabling a better understanding of the influence of the ionic liquid anion on the surface tension.
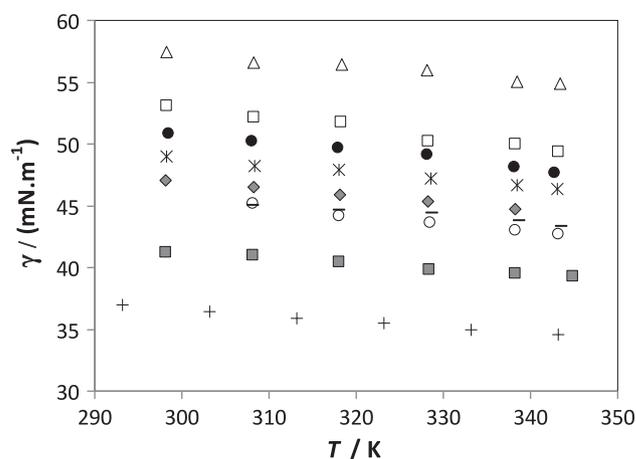
FIGURE 2. Surface tension values as a function of temperature for the ionic liquids: △, $[C_2mim][N(CN)_2]$; □, $[C_2mim][SCN]$; ●, $[C_2mim][CH_3SO_3]$; ∗, $[C_2mim][CH_3OHPO_2]$; ♦, $[C_2mim][CH_3CO_2]$; −, $[C_2mim][(OCH_3)_2PO_2]$; ○, $[C_2mim][Tos]$; ■, $[C_2mim][CF_3SO_3]$; +, $[C_2mim][Ntf_2]$ [27].

Despite the importance of surface tension data in a wide range of applications in pure and applied sciences, the data available are scarce when considering the large number of possible ionic liquids that can be synthesized. Moreover, the surface tension data are highly affected by the presence of impurities, and even by small amounts of water. Therefore, discrepancies inevitably exist among different authors. Among the ionic liquids here studied, surface tension data for $[C_2mim][CF_3SO_3]$ [28–31], $[C_2mim][N(CN)_2]$ [28,32,33], $[C_2mim][SCN]$ [28,34], $[C_2mim][CH_3SO_3]$ [35], and $[C_2mim][CH_3OHPO_2]$ [35] were found in literature. While most of the studies only reported the surface tension at room temperature [28,30,32,35], additional works have explored the influence of temperature in the surface tension of $[C_2mim][CF_3SO_3]$ [29,31], $[C_2mim][N(CN)_2]$ [33], and $[C_2mim][SCN]$ [34].
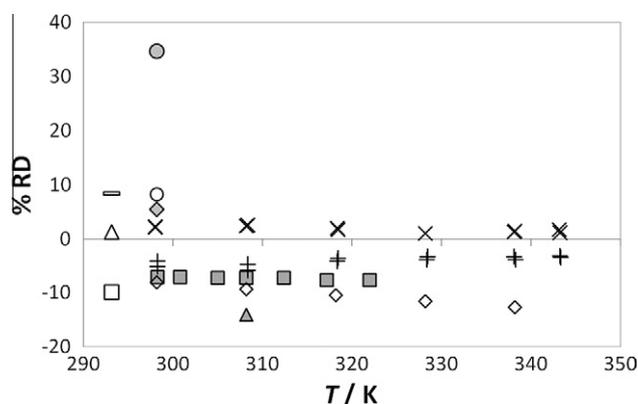
The percentage relative deviations (%RD) between our data and those from literature [28–35] are summarized in figure 3. Positive and negative relative deviations are found between our data and those already published. However, a close agreement between our data and those recently published by Pátek and co-workers was found [31,33]. It should be stressed that the authors employed both the du Noüy ring and Wilhelmy plate methods to confirm the accuracy of the measurements [31,33]. Although some large deviations exist between our data and literature data it must be noted that large deviations are still observed among the data from differ-

TABLE 2
Experimental surface tension values at several temperatures.

$[C_2mim][CH_3CO_2]$		$[C_2mim][SCN]$		$[C_2mim][N(CN)_2]$		$[C_2mim][Tos]$	
T/K	$(\gamma \pm 2u(\gamma)^a)/(mN \cdot m^{-1})$	T/K	$(\gamma \pm 2u(\gamma)^a)/(mN \cdot m^{-1})$	T/K	$(\gamma \pm 2u(\gamma)^a)/(mN \cdot m^{-1})$	T/K	$(\gamma \pm 2u(\gamma)^a)/(mN \cdot m^{-1})$
298.1	47.1 ± 0.1	298.2	53.3 ± 0.6	298.3	57.5 ± 0.6		
308.2	46.5 ± 0.1	308.2	52.3 ± 0.6	308.2	56.6 ± 0.7	308.1	45.2 ± 0.4
318.2	45.9 ± 0.1	318.2	51.8 ± 0.6	318.3	56.4 ± 0.6	318.0	44.2 ± 0.4
328.2	45.3 ± 0.1	328.2	50.5 ± 0.7	328.2	56.0 ± 0.3	328.5	43.6 ± 0.4
338.3	44.7 ± 0.1	338.3	49.8 ± 0.7	338.5	55.0 ± 0.6	338.3	43.0 ± 0.3
		343.2	49.4 ± 0.7	343.4	54.9 ± 0.6	343.2	42.7 ± 0.3
$[C_2mim][CF_3SO_3]$		$[C_2mim][CH_3OHPO_2]$		$[C_2mim][(OCH_3)_2PO_2]$		$[C_2mim][CH_3SO_3]$	
T/K	$(\gamma \pm 2u(\gamma)^a)/(mN \cdot m^{-1})$	T/K	$(\gamma \pm 2u(\gamma)^a)/(mN \cdot m^{-1})$	T/K	$(\gamma \pm 2u(\gamma)^a)/(mN \cdot m^{-1})$	T/K	$(\gamma \pm 2u(\gamma)^a)/(mN \cdot m^{-1})$
298.2	41.3 ± 0.2	298.2	49.0 ± 0.3			298.5	50.9 ± 0.5
308.1	41.0 ± 0.1	308.4	48.3 ± 0.3	308.2	45.3 ± 0.6	308.0	50.3 ± 0.6
318.1	40.5 ± 0.2	318.0	47.9 ± 0.5	318.0	44.7 ± 0.6	317.9	49.7 ± 0.5
328.4	39.9 ± 0.3	328.6	47.2 ± 0.3	328.7	44.4 ± 0.6	328.1	49.1 ± 0.5
338.3	39.5 ± 0.5	338.5	46.7 ± 0.3	338.6	43.8 ± 0.5	338.1	48.1 ± 0.5
344.9	39.3 ± 0.1	343.1	46.3 ± 0.3	343.5	43.3 ± 0.3	342.7	47.7 ± 0.5

^a Expanded uncertainty at the 0.95 confidence level, $2u(\gamma)$, evaluated from the standard deviation and applying a coverage factor $k = 2$.

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FIGURE 3. Percentage relative deviations between the experimental surface tension data obtained in this work and those reported in literature: ♦, [C$_2$mim][CF$_3$SO$_3$] [28]; ■, [C$_2$mim][CF$_3$SO$_3$] [29]; ▲, [C$_2$mim][CF$_3$SO$_3$] [30]; ×, [C$_2$mim][CF$_3$SO$_3$] [31] ●, [C$_2$mim][N(CN)$_2$] [28]; □, [C$_2$mim][N(CN)$_2$] [32]; +, [C$_2$mim][N(CN)$_2$] [33]; ○, [C$_2$mim][SCN] [28]; ◇, [C$_2$mim][SCN] [34]; △, [C$_2$mim][CH$_3$SO$_3$] [35]; ─, [C$_2$mim][CH$_3$OHPO$_2$] [35].
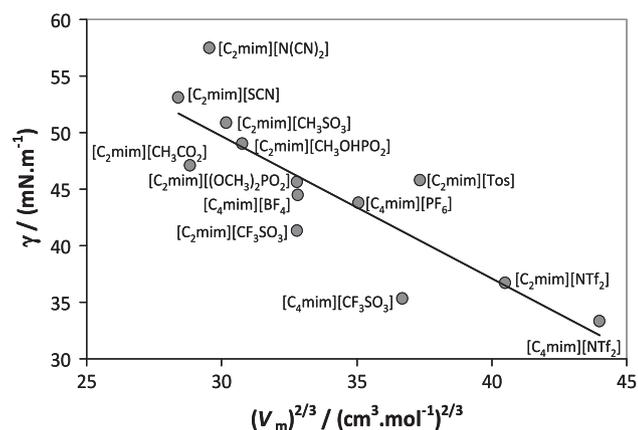
FIGURE 4. Dependence of the surface tensions of ionic liquids with their molar volumes (at 298 K). The solid line represents the data linear dependence.

ent authors. For instance, at 298 K, the surface tension of [C$_2$mim][SCN] was reported as 49.00 mN · m^{-1} or 57.76 mN · m^{-1} depending on the literature source [28,34]. These differences could be attributed to the ionic liquid purity level, including the amount of water, halides, volatile compounds, and other surface-active contaminants such as oxygen-containing carbohydrates and polysiloxanes [36,37]. Previously we have studied how the presence of water affects the surface tension of ionic liquids [26]. The effect of the water content further depends on the ionic liquid hydrophobicity [26]. In general, a decrease in the surface tension was observed for low water contents, while for higher water contents the surface tensions reach the values of "dry" ionic liquids – being this effect more relevant for hydrophilic ionic liquids [26]. We have explained this effect based on the structural rearrangement of the ionic liquids [26]. Water accommodates in the near-surface region of the ionic liquid by establishing hydrogen-bonding interactions with both the anion and cation (in this particularly example, imidazolium-based ionic liquids), reducing therefore the electrostatic interactions between the ions which further leads to a decrease of the cohesive energy. When significant amounts of water are present there is a complete solvation of the ions. The addition of more water leads to the appearance of water molecules not hydrogen-bonded to the ionic liquid and to the formation of water clusters, and to an increase in the surface tension values.

The gathered experimental surface tension values show that the ionic liquid anion plays a significant role in the structural organization of the ionic liquid at the air-liquid interface. For a common temperature, and making use of data previously reported for [C$_2$mim][Ntf$_2$] [27], the surface tension decreases in the following sequence: [C$_2$mim][N(CN)$_2$] > [C$_2$mim][SCN] > [C$_2$mim][CH$_3$SO$_3$] > [C$_2$mim][CH$_3$OHPO$_2$] > [C$_2$mim][CH$_3$CO$_2$] > [C$_2$mim][(OCH$_3$)$_2$PO$_2$] > [C$_2$mim][Tos] > [C$_2$mim][CF$_3$SO$_3$] > [C$_2$mim][Ntf$_2$].

Investigations involving the effect of the ionic liquid anion towards the surface tension values have leaded to conflicting conclusions. While Santos and Baldelli [38] showed that an increase in the length of the aliphatic chain of the anion decreases the surface tensions (behavior analogous to that observed with the aliphatic chain of the cation), Martino et al. [28] did not found a general trend regarding the effect of the anion size. The data obtained in this work suggest that an increase in the anion size leads to a decrease on the surface tensions as previously observed by us [26] and others [39,40] – see the results and discussion below. In fact, this trend is the opposite of what is commonly observed with organic compounds where an increase in the size of the molecules leads to an increase in the surface tension. This is a direct result of the complex nature of ionic liquids where Coulombic forces, hydrogen-bonding and dispersive interactions are present. While for common solvents an increase in the aliphatic chain enhances the van der Waals interactions, in ionic liquids this trend will be "negatively" compensated by an enhanced dispersion of the ions charge, thus lowering the strength of the Coulombic interactions, and by a decrease on the hydrogen-bonding strength.

The development of quantitative structure-property relationships and predictive methods for ionic liquids is a vital issue in the characterization of these fluids, as well as to estimate their thermophysical properties when related data are not available. Larriba et al. [41], based on the cavity theory, provided a correlation between the surface tension and void fraction in ionic liquids. The void fraction accounts with the difference between the liquid volume occupied by an ion pair (known from cationic and anionic weights and liquid density measurements) and the sum of the cationic and anionic volumes (known from crystal structures). In addition, Gardas and Coutinho [10] proposed a quantitative structure-property relationship correlation for the calculation of the surface tension of ionic liquids based on parachors and density data, and another correlation based on the ionic volumes of the fluids to estimate the surface tension of ionic liquids at room temperature. Taking into account that the surface enthalpy varies within a narrow range of values for most of the studied imidazolium-based ionic liquids, a new equation relating the surface tension and the molar volume was proposed by Gardas and Coutinho [10],

$$\gamma = \frac{d}{V^{2/3}} \tag{1}$$

where γ is the surface tension in mN · m^{-1}, V is the molecular volume in Å^3 and d is a fitted constant.

With the aim of allowing a visual comparison and to test the dependence of the surface tension of ionic liquids with their molar volumes, the surface tension is plotted as a function of the ionic liquid molar volume in figure 4. Besides the novel surface tension data for [C$_2$mim]-based ionic liquids, the data obtained in this work for [C$_4$mim]-based ionic liquids are also included in order to gather a broader picture of the possible correlation. The molar volume of each ionic liquid was calculated from experimental density data at 298.15 K [19,23–25,42]. Although the scattering of the data reveals that other ionic liquid characteristics play a role on the surface tension of the fluids, the general trend observed in figure 4 clearly suggests that the molar volume has a major influence on the surface tension of ionic liquids. Kolbeck et al. [39] previously

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TABLE 3
Surface thermodynamic functions of the studied ionic liquids.

Ionic liquid	$(S^\gamma \pm 2u(S^\gamma)^a) \cdot 10^{-5}/$ $(J \cdot m^{-2} \cdot K^{-1})$	$(H^\gamma \pm 2u(H^\gamma)^A) \cdot 10^{-2}/$ $(J \cdot m^{-2})$
$[C_2mim][CH_3CO_2]$	5.8 ± 0.1	6.44 ± 0.03
$[C_2mim][SCN]$	8.7 ± 0.4	7.9 ± 0.1
$[C_2mim][N(CN)_2]$	5.5 ± 0.5	7.4 ± 0.2
$[C_2mim][Tos]$	6.9 ± 0.5	6.6 ± 0.2
$[C_2mim][CF_3SO_3]$	4.5 ± 0.2	5.46 ± 0.08
$[C_2mim][CH_3OHPO_2]$	5.8 ± 0.2	6.63 ± 0.08
$[C_2mim][(OCH_3)_2PO_2]$	5.3 ± 0.5	6.2 ± 0.2
$[C_2mim][CH_3SO_3]$	7.1 ± 0.5	7.2 ± 0.2

^a Expanded uncertainty at the 0.95 confidence level, $2u(S^\gamma)$ and $2u(H^\gamma)$, evaluated from the standard deviation and applying a coverage factor $k = 2$.

described a dependence of the surface tension with the ionic volume of the anion for 12 ionic liquids with the common 1-methyl-3-octylimidazolium cation. Due to the variety of the studied anions with different size, shape, basicity and coordination ability, the authors divided the anion results by subgroups of chemical similarity: halides, spherical anions and perfluorinated anions. Although more clear trends were observed with the subgroups division [39], our data indicate that a general trend exists when the surface tension is plotted against the ionic liquids molar volume. In fact, the division on subgroups or categories of ionic liquids is not clear in figure 4.

Albeit it is safe to admit that the surface tension of ionic liquids depends on their molar volume, the orientation of the ions at the surface cannot be discarded. It is well known that the hydrogen-bonding ability between the ions plays a crucial task at the liquid bulk; yet, at the interface, it seems that the hydrogen-bonding ability is less relevant than the loss/gain of entropy and surface organization. For instance, the anion acetate is known to present an enhanced hydrogen-bonding acceptor character, the fluorinated anions are on the opposite extreme, and the cyano-based compounds are on a middle rank [43]. Therefore, from the obtained trend on the surface tensions according to the anion influence, it seems that the hydrogen-bonding capability between the ions plays a minor role in their surface properties.

According to the Langmuir principle, only the parts of the ions that are at the outer surface will primarily contribute to the surface tension values. Most of the results have shown that although both cations and anions are present at the interface there is a general segregation between the polar and non-polar parts of the ions and that the longer alkyl side chains point towards the vapor phase [44–46]. Recently, Hantal et al. [47] discussed the possibility and presence of a relative prevalence of different molecular orientations at the surface of ionic liquids, and that the experimental data should be interpreted considering a distribution of molecular arrangements. Even though the simulation results [44–47] could be used in the interpretation of the experimental data it should be stressed that the ionic liquid anion largely contributes to the surface tension values (from experimental data), implying thus that they tend to organize themselves at the surface and/or contribute to the organization of the cation. Therefore, related works for the anion organization at the surface are mandatory.

3.2. Surface thermodynamics properties

The surface thermodynamic properties, namely the surface entropy and the surface enthalpy, were derived using the quasi-linear dependence of the surface tension with temperature. The surface entropy, S^γ, can be calculated according to [48,49],

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

and the surface enthalpy, H^γ, according to [48,49],

$$H^\gamma = \gamma - T\left(\frac{d\gamma}{dT}\right) \quad (3)$$

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

The values of the thermodynamic functions of all the ionic liquids investigated (and respective expanded uncertainties [50]) are presented in table 3.

Along with results previously reported for different ionic liquids [6,26,27], this class of fluids exhibits a remarkably low surface entropy when compared with molecular organic compounds. This evidence reflects a high surface organization, as well as an inherent highly structured liquid phase, in ionic liquids. In previous works we have evaluated the effect of the alkyl chain length at the cation (from ethyl to octyl [27]) and the effect of the cation core (with imidazolium-, pyridinium-, pyrrolidinium-, and phosphonium-based ionic liquids [6]) through the surface entropy and surface enthalpy of ionic liquids. From the data gathered before and the values obtained in this work it is clear that the surface enthalpy and surface entropy are primarily ruled by the anion nature that constitutes a specific ionic liquid. Indeed, this trend was previously shown by us, yet with a smaller number of ionic liquids [26]. Lower surface entropies are particularly observed for $[C_2mim][CF_3SO_3]$ and $[C_2mim][(OCH_3)PO_2]$ which reflect a higher surface ordering in these ionic liquids. On the other hand, $[C_2mim][Tos]$ and $[C_2mim][CH_3SO_3]$ display the higher surface entropy values.

3.3. Estimated critical temperature

The determination of the thermodynamic coordinates of the triple and critical points of a given substance allows the definition of its pressure-temperature liquid range, as well as the indication of the boundaries of the corresponding liquid-gas equilibrium curve. The critical temperature of fluids, T_c, is a recurrent property commonly used in corresponding states relations involving equilibrium and transport properties [51]. However, the determination of the critical temperatures of ionic liquids is a challenge assignment since they decompose before reaching those high temperature values. Rebelo et al. [52] proposed the use of the Eötvos [17] and Guggenheim [18] equations to estimate the hypothetical critical temperature of ionic liquids, and described accordingly,

$$\gamma\left(\frac{M}{\rho}\right)^{2/3} = K(T_c - T) \quad (4)$$

$$\gamma = K\left(1 - \frac{T}{T_c}\right)^{11/9} \quad (5)$$

where T_c is the critical temperature, M is the molecular weight, ρ is the density, and K is a fitted parameter. Both equations reflect the fact that the surface tension becomes null at the critical point [51].

The critical temperature values estimated from the surface tension data obtained in this work are reported in table 4. The higher critical temperature is observed for the $[C_2mim][N(CN)_2]$ ionic

TABLE 4
Estimated critical temperatures using both the Eötvos $((T_c)_{Eot})$ [17] and Guggenheim $((T_c)_{Gug})$ [18] empirical equations.

Ionic liquid	$(T_c)_{Eot}/K$	$(T_c)_{Gug}/K$
$[C_2mim][CH_3CO_2]$	1437	1281
$[C_2mim][SCN]$	1062	1034
$[C_2mim][N(CN)_2]$	2064	1578
$[C_2mim][Tos]$	1153	1108
$[C_2mim][CF_3SO_3]$	1752	1427
$[C_2mim][CH_3OHPO_2]$	1476	1325
$[C_2mim][(CH_3O)_2PO_2]$	1551	1358
$[C_2mim][CH_3SO_3]$	1250	1169

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liquid. As reported in previous works [6,27], the values for the critical temperatures of ionic liquids obtained by these approaches must be used with caution. Strategies to estimate the critical temperatures using data from a limited temperature range, and requiring a large extrapolation, inherently introduce an important source of uncertainty. A recent work published by Tariq et al. [53] tested the validity of these extrapolations by the measurements of surface tension and density data on an extended temperature range, while confronting their results with data on the vapor pressure and enthalpy of vaporization for the same ionic liquids. On the other hand, recently, Rai and Maggin [54] showed that the critical temperatures estimated by these simple methods are in good agreement with those obtained by molecular simulation calculations.

4. Conclusions

New experimental data were reported for the surface tension of eight ionic liquids with the common 1-ethyl-3-methylimidazolium cation combined with the anions acetate, dicyanamide, dimethylphosphate, methylphosphonate, methanesulfonate, thiocyanate, tosylate, and trifluoromethanesulfonate. The surface tension values were determined in the temperature range from (298 to 343) K and at atmospheric pressure. In general, the surface tension decreases with an increase in the ionic liquid molar volume. When compared with molecular solvents, ionic liquids reveal enhanced surface ordering. Moreover, the surface thermodynamic properties are mainly controlled by the anion which composes a given ionic liquid (if compared with the cation core and alkyl chain length effects). The hypothetical critical temperatures of the ionic liquids investigated were estimated making use of the Eötvos and Guggenheim equations.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jct.2012.03.008.

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