1346 *J. Chem. Eng. Data* **2008,** *53,* 1346–1350

Surface Tensions for the 1-Alkyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide Ionic Liquids

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This work addresses surface tension measurements of eight imidazolium-based ionic liquids (ILs) with the bis(trifluoromethylsulfonyl)imide, Tf_2N, common anion, and their dependence with temperature, from (293 to 353) K, at atmospheric pressure. The set of selected ionic liquids was chosen to provide a detailed and comprehensive study of the influence of the cation alkyl chain length on the surface tensions of the ionic liquids based on the Tf_2N anion. It is shown that, unlike other ionic liquids, the surface tensions of the Tf_2N family do not have a linear decrease with the chain length. The surface thermodynamic functions such as surface entropy and enthalpy were derived from the temperature dependence of the surface tension, and their values indicate the importance of the surface ordering in ionic liquids. The use of the Guggenheim and Eötvos correlations for the estimation of the critical temperatures of ionic liquids is discussed, and the applicability of the Stefan rule to ionic liquids is analyzed.

Introduction

Ionic liquids (ILs) are a class of neoteric solvents composed of large organic cations and organic or inorganic anions that cannot form an ordered crystal and thus remain liquid at or near room temperature. Unlike molecular liquids, the ionic nature of these compounds 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 high solvating capacity, for both polar and nonpolar compounds.[1–3] These outstanding characteristics catalogued ILs as "green" and "designer" solvents, due to the possibility of interchangeability between thousands of cations and anions. The IL's great potential attracts attention for new innovative processes, such as the BASIL process[4] and the hydrosilylation process,[5] bridging academia research with chemical industry applications.

Knowledge of interface tension is of importance in a wide range of problems in pure and applied sciences. To design industrial processes and new products based on ILs, the thermophysical properties must be adequately characterized. As an example, mass-transfer operations like distillation, extraction, absorption, adsorption, and metabolite extractive fermentation require the knowledge of the interface tension. Unfortunately, these thermophysical properties are still limited, inconsistent, and discrepant, and therefore the gathering of a sufficiently large data bank, not only for process and product design but also for development of new correlations, is indispensable.

In this work, the influence of the temperature and cation alkyl chain length on the surface tension of eight 1-alkyl-3-methylimidazolium, [$C_n$mim], based ionic liquids with the bis(trifluoromethylsulfonyl)imide, Tf_2N, common anion, viz., [C_2mim][Tf_2N], [C_3mim][Tf_2N], [C_4mim][Tf_2N], [C_5mim][Tf_2N], [C_6mim][Tf_2N], [C_7mim][Tf_2N], [C_8mim][Tf_2N], and [C_{10}mim][Tf_2N], was investigated.

Using the quasilinear surface tension variation with temperature, the surface thermodynamic properties, such as surface entropy and enthalpy, were derived and the critical temperatures, by means of Eötvos[6] and Guggenheim[7] equations, were estimated.

Enthalpies of vaporization are of very high importance to probe the molecular interactions of ionic liquids in the liquid phase and even to obtain information about the structure of the liquid phase itself. However, very limited information is available for this property due to the difficulties related to its measurement. Very few experimental data are available for enthalpies of vaporization of ionic liquids, and all pertain to the [$C_n$mim][Tf_2N] family of ionic liquids. In an attempt to generate estimations for the enthalpies of vaporization of ionic liquids, some authors have been trying to relate the enthalpies of vaporization with other thermophysical properties more readily available. One of these approaches is through the Stefan rule that relates the enthalpies of vaporization with surface tensions. Although this relationship is known to apply to many different organic compounds, there is no evidence that it may be applied to ionic liquids. The limited and unreliable data concerning surface tensions for the [$C_n$mim][Tf_2N] ionic liquids make difficult a rigorous check of the applicability of this relationship. In an attempt to verify the applicability of Stefan's rule to ionic liquids, the surface tensions measured in this work, for the [$C_n$mim][Tf_2N] ionic liquids, were used along with the enthalpies of vaporization by Santos et al.[8]

Experimental Section

Materials. Eight imidazolium based ILs, namely, 1-alkyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide, [$C_n$mim]-[Tf_2N], with the alkyl side chain ranging between 2 to 8 and 10 were used on this study. All the compounds were acquired at IoLiTec with mass fraction purities > 99 % and bromide

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10.1021/je800069z CCC: \$40.75

Table 1. Surface Tension, σ, of the Ionic Liquids

	$(\sigma \pm 0.03)/\mathrm{mN \cdot m^{-1}}$							
T/K	$[C_2mim][Tf_2N]$	$[C_3mim][Tf_2N]$	$[C_4mim][Tf_2N]$	$[C_5mim][Tf_2N]$	$[C_6mim][Tf_2N]$	$[C_7mim][Tf_2N]$	$[C_8mim][Tf_2N]$	$[C_{10}mim][Tf_2N]$
293.15	36.94	34.87	33.60	32.90	32.31	32.00	31.93	32.12
303.15	36.43	34.22	33.09	32.41	31.76	31.36	31.30	31.34
313.15	35.92	33.73	32.50	31.83	31.20	30.66	30.57	30.70
323.15	35.51	33.31	31.92	31.27	30.60	30.02	29.98	30.10
333.15	34.96	32.79	31.35	30.77	30.16	29.50	29.40	29.50
343.15	34.57	32.18	30.90	30.31	29.62	28.95	28.86	28.68
353.15						28.29		

impurity mass fraction > 10^{-4}. The purities stated by the supplier, of each ionic liquid, were checked by ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR.

It is well established that even low water contents have a great impact on IL physical properties.[9–12] To reduce the water content and volatile compounds to negligible values, vacuum (0.1 Pa), stirring, and moderate temperature (353 K) for at least 48 h were applied to all IL samples prior to the measurements. The IL water content was determined with a Metrohm 831 Karl Fischer coulometer, indicating very low levels of water mass fraction content, as $(42, 33, 44, 20, 43, 30, 21, \text{and } 50) \cdot 10^{-6}$ for $[C_2mim][Tf_2N]$, $[C_3mim][Tf_2N]$, $[C_4mim][Tf_2N]$, $[C_5mim][Tf_2N]$, $[C_6mim][Tf_2N]$, $[C_7mim][Tf_2N]$, $[C_8mim][Tf_2N]$, and $[C_{10}mim][Tf_2N]$, respectively.

Experimental Measurements. The surface tension of the ILs was measured with a NIMA DST 9005 tensiometer from NIMA Technology, Ltd., equipped with a precision balance able to measure down to 10^{-9} N, using the Pt/Ir Du Noüy ring at atmospheric pressure. 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 thermostatized 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, providing a minimum of at least 15 surface tension values, allowing the determination of an average surface tension value for each temperature as well as the expanded associated uncertainty.[13,14] Further details about the equipment and method can be found elsewhere.[15–17] The liquid densities of the pure compounds necessary for the surface tension measurements using the Du Noüy ring were obtained from the literature.[18–21]

Results and Discussion

Surface Tension Measurements. Previous measurements have confirmed the ability of the equipment to accurately measure interfacial tensions for hydrocarbons, fluorocarbon systems, and ionic liquids, validating the methodology and experimental procedure adopted in this work.[9,15–17,22] The surface tension data of the dry ILs studied are reported in Table 1. The percent average relative deviations (% ARD) between the experimental data obtained in this work and those reported by other authors[11,23–25] are presented in Figure 1

$$\%\ \mathrm{AAD} = \frac{1}{n} \sum \left| \frac{\sigma_{\mathrm{exptl}} - \sigma_{\mathrm{lit.}}}{\sigma_{\mathrm{lit.}}} \right| \cdot 100 \qquad (1)$$

where n is the number of data points; σ is the surface tension; and the subscripts exptl and lit. stand for the experimental and literature values, respectively. The data measured show percent average relative deviations of 7 % from the available literature data. These deviations are larger than those previously observed for hydrocarbons and fluorocarbon compounds,[15–17,22] using the same equipment and methodology, but similar to those observed previously for other ILs.[9] Surface tension data are scarce, and significant discrepancies among data from different authors[11,23–25] are common in the literature, since most authors perform measurements either using compounds of low purity or without careful attention toward the preparation of the sample, in particular drying, and often those measurements have been carried out for purposes other than an accurate determination of the surface tensions.

The experimental values presented in Figures 2 and 3 show that the surface tension decreases with increasing alkyl chain length, as previously observed for other ionic liquid families.[9,11,23,26,27] For most ionic liquids, the surface tension decreases almost linearly with the increasing chain length of the cation[9,26,28–31] as predicted by the group contribution method by Gardas and Coutinho.[21] However, as noticed before by Rebelo et al.[24] and Zhou et al.,[32] the surface tensions for the Tf_2N family do not follow a linear decrease with increasing chain length, but instead the surface tension decreases toward a constant value as the cation alkyl chain size increases as can be seen in Figure 3. This peculiar behavior seems to be related to the anion influence on the surface tension, but the information currently available is not enough to provide a molecular explanation for this fact.

Surface Thermodynamic properties. The surface thermodynamic properties, surface entropy, and surface enthalpy were

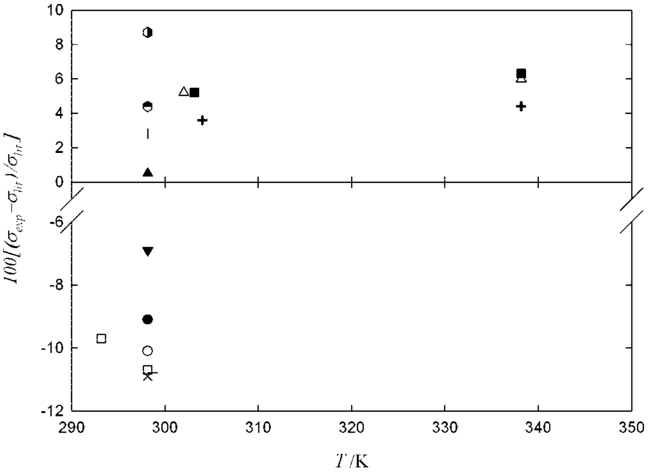

Figure 1. Percent average deviations between the experimental surface tension data of this work and those reported in the literature: ▼, $[C_2mim][Tf_2N]$;[23] Δ, $[C_2mim][Tf_2N]$;[24] ●, $[C_3mim][Tf_2N]$;[23] ×, $[C_4mim][Tf_2N]$;[11] ■, $[C_4mim][Tf_2N]$;[24] □, $[C_4mim][Tf_2N]$;[23] −, $[C_5mim][Tf_2N]$;[23] +, $[C_6mim][Tf_2N]$;[24] ○, $[C_6mim][Tf_2N]$;[23] ▲, $[C_7mim][Tf_2N]$;[23] ǀ, $[C_8mim][Tf_2N]$;[23] right-half-filled hexagon, $[C_{10}mim][Tf_2N]$;[24] top-half-filled hexagon, $[C_8mim][Tf_2N]$.[25]

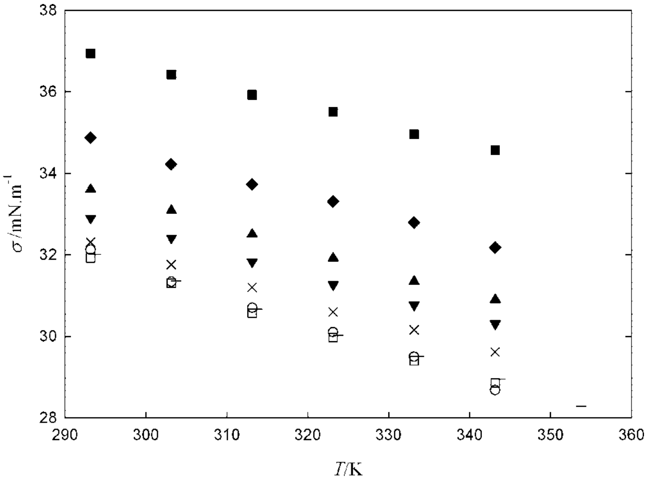

Figure 2. Surface tension vs temperature of ILs: ■, [C_2mim][Tf_2N]; ◆, [C_3mim][Tf_2N]; ▲, [C_4mim][Tf_2N]; ▼, [C_5mim][Tf_2N]; ×, [C_6mim][Tf_2N]; −, [C_7mim][Tf_2N]; □, [C_8mim][Tf_2N]; ○, [C_{10}mim][Tf_2N].

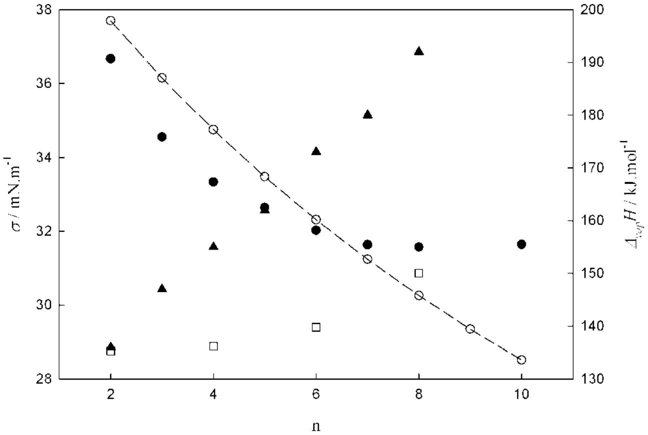

Figure 3. Enthalpy of vaporization (right axis) and surface tension (left axis) as a function of alkyl chain length, *n*, for 293.15 K: ●, this work surface tension data; ▲, Santos et al.[8] enthalpy of vaporization data; □, Zaitsau et al.[25] enthalpy of vaporization data; -○-, surface tensions predicted by the Gardas and Coutinho model.[2]

derived using the quasilinear surface tension variation with the temperature. The surface entropy, S^σ, can be obtained from[33,34]

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

and the surface enthalpy, H^σ, from[33,34]

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

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

The values of the thermodynamic functions for all the ILs studied and the respective expanded uncertainties, derived from the slope of the curve $\sigma = f(T)$ in combination with the law of propagation of uncertainty, are depicted in Table 2.[35]

In agreement with the results previously reported for other ILs,[9] [Tf_2N]-based ILs present a remarkably low surface entropy, when compared to other organic compounds. These low surface entropies are in agreement with results from our group[8] and by other authors using different techniques such as molecular simulation,[36] Direct Recoil Spectroscopy,[26,27,37] Sum Frequency Generation,[38] neutron reflectometry measurements,[39] and X-Ray reflectrometry[40] indicating a high surface organization as well as a highly structured liquid phase. The surface enthalpy by its turn seems to decrease with the increasing chain length, from C_2 to C_6, of the cation. This behavior, similar to what was observed before,[9] seems to follow the decrease in the strength of the hydrogen bonding. Nevertheless, for the higher alkyl chain length ILs, the surface enthalpy seems to also be affected by the dominant influence of the anion toward the IL surface organization. However, the information currently available is not enough to provide a molecular explanation.

Table 2. Surface Thermodynamic Functions for the Ionic Liquids

compound	$(S^\sigma \pm \gamma^a)\cdot 10^{-5}$ J·m^{-2}·K^{-1}	$(H^\sigma \pm \gamma^a)\cdot 10^{-2}$ J·m^{-2}
[C_2mim][Tf_2N]	4.8 ± 0.1	5.09 ± 0.03
[C_3mim][Tf_2N]	5.2 ± 0.1	5.00 ± 0.03
[C_4mim][Tf_2N]	5.5 ± 0.1	4.97 ± 0.03
[C_5mim][Tf_2N]	5.3 ± 0.1	4.83 ± 0.03
[C_6mim][Tf_2N]	5.4 ± 0.1	4.81 ± 0.03
[C_7mim][Tf_2N]	6.1 ± 0.1	4.98 ± 0.03
[C_8mim][Tf_2N]	6.2 ± 0.1	5.00 ± 0.03
[C_{10}mim][Tf_2N]	5.9 ± 0.1	4.93 ± 0.03

[a] Expanded uncertainty with an approximate 95 % level of confidence.

Applicability of Stefan's Equation to Ionic Liquids. Some authors,[30,41] following the suggestion of Zaitsau et al.,[25,42] are using an empirical equation based on the Stefan equation for the estimation of the standard enthalpy of vaporization, $\Delta_{vap}H_m^0$(298 K), of ionic liquids from their surface tension values.

The Stefan equation can be written as[25,43]

$$\sigma = \frac{\Delta_{vap}H_m^0}{V^{2/3}\cdot N_A^{1/3}}\frac{Z_s}{Z} \tag{4}$$

where V (cm^3·mol^{-1}) is the molar volume; N_A is Avogadro's number; and Z_s and Z are surface and bulk coordination numbers for the molecules in the liquid and can be derived based on statistical mechanics considerations for a simple cell model, which can be applied strictly to spherically symmetrical molecules.[43] Although this equation or some of its variations[42] can be applied to molecular liquids with some success, its applicability to complex fluids such as ionic liquids has not been addressed yet.

The version of the Stefan equation proposed by Zaitsau et al.[25] is presented in eq 5

$$\Delta_{vap}H_m^0/(\mathrm{J\cdot mol^{-1}}) = 1.121\cdot 10^{-2}(\sigma\cdot V^{2/3}\cdot N_A^{2/3}) + 2.4 \tag{5}$$

where the first term is related to the dispersive interactions and the second to the nondispersive interactions (dipole−dipole, Coulomb, etc.). It must be emphasized that this correlation was derived based just on data for the [$C_n$mim][Tf_2N] ionic liquids for which limited surface tension data[24] were available at that time, and the enthalpies of vaporization of ionic liquids used were derived from vapor pressure measurements using the integral effusion Knudsen method.[25]

Unlike molecular liquids,[17,22,44] for which surface tensions and enthalpies of vaporization usually follow the same trend with increasing molecular size,[42] for ionic liquids they clearly do not. As shown in Figure 3, both the surface tensions measured here and/or reported by other authors for the same ionic liquids[11,23–25] and the enthalpies of vaporization reported by Santos et al.[8] and Zaitsau et al.[25] vary inversely with increasing cation chain length. The large uncertainty in the enthalpies of vaporization prevents the proposal of any reliable relation between surface tensions and enthalpies of vaporization, and thus it is highly questionable if the Stefan equation is applicable

Table 3. Estimated Critical Temperatures, T_c/K, using both the Eötvos[42] (Eot) and the Guggenheim[7] (Gug) Equations, Comparison, and Relative Deviation from the Literature

	this work data		Rebelo et al.[24]			
	$(T_c)_{\text{Eot}}$	$(T_c)_{\text{Gug}}$	$(T_c)_{\text{Eot}}$	RD	$(T_c)_{\text{Gug}}$	RD
compound	K	K	K	%	K	%
$[C_2mim][Tf_2N]$	1039 ± 15	1236 ± 19	1209	14.1	1100	−12.4
$[C_3mim][Tf_2N]$	1239 ± 46	1109 ± 25				
$[C_4mim][Tf_2N]$	1110 ± 18	1032 ± 13	1077	−3.1	1012	−2.0
$[C_5mim][Tf_2N]$	1146 ± 15	1052 ± 24				
$[C_6mim][Tf_2N]$	1098 ± 22	1021 ± 14	967	−1.4	932	−9.5
$[C_7mim][Tf_2N]$	979 ± 12	932 ± 10				
$[C_8mim][Tf_2N]$	971 ± 16	918 ± 14				
$[C_{10}mim][Tf_2N]$	895 ± 32	870 ± 25	797	−1.2	800	−8.8

to ionic liquids since the approach described by eq 4 requires that the surface tension and enthalpy are related by a factor Z_s/Z.

Estimated Critical Temperatures. Critical temperatures T_c are one of the most relevant thermophysical properties since they can be used in many corresponding state correlations for equilibrium and transport properties of fluids.[45] Nevertheless, due to the IL's intrinsic nature, with negligible vapor pressures and low decomposition temperatures, the direct determination of critical temperatures is impossible. To estimate critical temperature for the compounds under study, two empirical methodologies, based on the temperature dependence of the surface tension and liquid density, were tested by means of the Eötvos[6] and Guggenheim[7] equations described below and are reported in Table 3.

$$\sigma\left(\frac{M}{\rho}\right)^{(2/3)} = K(T_c - T) \qquad (6)$$

$$\sigma = K'\left(1 - \frac{T}{T_c}\right)^{11/9} \qquad (7)$$

where M is the molecular weight and ρ is the density of the ionic liquid. Both equations reflect the fact that the surface tension becomes null at the critical point.[45]

The critical temperature values estimated in this work are compared in Table 3 with the values reported by Rebelo et al.[24] estimated using the same approach. Rebelo's values are in good agreement with the critical temperatures reported here.

As reported in a previous work,[9] the values for the critical temperatures obtained by these approaches are to be used with care since predictions of relative volatilities based on these data were found contrary to the experimental observations for a number of cases. These approaches for estimating the critical temperatures, using data from a limited temperature range and requiring a large extrapolation, can introduce a large uncertainty. It is well established that both Eötvos and Guggenheim empirical equations break down in the immediate neighborhood of the critical point since at this point the system is at critical pressure and not atmospheric, as supposed by the methodology. Therefore, higher values of the critical temperatures would be expected.

Conclusions

New experimental data are reported for the surface tension of eight imidazolium-based ionic liquids with the common $[Tf_2N]$ anion in the temperature range from (293 to 353) K, at atmospheric pressure, using the Du Noüy ring method. Very low surface entropies were observed for all ionic liquids indicating a high surface ordering. Similarly to what is commonly observed for most organic compounds, the increase in size of the ionic liquid molecule leads to an increase of the interaction forces between the IL ion pairs[40] that results in an increasing enthalpy of vaporization, but this size increase leads to a decrease of the surface tension due to the dispersion of the ion charge and the reduction on the hydrogen bond strength between the anion and cation. This peculiar behavior seems to preclude the application of the Stefan equation to obtain a relation between the surface tension and the enthalpies of vaporization for ionic liquids.

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Received for review January 30, 2008. Accepted March 26, 2008. The authors are thankful for financial support from Fundação para a Ciência e a Tecnologia (Project POCI/EQU/58152/2004) and the Ph.D. grant (SFRH/BD/41562/2007) of Pedro J. Carvalho.

JE800069Z