Surface Tensions of Bis(trifluoromethylsulfonyl)imide Anion-Based Ionic Liquids

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Experimental measurements of the surface tension of six imidazolium-, pyridinium-, pyrrolidinium-, and phosphonium-based ionic liquids (ILs) with NTf_2 as the common anion and their dependence with the temperatures of (293 to 353) K at atmospheric pressure are presented. The set of selected ILs was chosen to investigate the influence of the length and position of the cation alkyl chain and the cation family on the surface tension of the ILs based on the NTf_2 anion. 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 ILs. The use of the Guggenheim and Eötvos correlations for the estimation of the critical temperatures of ILs is discussed, and a quantitative structure-property relationship (QSPR) correlation, previously extended for ILs, is here extended for the studied cations.

Introduction

Large asymmetric organic cations with organic or inorganic anions, unable to easily form an ordered crystal, compel ionic liquids (ILs) to remain liquid at or near room temperature. Unlike molecular liquids, the ionic nature of these compounds, along with the possibility of interchange between thousands of cations and anions, 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]

The design of industrial processes and new products based on ILs requires an adequate characterization of their thermophysical properties. In particular, in mass-transfer operations such as distillation, extraction, absorption, adsorption, and extractive fermentation the knowledge of interfacial and surface tensions are highly relevant. Unfortunately, the knowledge of the thermophysical properties of ILs, in particular of surface and interfacial tensions, is 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 and predictive methods, is indispensable.

Despite their attractive characteristics, such as compatibility with strong alkaline solutes, stabilizing effect on palladium catalysts, effective media for Heck and Suzuki reactions, and their low cost, the phosphonium-, pyridinium-, and pyrrolidinium-based ILs have received surprisingly little attention.[1−5] Far from covering a broad set of IL families, the surface tension data available have been focused primordially on the imidazolium family.[6−15] Few authors have reported surface tension data for ILs other than the imidazolium-based ILs. Anouti et al.,[16] while studying the aggregation behavior of ILs in water, reported surface tension, at 298 K, for imidazolium and pyrrolidinium alkylcarboxylate protic ILs. Sánchez et al.[17] reported surface tension data for 13 ILs formed by imidazolium, pyridinium, and pyrrolidinium cations paired with dicyanamide, tetrafluoroborate, thiocyanate, methylsulfate, and trifluoroacetate anions, while Bandrés et al.[18,19] reported surface tension data for the 1-butyl-2-methylpyridinium tetrafluoroborate and for the *n*-butyl-3-methylpyridinium dicyanamide ILs. Kilaru et al.[12] reported surface tension measurements of imidazolium-, quaternary phosphonium-, and ammonium-based ILs in the temperature range of (298 to 350) K. On this narrow set of sources only Kilaru et al.[12] has reported surface tension data for ILs with the bis(trifluoromethylsulfony)imide (NTf_2) anion.

Succeeding a previous study[6] on the temperature and cation alkyl chain length influence on the surface tension of the 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ILs, the influence of the temperature, cation alkyl chain length, and isomerism on the surface tension of six imidazolium-, pyridinium-, pyrrolidinium-, and phosphonium-based ILs with the bis(trifluoromethylsulfonyl)imide, NTf_2, common anion, namely, $[C_4mmim][NTf_2]$, $[C_2C_2im][NTf_2]$, $[C_3mpy][NTf_2]$, $[C_3mpyr][NTf_2]$, $[C_4mpyr][NTf_2]$, and $[THTDP][NTf_2]$, was investigated.

Using the quasi-linear surface tension variation with temperature, the surface thermodynamic properties, such as surface entropy and enthalpy, were derived, and the critical temperatures, by means of Etövos[20] and Guggenheim[21] equations, were estimated.

The quantitative structure-property relationship (QSPR) correlation proposed by Knotts et al.[22] and later extended to ILs by Gardas and Coutinho[23] is here extended to these new IL cations.

Experimental Section

Material. Six ILs with the common bis(trifluoromethylsulfonyl)imide, NTf_2, anion, namely, 1-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide, $[C_4mmim][NTf_2]$, 1,3-diethylimidazolium bis(trifluoromethylsulfonyl)imide, $[C_2C_2im][NTf_2]$, 3-methyl-1-propylpyridinium bis(trifluoromethylsulfonyl)imide, $[C_3mpy][NTf_2]$, 1-methyl-1-propylpyrrolidinium bis(trifluoromethylsulfonyl)imide, $[C_3mpyr][NTf_2]$, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, $[C_4mpyr][NTf_2]$, and trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide, $[THTDP][NTf_2]$, were used on this study (see Figure 1). The imidazolium-, pyridinium-, and pyrrolidinium-based ILs were acquired from IoLiTec with mass fraction purities > 99 % and bromide

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10.1021/je100253m

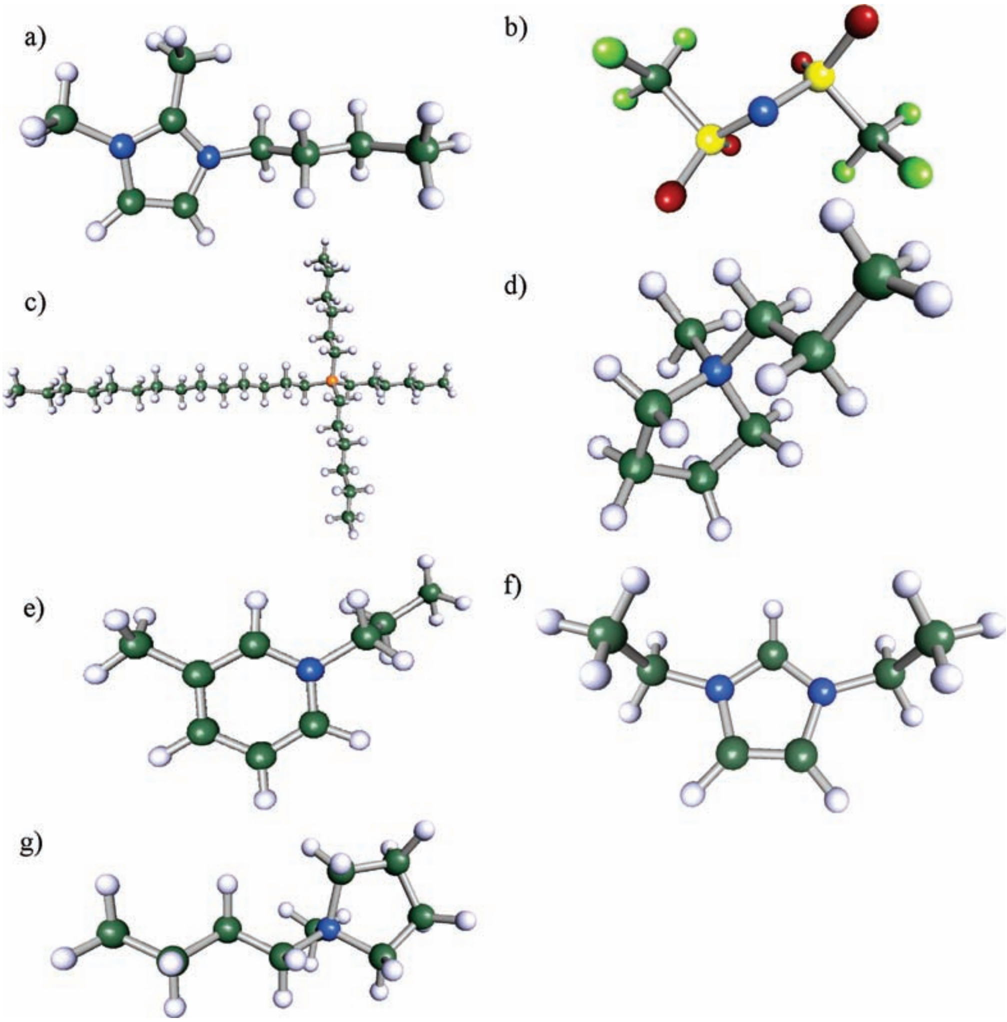

Figure 1. Chemical structures of (a) 1-butyl-2,3-dimethylimidazolium, $[C_4mmim]^-$; (b) bis(trifluoromethylsulfonyl)imide $[NTf_2]^-$; (c) trihexyltetradecylphosphonium, $[THTDP]^-$; (d) 1-methyl-1-propylpyrrolidinium, $[C_3mpyr]^-$; (e) 3-methyl-1-propylpyridinium, $[C_3mpy]^-$; (f) 1,3-diethylimidazolium, $[C_2C_2im]^-$; (g) 1-butyl-1-methylpyrrolidinium, $[C_4mpyr]^-$.

impurity mass fraction < 100 ppm. The $[THTDP][NTf_2]$ was supplied by Cytec and further purified by washing it with ultra pure water followed by drying under high vacuum ($1 \cdot 10^{-3}$ Pa) and moderate temperature (353 K) for a period of 48 h. The water used was double-distilled, passed through a reverse osmosis system, and further treated with a Milli-Q plus 185 water purification apparatus. It has a resistivity of 18.2 $M\Omega \cdot cm$ and a TOC smaller than 5 $\mu g \cdot L^{-1}$, and it is free of particles greater than 0.22 μm. The purities of the $[THTDP][NTf_2]$ were checked by ^1H NMR, ^{13}C NMR, ^{31}P NMR, and ^{19}F NMR after each purification step, and the purification was repeated until no impurities were observed in the ILs by NMR analysis. Along the purification process the IL initial coloration disappeared, and at the final stage the IL was almost colorless with a final purity estimated by NMR to be better than 99 %.

It is well-established that even low water contents have a great impact on IL physical properties.[7,24−26] To reduce the water content and volatile compounds to negligible values, high vacuum ($1 \cdot 10^{-3}$ Pa), stirring, and moderate temperature (343 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, at the end of the surface tension measurements, with levels of water mass fraction content of (70, 54, 113, 108, 55, and 34)$\cdot 10^{-6}$ for $[C_4mmim][NTf_2]$, $[C_2C_2im][NTf_2]$, $[C_3mpy][NTf_2]$, $[C_3mpyr][NTf_2]$, $[C_4mpyr][NTf_2]$, and $[THTDP][NTf_2]$, respectively.

Experimental Measurements

The surface tension of the ILs was measured with a NIMA DST 9005 tensiometer from NIMA Technology, Ltd. using 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 343) K and at atmospheric pressure. The sample under measurement was 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 that is 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.[27,28] Further details about the equipment and method can be found elsewhere.[6,7,29−32] The liquid densities of the pure compounds

Table 1. Ionic Liquid Surface Tension, γ, as a Function of Temperature

	$(\gamma \pm 0.05^a)/\mathrm{mN \cdot m^{-1}}$					
T/K	$[C_4mmim][NTf_2]$	$[C_2C_2im][NTf_2]$	$[C_3mpy][NTf_2]$	$[C_3mpyr][NTf_2]$	$[C_4mpyr][NTf_2]$	[THTDP]$[NTf_2]$
293.15	37.40	35.76	36.00	32.54	34.93	30.75
303.15	35.54	35.37	35.53	31.95	34.35	30.25
313.15	33.83	34.94	35.10	31.50	33.65	29.52
323.15	32.20	34.56	34.53	31.00	33.17	28.87
333.15	30.49	34.15	34.05	30.47	32.61	28.21
343.15	28.74	33.70	33.55	29.97	31.96	27.59

[a] Standard deviations.

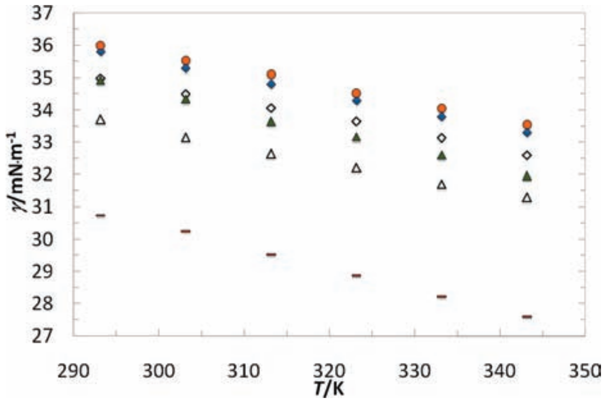

Figure 2. Surface tension vs temperature for the studied ILs and comparison with the $[C_3mim][NTf_2]$ and $[C_4mim][NTf_2]$ ILs, previously measured.[6] ◇, $[C_3mim][NTf_2]$; ♦, $[C_3mpyr][NTf_2]$; ●, $[C_3mpy][NTf_2]$; △, $[C_4mim][NTf_2]$; ▲, $[C_4mpyr][NTf_2]$; —, [THTDP]$[NTf_2]$.

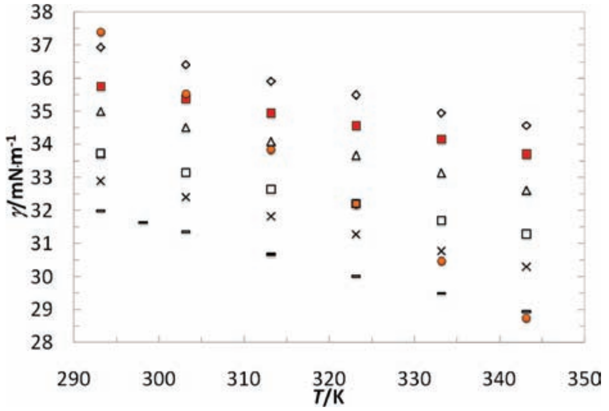

Figure 3. Surface tension vs temperature of the studied imidazolium-based ILs and comparison with the $[C_nmim][NTf_2]$ ILs, previously measured.[6] ●, $[C_4mmim][NTf_2]$; ■, $[C_2C_2im][NTf_2]$; ◇, $[C_2mim][NTf_2]$; △, $[C_3mim][NTf_2]$; □, $[C_4mim][NTf_2]$; ×, $[C_5mim][NTf_2]$; —, $[C_7mim][NTf_2]$.

necessary for the surface tension measurements using the Du Noüy ring were obtained from the literature.[12,33−35]

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 ILs, validating the methodology and experimental procedure adopted in this work.[6,7,29−32] The surface tension data of the ILs here studied are reported in Table 1 and plotted in Figures 2 and 3. To allow a better understanding of the influence of the cation on the surface tension, the measured data here are plotted along with that of the 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ILs, with the alkyl chain length varying from ethyl to hepthyl, previously published.[6] Despite the importance of the surface tension, in a wide range of problems in pure and applied sciences, the data available in literature are scarce and present significant discrepancies among different authors.[6,7] Among the set of ILs studied only surface tension data for the [THTDP]$[NTf_2]$ are available.[12] The experimental surface tension obtained in this work presents a percent average relative deviation of 7 % from the available literature data.

It is well-established that the surface tension is intrinsically related with the part of the molecule that is present at the interface.[6,7] In previous works[6,7] we have shown that, for the imidazolium-based ILs with alkyl chain lengths up to C_{10}, the surface tension is affected both by the anion and the cation, while for large alkyl chain lengths the cation has a dominant role on the surface tension.[6] The very low value of the surface tension, of the [THTDP]$[NTf_2]$, seems to confirm these observations. For the [THTDP]$[NTf_2]$ the large alkyl chains lead to surface tension values equivalent to those observed for heavy alkanes.[36]

The IL cation family seems to have a limited influence on the surface tension. Changing it from an aromatic pyridinium to a nonaromatic pyrrolidinium leads to a marginal decrease of the surface tension. Furthermore, both pyridinium and pyrrolidinium ILs present higher surface tensions than those reported for the corresponding imidazolium-based ILs. Sánchez et al.[17] has reported the same behavior for this IL family but with the thiocyanate as the common anion, while Anouti et al.[16] reported it for imidazolium and pyrrolidinium carboxylates.

As shown in Figures 2 and 3, within an IL cation family, the surface tension decreases with the increase of alkyl chain length. This behavior, previously reported for other ILs families,[7,14,25,37,38] is here also observed for the pyrrolidinium-based ILs.

In a previous work[7] it was shown that the $[C_4mmim][PF_6]$ had an intermediate behavior between $[C_4mim][PF_6]$ and $[C_5mim][PF_6]$. Surprisingly, the introduction of a methyl group on the $[C_4mim][NTf_2]$ IL, substituting the most acidic hydrogen at the C_2 position in the imidazolium ring,[39] does not lead just to an increase in the surface tension values, as observed for the $[C_4mmim][PF_6]$ but leads to a complete change on the surface tension behavior as a function of the temperature. The introduction of an extra CH_3 group produces not only an increase of the surface tension at low temperatures, but also a higher temperature dependency, when compared to what is observed for most ILs. This peculiar behavior seems to be related not only with the increase of the van der Waals forces but also with the dispersion of the ion charge and reduction on the hydrogen bond strength, but the information currently available is not enough to provide a molecular explanation for this fact.

For the $[C_2C_2im][NTf_2]$, the shorter alkyl chains of the molecule lead to an increase of the surface tension values when compared with its isomer $[C_3mim][NTf_2]$. However,

Table 2. Surface Thermodynamic Functions for the Studied Ionic Liquids

compound	$(S^{\gamma} \mp \sigma^{a})\cdot 10^{-5}$ J·m^{-2}·K^{-1}	$(H^{\gamma} \mp \sigma^{a})\cdot 10^{-2}$ J·m^{-2}
[C$_4$mmim][NTf$_2$]	17.2 ± 0.1	8.77 ± 0.04
[C$_2$C$_2$im][NTf$_2$]	4.78 ± 0.01	4.10 ± 0.04
[C$_3$mpy][NTf$_2$]	4.9 ± 0.1	5.05 ± 0.04
[C$_3$mpyr][NTf$_2$]	5.02 ± 0.01	5.05 ± 0.04
[C$_4$mpyr][NTf$_2$]	5.9 ± 0.1	5.21 ± 0.04
[THTDP][NTf$_2$]	6.5 ± 0.1	4.97 ± 0.04

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

contrary to what is observed for the [C$_4$mmim][NTf$_2$], where the molecule symmetry has a strong effect on its viscosity,[34] for the surface tensions the molecule structure and consequently the structure of the liquid phase do not result in a change in the dependency of the surface tension with the temperature.

Surface Thermodynamic Properties. The surface thermodynamic properties, surface entropy, and surface enthalpy were derived using the quasi-linear surface tension variation with the temperature. The surface entropy, S^{γ}, can be obtained from[40,41]

$$S^{\gamma} = -\left(\frac{d\gamma}{dT}\right) \tag{1}$$

and the surface enthalpy, H^{γ}, from[40,41]

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

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

The values of the thermodynamic functions for all of the ILs studied 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.[42]

In agreement with the results previously reported for other ILs,[6,7] these ILs present a remarkably low surface entropy when compared with other organic compounds. These low surface entropies are an indication of a high surface organization as well as a highly structured liquid phase.

Apart from the [C$_4$mmim][NTf$_2$] IL, where the substitution of the most acidic hydrogen at the C$_2$ position in the imidazolium ring leads to a strong increase on both the surface enthalpy and the surface entropy, denoting a less organized liquid structure, the remaining ILs present similar surface enthalpies and entropies to those previously reported for other ILs.[6,7] Moreover, as discussed above, the similar dependency of the surface tension with the temperature of the different IL families results on similar surface entropy and surface enthalpy values. This behavior is not surprising and reinforces a previous observation that the surface enthalpy and surface entropy are primarily dominated by the IL's anion influence on the surface organization.[6,7] Since the ILs studied have a common anion, they have similar surface enthalpy and entropy values. Furthermore, in agreement with the surface tension value increase, the lower surface enthalpy and entropy of the [C$_2$C$_2$im][NTf$_2$] IL suggests a more organized liquid surface structure than for the [C$_3$mim][NTf$_2$] (5.00 J·m^{-2} and 5.2 J·m^{-2}·K^{-1}, respectively)[6] that must certainly result from the symmetric shape of the IL.

Estimated Critical Temperatures. Being used in many corresponding states correlations for equilibrium and transport properties of fluids, critical temperatures T_c are one of the most relevant thermophysical properties.[43] Nonetheless, due to IL intrinsic nature, with negligible vapor pressures and relatively low decomposition temperatures, the direct determination of critical temperatures is not possible. Thus, to estimate critical temperatures for the compounds under study, two empirical methodologies, based on the temperature dependence of the surface tension and liquid density, were tested using the Eötvos[20] and Guggenheim[21] equations described below and are reported in Table 3.

Table 3. Estimated Critical Temperatures, T_c/K, Using Both the Eotvos[20] (Eot) and the Guggenheim[21] (Gug) Equations

compound	$(T_c)_{Eot}$/K	$(T_c)_{Gug}$/K
[C$_4$mmim][NTf$_2$]	526 ± 2	553 ± 2
[C$_2$C$_2$im][NTf$_2$]	1729 ± 32	1354 ± 12
[C$_3$mpy][NTf$_2$]	1337 ± 30	1179 ± 16
[C$_3$mpyr][NTf$_2$]	1328 ± 5	1159 ± 1
[C$_4$mpyr][NTf$_2$]	1095 ± 22	1014 ± 15
[THTDP][NTf$_2$]	875 ± 14	872 ± 11

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

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

where M is the molecular weight and ρ the density of the IL. Both equations reflect the fact that the surface tension becomes null at the critical point.[43]

As a result of the higher surface tensions, compared to those of the imidazolium with the exception of the [C$_2$C$_2$im][NTf$_2$], the pyridinium and pyrrolidinium ILs present a slightly higher T_c, while the phosphonium IL presents one of the lowest critical temperatures among the studied compounds. The substitution of the most acidic hydrogen at the C$_2$ position in the imidazolium ring and the consequent higher surface tension dependency with the temperature lead to an important decrease in the critical temperature. The [C$_2$C$_2$im][NTf$_2$] critical temperature is considerably higher than those reported for its isomer [C$_3$mim][NTf$_2$] ((1239 and 1109) K for the critical temperature estimated by the Eötvos and Guggenheim equations, respectively).

As reported in a previous work,[7] 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 introduce an important error on the critical temperatures. 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 would be expected for the critical temperatures.

QSPR Correlation to the Prediction of Surface Tensions. The approach to the prediction of the surface tension of ILs proposed by Gardas and Coutinho,[23] based on the QSPR correlation proposed by Knotts et al.[22] is here extended to the new IL cations. That correlation was previously applied for a wide number of imidazolium-based ILs, using data measured by ourselves along with a database of ILs surface tensions obtained from the literature. Using parachors the prediction of surface tension (mN·m^{-1}) can be described by

$$\gamma = \left(\frac{P_{ch}\cdot\rho}{M_w}\right)^4 \tag{5}$$

The parachors estimated on this work are shown in Table 4, and the calculated surface tensions display a relative good

Table 4. Calculated Parachor, P, for the Studied IL Cations and Percent Absolute Average Deviations, ARD, between the Experimental and the Parachor Estimated Surface Tensions

compound	P $(\mathrm{mN \cdot m^{-1}})^{1/4}/\mathrm{cm^3 \cdot mol^{-1}}$	ARD
$\mathrm{C_4mmim^+}$	405.20	4.1
$\mathrm{C_2C_2im^+}$	335.27	2.5
$\mathrm{C_3mpy^+}$	361.10	1.8
$\mathrm{C_3mpyr^+}$	353.71	2.0
$\mathrm{C_4mpyr^+}$	387.01	1.6
$\mathrm{THTDP^+}$	1364.96	0.4
$\mathrm{NTf_2^-}$	346.27[a]	

[a] From ref 23.

agreement (less than 4.2 %) with the experimental surface tension data measured in this work. Nonetheless and despite their low deviations, the slope obtained from the surface tension determined by the parachor is higher than that described by the experimental data. Extrapolations of the model values to high temperatures are thus not advisible.

Conclusions

New experimental data are reported for the surface tension of six imidazolium-, pyridinium-, pyrrolidinium-, and phosphonium-based ILs with the common [NTf$_2$] anion in the temperature range from (293 to 353) K, at atmospheric pressure, using the Du Noüy ring method.

The results obtained indicate that the IL family seems to have a low influence on the surface tension. While both pyridinium- and pyrrolidinium-based ILs present slight higher surface tensions than those reported for their homologous imidazolium, changing from an aromatic pyridinium to a nonaromatic pyrrolidinium leads to a small decrease of the surface tension. Surprisingly the introduction of a methyl group on the [C$_4$mim][NTf$_2$] IL, substituting the most acidic hydrogen at the C$_2$ position in the imidazolium ring, not only leads to an increase in the surface tension values but also to a complete change on the surface tension dependency with the temperature. Furthermore, the [C$_2$C$_2$im][NTf$_2$] smaller alkyl chains lead to a higher surface tension than that reported for its [C$_3$mim][NTf$_2$] isomer.

These changes on the surface tension behavior have a direct influence on both their surface thermodynamic properties and critical temperatures. Thus, while imidazolium, pyridinium, and pyrrolidinium all present similar derived properties, the substitution of the most acidic hydrogen at the C$_2$ position in the imidazolium ring by a methyl group and the increase of the alkyl chain at the position N$_1$ of the imidazolium ring has a great influence on the derived properties. Very low surface entropies were observed for all ILs, with the exception of the [C$_4$mmim][NTf$_2$], indicating a high surface ordering. For the [C$_4$mmim][NTf$_2$] the substitution of the most acidic hydrogen at the C$_2$ position in the imidazolium ring leads to a strong increase on both the surface enthalpy and the surface entropy, denoting a less organized liquid surface structure and corroborating the strong influence of the temperature on the surface tension of the compound.

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Received for review March 31, 2010. Accepted April 23, 2010. The authors are thankful for financial support from Fundação para a Ciência e a Tecnologia (Project PTDC/EQU-FTT/102166/2008) and Ph.D. Grant (SFRH/BD/41562/2007) of P.J.C.

JE100253M