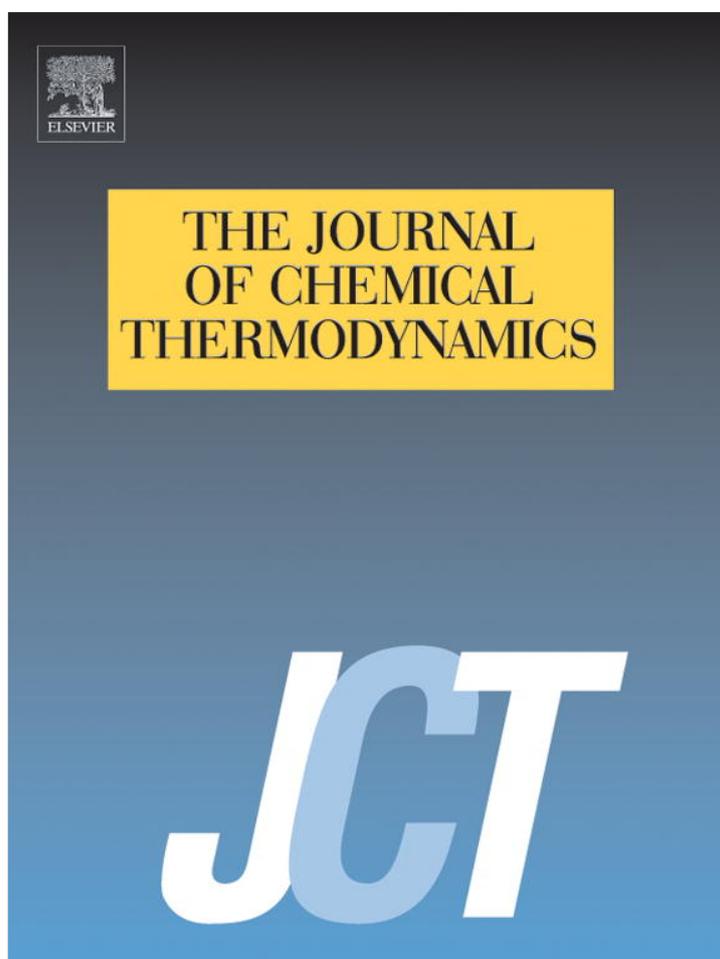


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Surface tensions of binary mixtures of ionic liquids with bis(trifluoromethylsulfonyl)imide as the common anion

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ABSTRACT

While values for thermophysical properties of ionic liquids are becoming widely available, data for ionic liquid mixtures are still scarce. In an effort to overcome this limitation and understand the behavior of ionic liquid mixtures, novel data for the surface tension of mixtures composed of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C₄mim][NTf₂], with other ionic liquids with a common anion, namely 1-butyl-2,3-dimethylimidazolium, [C₄C₁mim]⁺, 3-methyl-1-propylpyridinium, [C₃mpy]⁺, 1-methyl-1-propylpyrrolidinium, [C₃mpyr]⁺, and 1-methyl-1-propylpiperidinium, [C₃mpip]⁺, were measured at $T = 298.2$ K and atmospheric pressure over the entire composition range. From the surface tension deviations derived from the experimental results, it was possible to infer that the cation alkyl chain length of the second ionic liquid constituting the mixture has a stronger influence in the ideal mixture behavior than the type of family the ionic liquid cation belongs to. The Gibbs adsorption isotherms, estimated from the experimental values, show that the composition of the vapor–liquid interface is not the same as that of the bulk and that the interface is richer in the ionic liquid with the lowest surface tension, [C₄mim][NTf₂].

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1. Introduction

The increasing number of works concerning ionic liquids (ILs) during the last decade reveals the great interest that both academia and industry place on these molten salts [1,2]. Their unique properties resulting from the combination of large organic cations with dispersed charge, and organic or inorganic anions, justify their interest for application in different areas [2–5]. These unusual characteristics make ionic liquids a reliable alternative to conventional solvents in synthesis protocols [6] or as extractive media in separation processes [7]. The use of ionic liquid mixtures can further enhance the range of ionic liquid properties and allow the fine tuning of their properties [1]. Ionic liquid mixtures composed of specified and selected ions may be used to expand their *liquidus* range and to overcome the unwanted high viscosity and low conductivity of some ionic liquids which can somehow hamper their use in chemical reactions [2] or electrolyte applications [8]. The use of ionic liquids mixed with common organic solvents has been addressed; yet, the valuable ionic liquid characteristics of negligible volatility and high thermal and chemical stabilities are lost by the use of these molecular compounds [9].

Plechkova and Seddon [10] stated that “if there are one million possible simple systems, then there are one billion (10^{12}) binary

combinations of these, and one trillion (10^{18}) ternary systems possible!”. Though the trillion number (10^{18}) caught the community attention and keeps being (wrongly) cited as the total number of potential ionic liquids, the surprising reality is that, in spite of having today more than 1000 ionic liquids reported, very little effort has been addressed at studying their binary, let alone ternary, combinations. As discussed in a recent review by Welton and co-workers [11], only a handful of researchers have been measuring the thermophysical properties and phase equilibria of ionic liquids mixtures in spite of their interesting properties. As the review shows [11], the amount of data on the thermophysical properties of ionic liquids mixtures is still quite scarce. Only some densities, electromotive forces, phase behavior, viscosities and conductivities have been experimentally measured or studied by molecular simulation techniques. However, these data are essential in process design and optimization where ionic liquid mixtures have found wide applicability.

One important ionic liquid property is the surface tension. Early works concerning this subject were mainly devoted to the characterization of surface tension of ionic liquids mixtures with water and alcohols [12–14], and some of them with the aim of determining the critical micelle concentration of surfactant-like ionic liquids in aqueous media [15–17]. Later works on surface and interfacial tensions measurements have been focused on providing information about how ionic liquids are structured at the interface [11,18,19]. Ionic liquids surface tensions can provide valuable

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TABLE 1

Water content, provenance, purity and experimental (γ_{exp}) and literature (γ_{lit}) [26,27,37] surface tension of pure ionic liquids.

Compound	Provenance	Mass fraction purity	Water content/ 10^{-6}	γ_{exp} at $T = 298.2 \text{ K}/(\text{mN} \cdot \text{m}^{-1})$	$\gamma_{\text{lit}}/(\text{mN} \cdot \text{m}^{-1})$
[C ₄ mim][NTf ₂]	Iolitec	0.99	235	33.15	33.60 (293.15 K) [26] 33.09 (303.15 K) [26]
[C ₄ C ₁ mim][NTf ₂]	Iolitec	0.99	291	34.50	37.40 (293.15 K) [27] 35.54 (303.15 K) [27]
[C ₃ mpyr][NTf ₂]	Iolitec	0.99	253	35.35	35.56 (298.15 K) [26]
[C ₃ mpy][NTf ₂]	Iolitec	0.99	237	35.02	36.00 (293.15 K) [27] 35.53 (303.15 K) [27]
[C ₃ mpip][NTf ₂]	Iolitec	0.99	318	35.17	34.50 (303.15 K) [37]

information on the cohesive forces between liquid molecules present at the air–liquid boundary, intrinsic energies and their structural nature and, ultimately, the preferential migration and organization of ionic liquids at the surface. As shown in two recent reviews on ionic liquids most of these studies address neat ionic liquids while ionic liquids mixtures were seldom investigated [11,20].

In what concerns the study of surface tensions of ionic liquid mixtures, the determination of the critical micelle concentration of surface active ionic liquids in ionic liquid media and the measure of surface tension of binary mixtures composed of imidazolium/ammonium and ammonium/ammonium or imidazolium/imidazolium were carried out, albeit only within a narrow composition range [16,17,21]. Alam *et al.* [22] also measured the surface tension along with the differential capacitance of the 1-ethyl-3-methylimidazolium tetrafluoroborate/1-octyl-3-methylimidazolium tetrafluoroborate system to understand the mixture interfacial structure at the Hg electrode surface, and Freire *et al.* [23] reported the surface tension of the mixture 1-ethyl-3-methylimidazolium acetate/1-decyl-3-methylimidazolium chloride for the production of nanosized cellulose fibers by electrospinning. These studies are, nevertheless, not extensive in what concerns the number of mixtures studied, their type and composition range. In addition, most of them only considered imidazolium-based ionic liquids.

In a previous work [24], we reported, for the first time, a comprehensive study of the surface tension of binary mixtures of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C₄mim][NTf₂]) with other 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquids, [C_nmim][NTf₂] (with $n = 1, 2, 5, 6, 8,$ and 10), over the whole composition range, overcoming the lack of information regarding the surface tension of ionic liquids mixtures. Through the calculation of surface tension deviations and relative Gibbs adsorption isotherms it was possible to conclude that the composition of the vapor–liquid interface is not the same as that of the bulk and that this interface is richer in the compound with the longest alkyl chain length, confirming the segregation between the polar and non-polar parts of the ionic liquid ions with the longer alkyl side chains pointing towards the vapor phase.

Following this previous work [24], novel data for the surface tension of mixtures composed of [C₄mim][NTf₂] with [NTf₂]-based ionic liquids combined with a different number of substituent aliphatic chains at the imidazolium cation or with a different cation core, namely 1-butyl-2,3-dimethylimidazolium, [C₄C₁mim]⁺, 3-methyl-1-propylpyridinium, [C₃mpy]⁺, 1-methyl-1-propylpyrrolidinium, [C₃mpyr]⁺, and 1-methyl-1-propylpiperidinium, [C₃mpip]⁺, were measured at $T = 298.2 \text{ K}$ and atmospheric pressure, in the entire composition range. In this work, the anion and the cation side alkyl chain length were kept constant whereas the number of alkyl substitutions at the imidazolium cation or the cation core was changed to evaluate its effect towards the binary surface tensions. Surface tension deviations and relative Gibbs adsorption isotherms were further determined showing the preferential adsorption of one ionic liquid over the other at the surface

and the near ideal behavior of the selected mixtures. A comparison with the results previously obtained [24] is also presented and discussed.

2. Experimental

2.1. Materials

Five ionic liquids with the anion bis(trifluoromethylsulfonyl)imide, [NTf₂]⁻, namely 3-methyl-1-propylpyridinium, [C₃mpy][NTf₂], 1-methyl-1-propylpyrrolidinium, [C₃mpyr][NTf₂], 1-methyl-1-propylpiperidinium, [C₃mpip][NTf₂], 1-butyl-2,3-dimethylimidazolium, [C₄C₁mim][NTf₂], and 1-butyl-3-methylimidazolium, [C₄mim][NTf₂], were studied in this work. All the compounds were acquired at Iolitec (IoLiTec Ionic Liquids Technologies GmbH, Germany) with stated mass fraction purity >0.99. See table 1.

To remove traces of water and volatile compounds all the ionic liquid samples were dried before use at moderate temperature ($\approx 343 \text{ K}$) and at high vacuum ($\approx 10^{-5} \text{ Pa}$) for a minimum period of 48 h under constant stirring. After the purification procedure, the purity of all ionic liquid samples was further checked by ¹H, ¹³C and ¹⁹F NMR, and showed to agree with the purities given by the supplier. Moreover, the water content of each ionic liquid, after the drying step and immediately before the measurements of densities and surface tensions, was determined by Karl Fischer titration using a Metrohm 831 Karl Fischer coulometer. The reagent used was Hydranal–Coulomat AG from Riedel-de Haën. The average water content of each ionic liquid is reported in table 1.

2.2. Experimental procedure

The surface tension and density of the mixtures [C₄mim][NTf₂] + [C₃mpy][NTf₂], [C₄mim][NTf₂] + [C₃mpyr][NTf₂], [C₄mim][NTf₂] + [C₃mpip][NTf₂] and [C₄mim][NTf₂] + [C₄C₁mim][NTf₂], over the whole mole fraction range, were measured at $T = 298.2 \text{ K}$ and at atmospheric pressure.

2.2.1. Surface tension

The surface tension of each ionic liquid and respective mixture were determined through the analysis of the shape of a pendant drop using a Dataphysics contact angle system OCA-20 (DataPhysics Instruments GmbH, Germany). Drop volumes of $(14 \pm 1) \mu\text{L}$ 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 $\pm 0.1 \text{ K}$. The temperature was attained by circulating water in the double jacketed aluminium cell by means of a Julabo F-25 water bath. The temperature inside the aluminium chamber was measured with a Pt100 within $\pm 0.1 \text{ K}$ which is placed at a distance of approximately 2 cm of the liquid drop. After reaching a temperature of 298.2 K, the surface tension measurements were carried out after 30 min to guarantee the thermal equilibrium. At least 7 drops were formed and analysed, and, for each drop, an average of 100 images

TABLE 2
Density (at $T = 298.15$ K) and surface tension (at $T = 298.2$ K) of binary ionic liquid mixtures (compositions in mole fraction, x_2) at $p = 101.325$ kPa.

x_2	$\rho/(\text{g} \cdot \text{cm}^{-3})^b$	$\gamma/(\text{mN} \cdot \text{m}^{-1})^a$	x_2	$\rho/(\text{g} \cdot \text{cm}^{-3})^b$	$\gamma/(\text{mN} \cdot \text{m}^{-1})^a$
[C ₄ C ₁ mim][NTf ₂] (2) + [C ₄ mim][NTf ₂] (1)			[C ₃ mpyr][NTf ₂] (2) + [C ₄ mim][NTf ₂] (1)		
0.0000	1.4369	33.15	0.0000	1.4369	33.15
0.2193	1.4338	33.38	0.2094	1.4369	33.63
0.3981	1.4312	33.59	0.3935	1.4364	34.04
0.4962	1.4296	33.72	0.5004	1.4359	34.28
0.5995	1.4280	33.87	0.5943	1.4354	34.48
0.7896	1.4249	34.16	0.7854	1.4339	34.89
1.0000	1.4212	34.50	1.0000	1.4317	35.35
[C ₃ mpy][NTf ₂] (2) + [C ₄ mim][NTf ₂] (1)			[C ₃ mpip][NTf ₂] (2) + [C ₄ mim][NTf ₂] (1)		
0.0000	1.4369	33.15	0.0000	1.4369	33.15
0.2093	1.4402	33.42	0.2156	1.4343	33.53
0.3996	1.4429	33.73	0.4069	1.4289	33.90
0.4995	1.4442	33.91	0.4988	1.4252	34.08
0.6047	1.4455	34.12	0.5955	1.4207	34.28
0.8024	1.4477	34.55	0.7958	1.4090	34.71
1.0000	1.4497	35.02	1.0000	1.3941	35.17

^a Uncertainty of the measured surface tension is within $5 \cdot 10^{-2} \text{ mN} \cdot \text{m}^{-1}$.

^b Uncertainty of the density measured is within $5 \cdot 10^{-4} \text{ g} \cdot \text{cm}^{-3}$.

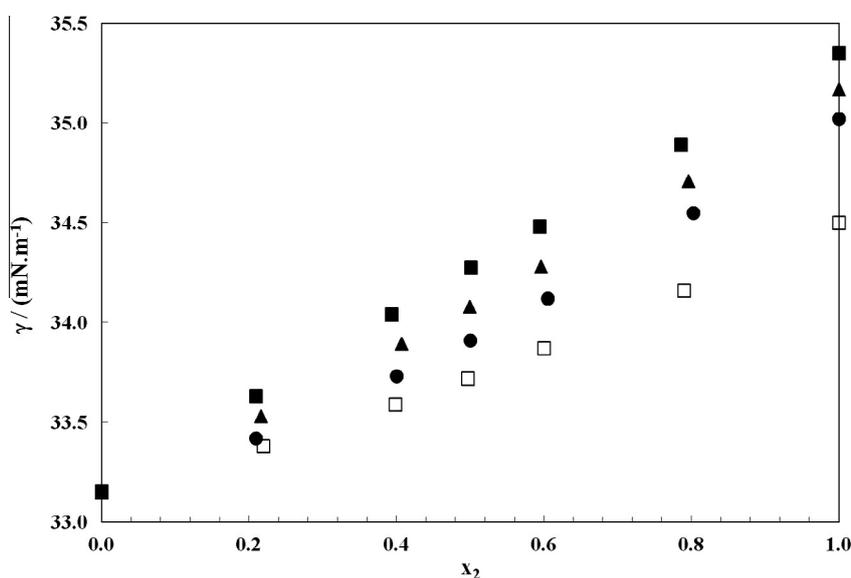


FIGURE 1. Experimental surface tension data at $T = 298.2$ K of the binary systems composed of [C₄mim][NTf₂] (1) and: □, [C₄C₁mim][NTf₂] (2); ■, [C₃mpyr][NTf₂] (2); ●, [C₃mpy][NTf₂] (2); ▲, [C₃mpip][NTf₂] (2).

was captured. The analysis of the drop shape was executed with the software modules SCA 20, where gravitational acceleration (g) and latitude (lat) were also provided, according to the location of assay ($g = 9.8018 \text{ m} \cdot \text{s}^{-2}$; $lat = 40^\circ$). The uncertainty of the surface tension measured is within $5 \cdot 10^{-2} \text{ mN} \cdot \text{m}^{-1}$. Silica gel was kept inside the air chamber to maintain a dry environment and to avoid the adsorption of moisture by the ionic liquids. Further details on the equipment and its validity to measure surface tension of ionic liquids and ionic liquid mixtures were previously reported [25–27]. The density of the pure ILs and their mixtures used to calculate the surface tensions based on the pendant drop method were determined in this work and are described below (ambient phase density (air) is available from the software modules SCA 20 data base).

2.2.2. Density

The density of the pure ILs and their mixtures was determined using an automated SVM 300 Anton Paar rotational Stabinger viscometer-densimeter. The absolute uncertainty in density is $\pm(5 \cdot 10^{-4}) \text{ g} \cdot \text{cm}^{-3}$. The relative uncertainty in temperature is

within ± 0.02 K. Further details on the equipment for the determination of densities of ionic liquids can be found elsewhere [28,29].

2.3. Analysis of the surface tension data

From the experimental values obtained, the surface tension deviations were further estimated according to equation (1),

$$\delta\gamma = \gamma - (x_1\gamma_1 + x_2\gamma_2), \quad (1)$$

where γ and γ_i are the values of the surface tension of the mixture and of the pure component i , respectively, and x_i is the mole fraction of the ionic liquid i . The surface tension deviations were correlated with a Redlich–Kister-type equation [30].

$$\delta\gamma = x_1x_2 \sum_{K=0}^n A_K (x_1 - x_2)^K, \quad (2)$$

where A_K denotes the polynomial coefficients. The degree of the polynomial Redlich–Kister equation, n , was optimized by application of the F-test [31].

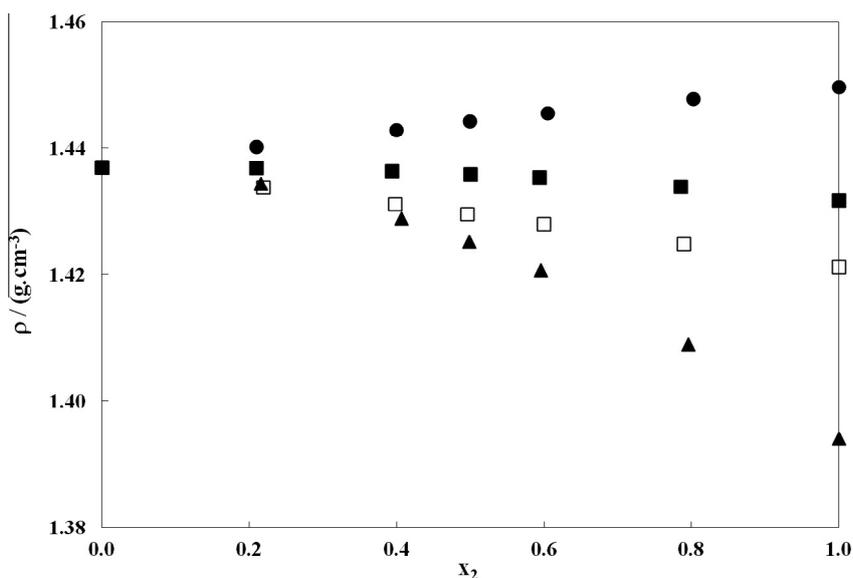


FIGURE 2. Experimental density data at $T = 298.15$ K of the binary systems composed of $[\text{C}_4\text{mim}][\text{NTf}_2]$ (1) and: \square , $[\text{C}_4\text{C}_1\text{mim}][\text{NTf}_2]$ (2); \blacksquare , $[\text{C}_3\text{mpyr}][\text{NTf}_2]$ (2); \bullet , $[\text{C}_3\text{mpy}][\text{NTf}_2]$ (2); \blacktriangle , $[\text{C}_3\text{mpip}][\text{NTf}_2]$ (2).

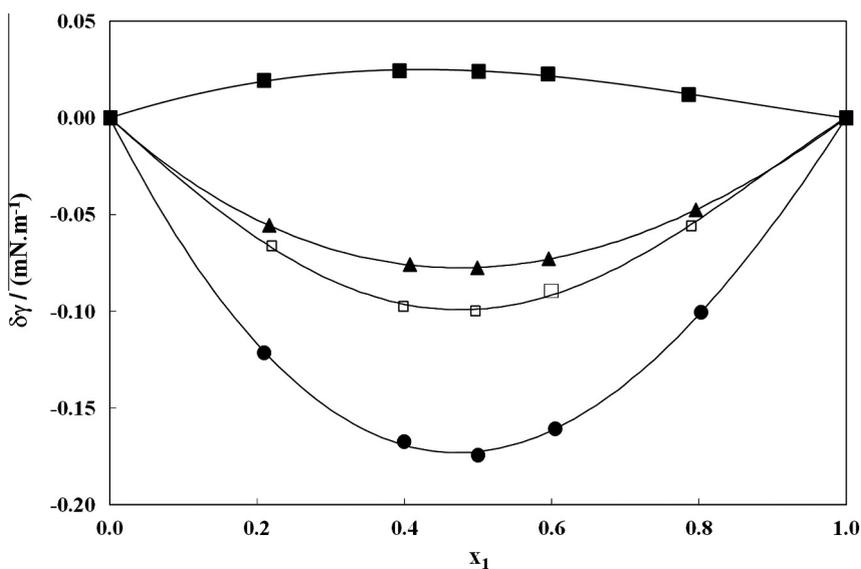


FIGURE 3. Surface tension deviations at $T = 298.2$ K of the binary systems composed of $[\text{C}_4\text{mim}][\text{NTf}_2]$ (1) and: \square , $[\text{C}_4\text{C}_1\text{mim}][\text{NTf}_2]$ (2); \blacksquare , $[\text{C}_3\text{mpyr}][\text{NTf}_2]$ (2); \bullet , $[\text{C}_3\text{mpy}][\text{NTf}_2]$ (2); \blacktriangle , $[\text{C}_3\text{mpip}][\text{NTf}_2]$ (2). Lines represent the fittings obtained by the Redlich–Kister equation.

Torres *et al.* [32] were the first to show that homogeneous binary mixtures of ionic liquids are approximately ideal. The experimental data of Canongia Lopes *et al.* [33] and Navia *et al.* [34] further confirmed that binary mixtures of ILs containing the same cation or anion behave like ideal liquid mixtures. Based on this hypothesis the relative Gibbs adsorption isotherm was estimated according to [35,36],

$$\Gamma_2^{(1)} = -\frac{1}{RT} \frac{d\gamma}{d\ln x_2}, \quad (3)$$

where $\Gamma_2^{(1)}$ is the relative adsorption of component 2 in respect to component 1, being component 1 the one with the highest surface tension.

3. Results and discussion

Previous studies confirmed the adequacy of the experimental equipment to measure the surface tension of pure ionic liquids [25–27] and their mixtures [24]. The results obtained in this work for the pure ionic liquids are reported in table 1 and compared with previous literature data [26,27,37].

The experimental surface tension (γ) and density (ρ) data measured for all the studied ionic liquid binary mixtures are presented

TABLE 3
 A_k coefficients obtained from the Redlich–Kister equation (2) and standard deviation of the fitting (σ).

Binary System	A_0	A_1	A_2	σ
$[\text{C}_4\text{C}_1\text{mim}][\text{NTf}_2] + [\text{C}_4\text{mim}][\text{NTf}_2]$	−0.396	0.050	0.105	0.0010
$[\text{C}_3\text{mpyr}][\text{NTf}_2] + [\text{C}_4\text{mim}][\text{NTf}_2]$	0.097	−0.035	−0.010	0.0010
$[\text{C}_3\text{mpy}][\text{NTf}_2] + [\text{C}_4\text{mim}][\text{NTf}_2]$	−0.690	0.079	0.020	0.0012
$[\text{C}_3\text{mpip}][\text{NTf}_2] + [\text{C}_4\text{mim}][\text{NTf}_2]$	−0.309	0.031	−0.007	0.0002

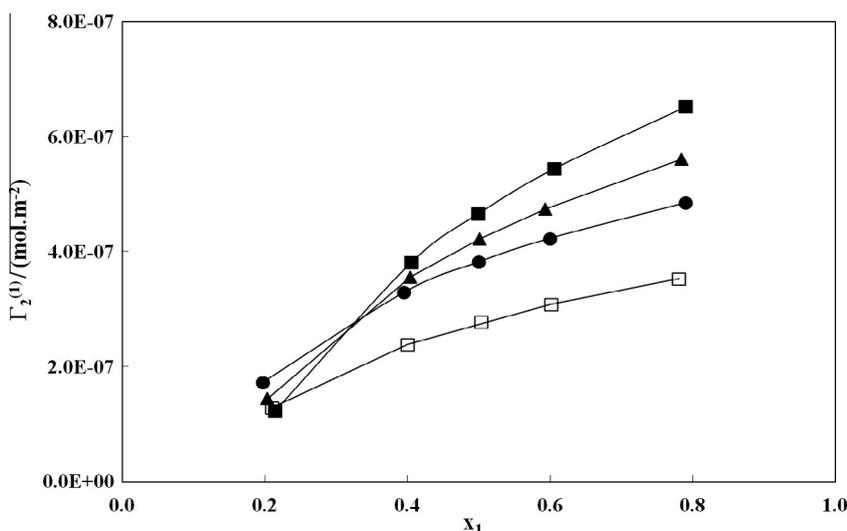


FIGURE 4. Relative Gibbs adsorption isotherms of the binary systems composed of $[C_4mim][NTf_2]$ (1) and: \square , $[C_4C_1mim][NTf_2]$ (2); \blacksquare , $[C_3mpyr][NTf_2]$ (2); \bullet , $[C_3mpy][NTf_2]$ (2); \blacktriangle , $[C_3mpip][NTf_2]$ (2).

in table 2, and depicted in figures 1 and 2. As shown in figure 1, the surface tension of the mixtures follow a quasi linear behavior unlike what is observed for the mixture densities presented in figure 2. The deviations from an ideal mixture behavior, regarding the density, increase in the sequence: $[C_3mpy][NTf_2] < [C_3mpyr][NTf_2] < [C_4C_1mim][NTf_2] \ll [C_3mpip][NTf_2]$. The deviation from the ideal behavior is particularly notorious for the mixture with $[C_3mpip][NTf_2]$, the only ionic liquid among the selected fluids for this work composed of a cation with a non-aromatic and 6 carbon ring. This is a quite different behavior from the one previously observed for $[C_4mim][NTf_2] + [C_nmim][NTf_2]$ mixtures [24] where the density values as a function of the mole fraction of $[C_nmim][NTf_2]$ followed a quasi linear behavior. Interestingly, contrarily to what is observed for the surface tensions, the nature of the cation core seems to have a strong influence on the density behavior of mixtures of ionic liquids.

The surface tension deviations, $\delta\gamma$, determined through equation (2), are shown in figure 3, for all the mixtures studied. Surface tension deviations can provide some insights regarding the mixtures ideal behavior and composition in the bulk and across the surface. The Redlich–Kister fittings (equation (2)) are also depicted in figure 3. The fitted A_K parameters and the corresponding standard deviations are presented in table 3.

Since, in this work, $[C_4mim][NTf_2]$ binary mixtures with $[NTf_2]$ -based ionic liquids having different cation cores but similar alkyl chain lengths were studied, it is now possible, comparing with the surface tension deviations reported in a previous work where $[C_4mim][NTf_2]$ binary mixtures with $[C_nmim][NTf_2]$ ILs, with n varying from 1 to 10, were investigated [24], to infer which IL characteristics have the strongest effect on mixture surface tensions and mixture behavior: the IL cation family, the number of alkyl substitutions at the cation or its alkyl side chain length. Surface tension deviations for the $[C_4mim][NTf_2]$ mixtures containing ionic liquids with a different cation core have absolute surface tension deviations much lower than those observed for the ionic liquid mixtures composed of ionic liquids having the same cation core but different chain lengths [24], being the higher deviations observed for the $[C_4mim][NTf_2]$ binary mixtures with $[C_nmim][NTf_2]$ ionic liquids with the lowest and the highest chain lengths. Mixtures composed of ionic liquids having cations belonging to different families but with similar alkyl chain lengths behave almost ideally, in contrast to what occurs when the second compound is

a similar IL but with a different chain length. The alkyl chain length effect is dominant on the surface tensions of mixtures, overcoming the influence of the cation family, feature to be taken into account when tailoring an ionic liquid mixture for a specific application.

All the $\delta\gamma$ values presented in figure 3 are nearly symmetric. A minimum is observed for the equimolar composition of the binary mixtures composed of $[C_4mim][NTf_2] + [C_3mpy][NTf_2]$, $[C_4C_1mim][NTf_2]$ or $[C_3mpip][NTf_2]$. The negative $\delta\gamma$ values observed for the systems containing $[C_3mpy][NTf_2]$, $[C_4C_1mim][NTf_2]$ and $[C_3mpip][NTf_2]$ show an unequal distribution of the mixture components between the bulk and the interface, being the composition of the surface, for these particular ionic liquid mixtures, somewhat different from that in the bulk composition. The surface can be considered richer in the component with the lower surface tension corresponding, in this case to the $[C_4mim][NTf_2]$ ionic liquid. A different behavior was observed with the mixture constituted by $[C_3mpyr][NTf_2]$ where small and positive values of the surface tension deviations were found. However, being the surface tension deviation values relatively small it is necessary to evaluate other mixture properties such as the Gibbs adsorption isotherms to infer about the distribution of the several components at the interface and at the bulk.

Figure 4 depicts the relative Gibbs adsorption isotherms, $\Gamma_2^{(1)}$, obtained from equation (3), for all the mixtures studied in this work. Values of the $\Gamma_2^{(1)}$ increase as a function of the $[C_4mim][NTf_2]$ content in all the systems studied and reveals the tendency of the ionic liquid with the lowest surface tension value, $[C_4mim][NTf_2]$, to migrate preferentially to the liquid–vapor interface, as previously observed [24].

The surface tension of the binary mixtures composed of $[C_4mim][NTf_2]$ and $[C_3mpy][NTf_2]$, $[C_3mpyr][NTf_2]$ or $[C_3mpip][NTf_2]$ present similar behavior according to the results obtained from the Gibbs adsorption isotherm. The mixture with $[C_4C_1mim][NTf_2]$ shows the smallest value for the relative Gibbs adsorption isotherms, as expected due to the similarity between the two compounds constituting the mixture. Therefore, the elimination of the most acidic hydrogen at the imidazolium cation and substitution by an aliphatic chain has no significant impact towards a preferential migration for the vapor–liquid interface. Still, even for this mixture the surface seems to be richer in $[C_4mim][NTf_2]$ since the positive value of $\Gamma_2^{(1)}$ increases with the $[C_4mim][NTf_2]$ concentration as observed in figure 4.

Finally, it is still possible to observe that the Gibbs adsorption isotherm lines intersect at a [C₄mim][NTf₂] composition approximately of 0.3, meaning that the [C₄mim][NTf₂] adsorption behavior at the surface in the different mixtures changes with the [C₄mim][NTf₂] composition – for lower compositions the [C₄mim][NTf₂] adsorption at the surface is stronger for the mixture with [C₃mpy][NTf₂] whereas for higher [C₄mim][NTf₂] concentrations the adsorption phenomena are more efficient for the [C₄mim][NTf₂] + [C₃mpyr][NTf₂] system.

4. Conclusions

For the first time, the surface tension of binary mixtures composed of [C₄mim][NTf₂] with other [NTf₂]-based ionic liquids with a different cation core or a different number of alkyl chains at the cation (1-butyl-2,3-dimethylimidazolium, [C₄C₁mim]⁺, 3-methyl-1-propylpyridinium, [C₃mpy]⁺, [C₃mpyr]⁺, 1-methyl-1-propylpyrrolidinium, [C₃mpyr]⁺, and 1-methyl-1-propylpiperidinium, [C₃mpip]⁺) were determined and presented. The surface tension was determined at a fixed temperature, 298.2 K, and at atmospheric pressure, for the whole composition range.

This work completes the study concerning surface tension and mixture behavior of [C₄mim][NTf₂] binary mixtures initiated with the investigation of [C₄mim][NTf₂] + [C_nmim][NTf₂] (*n* = 1, 2, 5, 6, 8, and 10) systems [24]. Unlike what was observed in that previous work, small values of the surface tension deviations were obtained for all the selected mixtures indicating that the IL cation core seems to have a limited influence on the mixtures behavior. The [C₄mim][NTf₂] binary systems containing [NTf₂]-based ionic liquids with a different cation core, but similar chain length, behave almost like ideal mixtures.

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