Surface Tension of Binary Mixtures of 1-Alkyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide Ionic Liquids: Experimental Measurements and Soft-SAFT Modeling

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Ⓢ *Supporting Information*

ABSTRACT: Ionic liquids have attracted a large amount of interest in the past few years. One approach to better understand their peculiar nature and characteristics is through the analysis of their surface properties. Some research has provided novel information on the organization of pure ionic liquids at the vapor—liquid interface; yet, a systematic study on the surface properties of mixtures of ionic liquids and their organization at the surface has not previously been carried out in the literature. This work reports, for the first time, a comprehensive analysis of the surface organization of mixtures of ionic liquids constituted by 1-alkyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide ionic liquids, $[C_n mim]$-$[NTf_2]$. The surface tension of mixtures composed of

$[C_4 mim][NTf_2] + [C_n mim][NTf_2]$ (n = 1, 2, 5, 6, 8, and 10) was experimentally determined, at 298.2 K and atmospheric pressure, in the whole composition range. From the experimental data, the surface tension deviations and the relative Gibbs adsorption isotherms were estimated showing how the surface composition of an ionic liquid mixture differs from that of the liquid bulk and that the surface is enriched by the ionic liquid with the longest alkyl chain length. Finally, the soft-SAFT equation of state coupled with the density gradient theory (DGT) was used, for the first time, to successfully reproduce the surface tension experimental data of binary mixtures of ionic liquids using a molecular-based approach. In addition, the DGT was used to compute the density profiles of the two components across the interface, confirming the experimental results for the components distribution at the bulk and at the vapor—liquid interface.
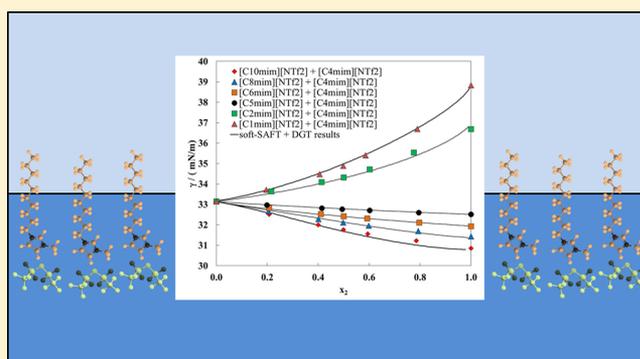
1. INTRODUCTION

In the past few years, ionic liquids (ILs) have been the focus of extensive research by academia, and they are finding their place in the chemical industry. These molten salts, constituted by large organic cations and organic or inorganic anions, are unable to form an ordered crystal, and thus keep their liquid state at or near room temperature.[1] Their exceptional thermophysical properties,[2−4] such as negligible vapor pressure, high thermal and chemical stability, nonflammability, and high solvation capacity for a wide range of organic compounds, have largely contributed to their recognition as potential alternatives to organic molecular solvents actually employed in a wide range of processes. Nowadays, the applications of ionic liquids range, among others, from their use as solvents in organic synthesis[5] to their use as extractive media in separation methodologies.[6]

In general, most applications concerning ionic liquids involve the presence of a second liquid/gas phase where the interface among the fluids plays a vital role. Because vapor absorption transfer rates are affected through that interface,[7] the knowledge of the surface tension of ionic liquids and their mixtures is essential for a proper design and operation of new industrial mass-transfer-based operations involving these fluids, such as distillation, extraction, and absorption.[8]

Considering the wide variety of ionic liquids that can be designed by combining different cations and anions, the knowledge of their interfacial properties, namely surface and interfacial tensions, and the connection of these properties with the chemical structure of the compounds are crucial requirements for designing or selecting an ionic liquid for a specific purpose.[9] Because surface tension is a measure of the cohesive

forces between liquid molecules present at the air−liquid boundary, the measurement of the surface tensions of ionic liquids is one of the most effective approaches to assess their intrinsic energies and their structural nature.

Despite all of the information that can be taken from the surface tension data of ionic liquids, this property has, however, been lagged behind. In fact, reliable and accurate measurements of surface tensions of ionic liquids are nontrivial. The presence of surface active impurities and the adsorption of water have been the major drawbacks which have led to large deviations in the acquisition of surface tension data. A review regarding the surface tensions of ionic liquids and ionic liquid solutions was recently reported and addresses these issues.[10]

One of the major features of ionic liquids is the possibility of tailoring their properties by a judicious choice of the ions that compose them. The term "designer solvents" has been used to describe this ability. Besides this primary tailoring, the properties of ionic liquids can be further tuned if mixtures of ionic liquids are considered. If a full database on the surface tensions of pure ionic liquids is far from being complete, the characterization of the surface properties of mixtures involving ionic liquids is even scarcer.[10] However, the surface tension of mixtures of ionic liquids can provide valuable information on the preferential migration and organization of ionic liquids at the surface. The local composition at a binary mixture interface differs from that in the bulk due to the preferential adsorption of one of the components (usually the compound with lower surface tension).[10]

The vast majority of literature dealing with ionic liquid mixtures or solutions has been devoted to the determination of the surface tension of aqueous solutions of ionic liquids aiming to establish the critical micelle concentration of surfactant-like ionic liquids. Besides water, other molecular solvents have been mixed with ionic liquids and their surface tensions determined, namely alcohols, n-alkanes, 1-octene, benzene, and n-perfluorohexane.[10] Additional studies have addressed the surface tensions of mixtures of ionic liquids combining both imidazolium−ammonium-, ammonium−ammonium-, and imidazolium−imidazolium-based pairs of ionic liquids.[11−13] Nevertheless, the main goal of those works was always the determination of the critical micelle concentration of surface active ionic liquids in ionic liquid media, and only very limited concentration ranges were investigated. In addition, and with a different purpose, we have previously evaluated the surface tension of mixtures of 1-ethyl-3-methylimidazolium acetate and 1-decyl-3-methylimidazolium chloride to obtain nanosized cellulose fibers by electrospinning making use of an ionic liquid dissolving medium.[14]

In this work we report, for the first time, a comprehensive study of the surface tensions of binary mixtures composed of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_4mim][NTf_2]$) and another 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquid, $[C_nmim][NTf_2]$ (with n = 1, 2, 5, 6, 8 and 10) in the whole composition range. The main goal of this work is to overcome the lack of information regarding the surface tension of ionic liquids mixtures and to better understand their behavior and their surface organization. In addition, the densities of all mixtures were also determined since they are required to calculate the surface tension values. The surface tension deviations were estimated and the relative Gibbs adsorption isotherms, describing the preferential adsorption of one ionic liquid over the other at the surface, are reported and discussed.

In addition, this work is completed by using the soft-SAFT equation of state, one of the most refined versions of SAFT (from statistical associating fluid theory) coupled with the density gradient theory (DGT) for the description of the new experimental binary data and the calculation of some interesting interface density profiles. Soft-SAFT[15] is a molecular-based accurate equation for the description of bulk thermodynamic properties of complex systems. The DGT approach[16,17] is a methodology that provides a path to account for the inhomogeneity of the interface and allows the calculation of interfacial properties when coupled to an equation of state for the bulk properties. The inclusion of a DGT treatment in soft-SAFT has been applied with success to model the surface tension of several families of pure ionic liquids, including several imidazolium-based ILs with the $[BF_4]^-$,[18] $[PF_6]^-$,[19] and $[NTf_2]^-$[20] anions and pyridinium-based ILs with the $[NTf_2]^-$ anion.[21] Soft-SAFT + DGT has also been used to obtain an excellent description of binary mixtures of hydrocarbons, carbon dioxide + n-alkanes, nitrile + alkanes, and blends of refrigerants.[22,23]

Although the current DGT methodology has been combined with other SAFT-type equations to provide the surface tension of pure fluids and mixtures, there are practically no works for the modeling of ionic liquids interfacial tensions (apart of the soft-SAFT contributions mentioned in previous paragraph). To our knowledge, only a recent contribution from Paduszyński and Domańska[24] provided the description of the surface tension of several $[C_nmim][NTf_2]$ ionic liquids using the perturbed-chain PC-SAFT + DGT approach. They compared the calculations using the characteristic DGT influence parameter c with and without temperature dependence. Their results were quantitative when the temperature dependence was added.

2. EXPERIMENTAL SECTION

2.1. Materials. Seven ionic liquids of the type 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, $[C_nmim][Tf_2N]$, were studied in this work, namely those with the cation 1-methyl-3-methylimidazolium, $[C_1mim]$-$[NTf_2]$; 1-ethyl-3-methylimidazolium, $[C_2mim][NTf_2]$; 1-butyl-3-methylimidazolium, $[C_4mim][NTf_2]$; 1-methyl-3-pentylimidazolium, $[C_5mim][NTf_2]$; 1-hexyl-3-methylimidazolium, $[C_6mim][NTf_2]$; 1-methyl-3-octylimidazolium, $[C_8mim]$-$[NTf_2]$; and 1-decyl-3-methylimidazolium, $[C_{10}mim][NTf_2]$. All of the compounds were acquired at Iolitec with mass fraction purities >99%.

To remove traces of water and volatile compounds, all the ionic liquid samples were dried before use at moderate temperature (∼313 K) and at high vacuum (∼10^{-5} 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, ^{13}C, and ^{19}F NMR and was shown to agree with the purities given by the supplier. Moreover, the water content of each ionic liquid, after the drying step, and before and after the measurements of densities and surface tensions, was determined by Karl Fischer titration making use of a Metrohm 831 coulometer. The reagent used was Hydranal-Coulomat AG from Riedel-de Haën. The average water content of each ionic liquid is presented in Table 1.

2.2. Experimental Procedure. Surface tensions and densities of the mixtures $[C_4mim][NTf_2]$ + $[C_nmim][NTf_2]$, in the whole mole fraction range, were measured at 298.2 and 298.15 K, respectively, and at atmospheric pressure.

Table 1. Water Content and Experimental (γ_{exp}) and Literature (γ_{lit})[36,37] Surface Tension of Pure Ionic Liquids

compound	water content/ ppm	γ_{exp} at 298.2 K/ (mN/m)	γ_{lit}/(mN/m)
$[C_1mim][NTf_2]$	125	38.83	no data found
$[C_2mim][NTf_2]$	178	36.68	36.94 (293.15 K)
			36.43 (303.15 K)
$[C_4mim][NTf_2]$	243	33.15	33.60 (293.15 K)
			33.09 (303.15 K)
$[C_5mim][NTf_2]$	289	32.51	32.90 (293.15 K)
			32.41 (303.15 K)
$[C_6mim][NTf_2]$	307	31.93	32.31 (293.15 K)
			31.76 (303.15 K)
$[C_8mim][NTf_2]$	440	31.44	31.93 (293.15 K)
			31.30 (303.15 K)
$[C_{10}mim][NTf_2]$	712	30.85	32.12 (293.15 K)
			31.34 (303.15 K)

Density. The measurements of densities (ρ) of the pure and ionic liquids mixtures were carried out using an automated SVM 300 Anton Paar rotational Stabinger viscometer-densimeter. The absolute uncertainty in density is $\pm 5 \times 10^{-4}$ g 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.[25−27]

Surface Tension. The surface tension of each pure ionic liquid and mixtures of ILs were determined through the analysis of the shape of a pendant drop using a Dataphysics contact angle system OCA-20. Drop volumes of ~14 ± 1 μL were obtained using a Hamilton DS 500/GT syringe connected to a Teflon coated needle placed inside an aluminum air chamber capable of maintaining the temperature within ±0.1 K. The temperature was attained by circulating water in the double jacketed aluminum cell by means of a Julabo F-25 water bath. After reaching a temperature of 298.2 K, the measurements on surface tensions were carried out after 30 min to guarantee the thermal equilibrium. Silica gel was kept inside the air chamber to avoid the adsorption of moisture by the ionic liquids. For the surface tension determination, at least 7 drops were formed and analyzed. For each drop, an average of 100 images was captured. The uncertainty of the surface tension measured is within 5×10^{-2} mN m^{-1}. The analysis of the drop shape was performed with the software modules SCA 20. Further details on the equipment and its validity to measure surface tensions of ionic liquids were previously reported.[14,28] The densities used to calculate the surface tensions based on the pendant drop method were those obtained in this work and described previously.

2.3. Analysis of the Surface Tension Data. From the experimental data obtained, the surface tension deviations were further estimated according to eq 1

$$\delta\gamma = \gamma - \sum_{i=1}^{n} x_i \gamma_i \tag{1}$$

where γ and γ_i are 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. For the case of binary mixtures, the surface tension deviations were correlated with a Redlich−Kister-type equation described by[29]

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

where subscripts 1 and 2 refer to ionic liquids 1 and 2 of the mixture and A_K denotes the polynomial coefficients. The degree, n, of the polynomial Redlich−Kister equation was optimized by application of the F-test.[30]

Torres[31] was the first to show that homogeneous binary mixtures of ionic liquids can be considered ideal. The experimental data of Lopes et al.[32] and Navia et al.[33] further confirmed that binary mixtures of ILs having the same cation or anion behave like ideal liquid mixtures. Based on this hypothesis the relative Gibbs adsorption isotherm was estimated according to[29]

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

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

3. SOFT-SAFT EOS AND DGT

The experimental data obtained in this work were also described using the DGT coupled to the soft-SAFT EoS.

Soft-SAFT[15] is a molecular-based equation of state derived from the original SAFT.[34] All SAFT versions consider explicitly physical interactions among the molecules through two specific terms (chain and association) coming from the thermodynamic perturbation theory of first order (TPT1) developed by Wertheim[35,36] and being particularly suitable to model complex systems like ionic liquids. In soft-SAFT, the residual Helmholtz energy of a compound is described as the sum of the different molecular contributions to the total energy of the system according to eq

$$a^{res} = a - a^{id} = a^{ref} + a^{chain} + a^{assoc} \tag{4}$$

where each term stands for different microscopic contributions to the total energy of the fluid: a^{res} is the system residual Helmholtz free energy and a^{id} is the ideal contribution. Consequently, *ref*, *chain*, and *assoc* represent respectively the reference term of the spheres making the chain, the chain formation, and the association interactions.

The reference term is based on a Lennard-Jones (LJ) monomer fluid accounting for the repulsive and attractive interactions of the monomers that constitute the chain. There are two molecular parameters which represent the monomer, the segment diameter, σ_{ii}, and the dispersive energy between segments, ε_{ii}/k_B (with k_B being the Boltzmann constant).[37] The reference term contribution is computed by the EoS of Johnson et al.[38]

The van der Waals one-fluid theory with the modified Lorentz−Berthelot combining rules is applied to the reference term when the soft-SAFT is extended to mixtures

$$\sigma_{ij} = \eta_{ij} \left(\frac{\sigma_{ii} + \sigma_{jj}}{2} \right) \tag{5}$$

$$\varepsilon_{ij} = \xi_{ij} (\varepsilon_{ii}\varepsilon_{jj})^{1/2} \tag{6}$$

where η_{ij} is the binary size parameter and ξ_{ij} is the binary energy parameter, accounting for size and energy asymmetries,

respectively. These values are set to one when using the equation in a predictive manner.

The chain and association terms are taken from the TPT1 Wertheim's theory.[35,36] They are formally identical in all SAFT equations, and the reader is referred to the original soft-SAFT publication for more details.[15] The association term description includes two additional parameters that define the strength of the associating interaction: $K_{\alpha\beta,ij}$, related to the site–site bonding volume of association, and $\varepsilon_{\alpha\beta}^{HB}/k_B$, the site–site association energy.

Hence, within the soft-SAFT framework, ionic liquids are represented as a single molecule (cation+anion) defined by five molecular parameters: the chain length, m_i, the segment diameter, σ_{ii}, the dispersive energy between segments, ε_{ii}/k_B, and the parameters that describe the association interactions $K_{\alpha\beta,ij}$ and $\varepsilon_{\alpha\beta}^{HB}/k_B$, taking into account the specific interactions between pairs of ionic liquids when they approach each other.

The DGT was used with the soft-SAFT EoS for predicting the interfacial properties. DGT was first proposed by van der Waals[16] and later on reformulated by Cahn and Hilliard.[17] It has been proven to be very accurate when coupled with soft-SAFT for simulation and experimental data, being a reliable tool to simultaneously describe phase and interface data.[22,39,40]

The expression for the total Helmholtz energy of the inhomogeneous system is given by

$$A = \int \left[a_0(\rho) + \sum_i \sum_j \frac{1}{2} c_{ij} \nabla \rho_i \nabla \rho_j \right] d^3r \tag{7}$$

where $a_0(\rho)$ is the Helmholtz free energy density of the homogeneous fluid at the local density ρ; ρ_i and ρ_j are the molar densities of components i and j; and c_{ij} is the influence parameter, which is treated as an adjustable temperature independent parameter regressed from experimental data.

Assuming a planar interface and neglecting the density dependence of c_{ij}, it is possible to derive an expression relating the surface tension γ and the square of the density gradient according to[41]

$$\gamma = \sum_i \sum_j \int_{-\infty}^{\infty} c_{ij} \frac{d\rho_i}{dz} \frac{d\rho_j}{dz} dz$$
$$= 2 \int_{-\infty}^{\infty} \left[a_0(\rho) - \sum_i \rho_i \mu_{0i} + p_0 \right] dz \tag{8}$$

where μ_{0i} and p_0 are the equilibrium chemical potential and pressure, respectively, and z is the direction perpendicular to the interface.

Poser and Sanchez[42] applied a transformation from local space to density space, the integration of which provides a way to calculate density profiles. For the case of a binary mixture the following expression can be obtained

$$z = z_0 + \int_{\rho_2(z_0)}^{\rho_2(z)} \sqrt{\frac{c'}{\Delta\Omega(\rho_1, \rho_2)}} d\rho_2 \tag{9}$$

where z_0 denotes an arbitrary chosen origin and $\Delta\Omega(\rho_1,\rho_2) = a_0(\rho) - \sum_i \rho_i \mu_{0i} + p_0$ is the reduced grand thermodynamic potential function; c' results from the influence parameters of the pure components and the density profiles across the interface and is described by

$$c' = c_2 + 2c_{12}\left(\frac{d\rho_1}{d\rho_2}\right) + c_1\left(\frac{d\rho_1}{d\rho_2}\right)^2 \tag{10}$$

For simplicity, the crossed parameter c_{12} is assumed to be given by the geometric mean combination rule, $c_{12} = \beta(c_1 c_2)^{1/2}$. β is an adjustable parameter, either fitted to the mixture experimental surface tension data or kept equal to one for predictive purposes. In this work, β has been set to unity in all cases.

Using the above-mentioned transformation, Poser and Sanchez[42] also derived an equation for the surface tension in binary mixtures that considers the change in the partial densities ρ_1 and ρ_2 within the interface

$$\gamma = \sqrt{2} \int_{\rho_2^I}^{\rho_2^{II}} \sqrt{c'\Delta\Omega(\rho_1, \rho_2)} d\rho_2 \tag{11}$$

where the limits of integration are the bulk densities of component 2 in the coexisting phases, indistinctly labeled by I and II. Further details concerning the computational performance of the grand thermodynamic potential for binary mixtures within the soft-SAFT framework can be found in the literature.[22]

3.1. Molecular Model Used in the Soft-SAFT EoS. The first step when applying a SAFT-type equation of state is to identify an appropriate association model able to represent a family of compounds. In the particular case of the 1-alkyl-3-methylimidazolium-[NTf₂] family of ionic liquids, a molecular model has previously been defined when applying the soft-SAFT equation to describe the thermophysical properties of pure ionic liquids and their phase behavior with water or gases.[20,43]

Experimental and theoretical studies[44,45] have shown that in the liquid phase anions and cations are associated together as ion pairs. Specific associating sites can be used to represent interactions between counterions since the ionic liquids bulky ions, with an asymmetric charge distribution, soften the Coulombic forces while generating short-range highly directional interactions.[47] In addition, dispersion forces, specific steric interactions, and short-lived ion pairs reduce the ionic character of these compounds.[47] The main interaction between counterions is due to the Coulombic forces as a consequence of their opposite electric charge. Moreover, the delocalization of the anion electric charge due to the oxygen groups enhances the possibility of interaction with the surrounding cations through them. Consequently, a simplified coarse-grained model, where the cation and the anion are together as a homonuclear Lennard-Jones chain, was defined for [NTf₂]-imidazolium ionic liquids to successfully describe experimental data.[20,43] Hence, the members of the alkyl-imidazolium-[Tf₂N] family are modeled as LJ chains with three associating sites in each molecule (let us say one "A" site and 2 "B" sites). According to these interactions we use an "A" site as a crude representation of the nitrogen atom interactions with the cation and a "B" site representing the delocalized charge due to the oxygen molecules on the anion. Each type of associating site is identically defined, but only AB interactions between different IL molecules are allowed, according to the modeled specific interactions on such systems.[20,43] For consistency, the same model is used here to represent the new mixtures experimental data.

4. RESULTS AND DISCUSSION

4.1. Surface Tension Data. The adequacy of the experimental equipment used to measure the surface tensions of ionic liquids, γ, was previously established.[14,28] The results obtained in this work for the pure ionic liquids are compiled in Table 1 and compared with previous literature data measured by a different technique (Du Noüy ring method).[8,48] No data were found for the surface tension of $[C_1mim][NTf_2]$.

In Table 2 and Figure 1, the experimental surface tension data measured for all of the ionic liquid binary mixtures of the

Table 2. Density (at 298.15 K) and Surface Tension (at 298.2 K) of the Binary Ionic Liquid Mixtures (Presented in Mole Fraction, x_2)

x_2	$\rho/(g/cm^3)$	$\gamma/(mN/m)$	x_2	$\rho/(g/cm^3)$	$\gamma/(mN/m)$
$[C_1mim][NTf_2]$ (2) + $[C_4mim][NTf_2]$ (1)			$[C_2mim][NTf_2]$ (2) + $[C_4mim][NTf_2]$ (1)		
0	1.4369	33.15	0	1.4369	33.15
0.1962	1.4596	33.72	0.2159	1.4469	33.64
0.4060	1.4857	34.48	0.4133	1.4595	34.09
0.4980	1.4980	34.89	0.4997	1.4661	34.32
0.5859	1.5096	35.40	0.6026	1.4749	34.71
0.7894	1.5387	36.86	0.7753	1.4920	35.54
1	1.5714	38.83	1	1.5193	36.68
$[C_5mim][NTf_2]$ (2) + $[C_4mim][NTf_2]$ (1)			$[C_6mim][NTf_2]$ (2) + $[C_4mim][NTf_2]$ (1)		
0	1.4369	33.15	0	1.4369	33.15
0.1989	1.4321	32.97	0.2070	1.4232	32.82
0.4149	1.4244	32.81	0.4106	1.4100	32.53
0.4943	1.4207	32.76	0.4999	1.4043	32.42
0.6019	1.4158	32.70	0.5927	1.3984	32.31
0.7946	1.4050	32.60	0.7966	1.3857	32.11
1	1.3917	32.50	1	1.3732	31.93
$[C_8mim][NTf_2]$ (2) + $[C_4mim][NTf_2]$ (1)			$[C_{10}mim][NTf_2]$ (2) + $[C_4mim][NTf_2]$ (1)		
0	1.4369	33.15	0	1.4369	33.15
0.2056	1.4096	32.67	0.2072	1.3963	32.52
0.4014	1.3857	32.29	0.4001	1.3628	32.00
0.4983	1.3743	32.12	0.4989	1.3469	31.76
0.5981	1.3634	31.96	0.5948	1.3326	31.56
0.7932	1.3428	31.70	0.7853	1.3059	31.21
1	1.3224	31.44	1	1.2788	30.85

type $[C_4mim][NTf_2] + [C_nmim][NTf_2]$ is shown. Information about the density values of those mixtures is also available as Supporting Information (Figure S1). As referred above, surface tensions were experimentally determined through the analysis of the shape of a pendant drop and, accordingly, Figure 1 also presents digital pictures of the droplets for the system $[C_4mim][NTf_2]$ (1) + $[C_{10}mim][NTf_2]$ (2) in the whole mixture composition range.

From the observation of Figure 1, it is deduced that the surface tensions do not follow an ideal linear trend. The mixtures composed of $[C_4mim][NTf_2]$ with the shorter alkyl chain ionic liquids, $[C_1mim][NTf_2]$ and $[C_2mim][NTf_2]$, are those which deviate most from the linearity. Conversely, for ionic liquids with $n > 4$, in $[C_nmim][NTf_2]$, the deviation to ideality increases with the length of the alkyl chain of the cation, although in a less significant manner than for $[C_1mim][NTf_2]$ and $[C_2mim][NTf_2]$.

For a better perception of the nonlinear trend of the surface tension as a function of the mole fraction of the components, the surface tension deviations, $\delta\gamma$, determined through eq 1, are
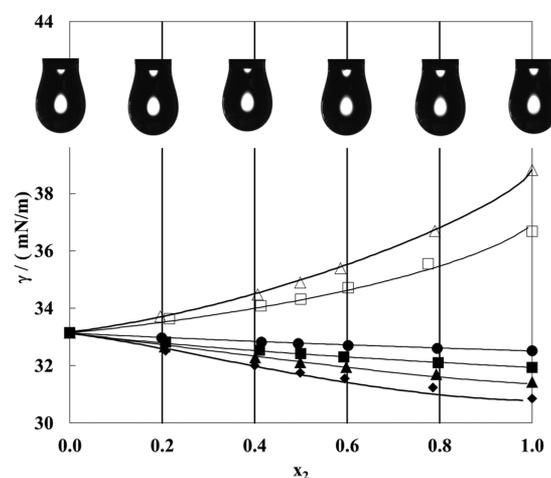

Figure 1. Experimental surface tension data at 298.2 K (symbols) and soft-SAFT + DGT results (lines) of the binary systems composed of $[C_4mim][NTf_2]$ (1) + $[C_nmim][NTf_2]$ (2): Δ, $[C_1mim][NTf_2]$; □, $[C_2mim][NTf_2]$; ●, $[C_5mim][NTf_2]$; ■, $[C_6mim][NTf_2]$; ▲, $[C_8mim][NTf_2]$; ◆, $[C_{10}mim][NTf_2]$. Digital pictures of the droplet shape in the whole mole fraction range for the system $[C_4mim][NTf_2]$ (1) + $[C_{10}mim][NTf_2]$ (2).

plotted in Figure 2, for all of the selected mixtures. Besides the experimental data deviations, the fittings obtained by the
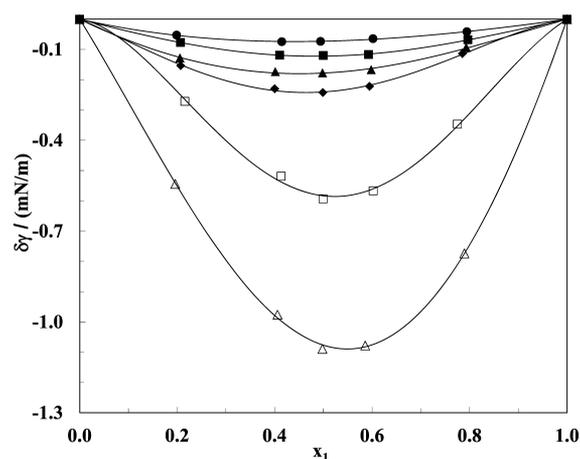

Figure 2. Surface tension deviations at 298.2 K of $[C_4mim][NTf_2]$ (1) + $[C_nmim][NTf_2]$ (2): Δ, $[C_1mim][NTf_2]$; □, $[C_2mim][NTf_2]$; ●, $[C_5mim][NTf_2]$; ■, $[C_6mim][NTf_2]$; ▲, $[C_8mim][NTf_2]$; ◆, $[C_{10}mim][NTf_2]$. Lines represent fittings obtained by the Redlich−Kister equation.

Redlich−Kister equation (described by eq 2) are also depicted for comparison purposes. The fitted A_K parameters and the corresponding standard deviations of the fitting are given in Table 3. All of the $\delta\gamma$ data presented in Figure 2 are nearly symmetric and present a minimum at the equimolar composition. The higher the difference between the surface tensions of the pure ionic liquids is, the higher the absolute value of $\delta\gamma$ becomes. Therefore, larger deviations are observed for the mixtures employing the short chain ionic liquids, $[C_1mim][NTf_2]$ and $[C_2mim][NTf_2]$, since they present substantially higher surface tension values than $[C_4mim]-[NTf_2]$. In contrast, for the mixtures containing $[C_nmim]-[NTf_2]$, with $n > 4$, these deviations increase with the length of the alkyl chain of the cation. The negative $\delta\gamma$ values observed in

Table 3. A_K Coefficients Obtained from the Redlich-Kister Equation (eq 2) and Standard Deviation of the Fitting (σ)

binary system	A_0	A_1	A_2	σ
$[C_1mim][NTf_2]$ + $[C_4mim][NTf_2]$	−4.310	−1.010	0.702	0.008
$[C_2mim][NTf_2]$ + $[C_4mim][NTf_2]$	−2.330	−0.375	1.710	0.011
$[C_5mim][NTf_2]$ + $[C_4mim][NTf_2]$	−0.291	0.071		0.001
$[C_6mim][NTf_2]$ + $[C_4mim][NTf_2]$	−0.488	0.039	0.116	0.001
$[C_8mim][NTf_2]$ + $[C_4mim][NTf_2]$	−0.712	0.160	0.098	0.003
$[C_{10}mim][NTf_2]$ + $[C_4mim][NTf_2]$	−0.957	0.116	0.279	0.002

all systems clearly indicate that the composition of the surface of the ionic liquid mixtures is not identical to the bulk composition; instead, the surface is richer in the component with the lower surface tension, which corresponds to the ionic liquid with the longer alkyl chain length.

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. Molecular simulation, spectrometry, X-ray, and spectroscopic studies, among others, are starting to provide an enlightenment and convergent opinion regarding the organization of the ions at the surface.[49−52] Some studies conclude that, although both cations and anions are present at the interface, there is generally a segregation between the polar and nonpolar parts of the ions and that the longer alkyl side chains point toward the vapor phase.[49−51] More recent molecular simulation results[52] are converging up to the idea that there are different relative molecular orientations at the surface of ionic liquids and that the experimental data should be interpreted considering a nonequal distribution of molecular arrangements. Nevertheless, this study still concludes that the most prevalent molecular orientation of the imidazolium cations is the one presenting the longer alkyl side chain pointing toward the vapor phase.

Besides all of the valuable conclusions provided by these studies,[49−52] further works are necessary for a clear picture of the ion orientation obtained from molecular simulation and experimental material characterization studies. Nonetheless, the notion that the composition of ionic liquids at the air−liquid boundary is not the same as in the bulk liquid and that this interface is preferentially composed of the longer alkyl chain ionic liquid is clearly supported by the experimental data gathered in this work, similarly to that observed in previous works reporting experimental data for pure ionic liquids.[28,53,54]

Figure 3 depicts the relative Gibbs adsorption isotherms, $\Gamma_2^{(1)}$, obtained from eq 3, for all the mixtures of this work. The trends on $\Gamma_2^{(1)}$ as a function of the composition of $[C_4mim][NTf_2]$ further confirm that the compound with the lower surface tension, i.e., the ionic liquid with the longer alkyl chain length, preferentially migrates to the liquid−vapor interface. Thus, for all systems, the relative Gibbs adsorption isotherm description tends to increase with the mole fraction content of $[C_4mim]$-$[NTf_2]$ (x_1) if the alkyl chain length of the other ionic liquid is <4 and decreases if the alkyl chain length of the other imidazolium fluid is >4.

4.2. Modeling Results with Soft-SAFT + DGT. The pure compound parameters, the chain length, m_i, the segment diameter, σ_{ii}, the dispersive energy between segments, ε_{ii}/k_B, the site−site association energy, $\varepsilon_{\alpha\beta}^{HB}/k_B$, and the site−site bonding-volume of association, $K_{\alpha\beta,ij}$, of the soft-SAFT EoS for the selected $[C_nmim][Tf_2N]$ ionic liquids were estimated in a previous work and are used here in a transferable manner.[16] All of the values of these parameters are presented in Table 4 for completeness.
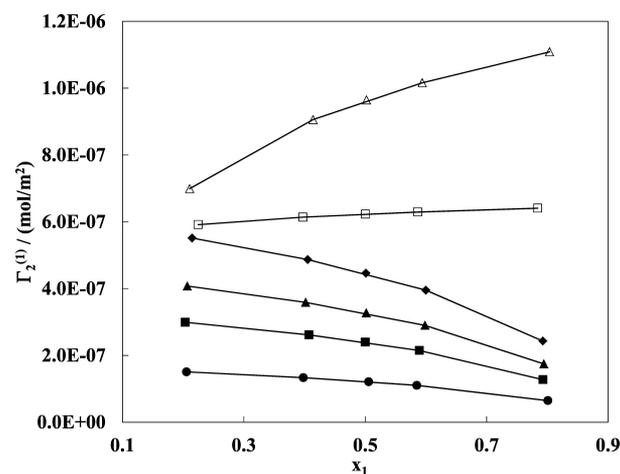

Figure 3. Relative Gibbs adsorption isotherms of $[C_4mim][NTf_2]$ (1) + $[C_nmim][NTf_2]$ (2) (symbols and lines): $\triangle$, $[C_1mim]$ $[NTf_2]$; $\square$, $[C_2mim][NTf_2]$; $\bullet$, $[C_5mim]$ $[NTf_2]$; $\blacksquare$, $[C_6mim][NTf_2]$; $\blacktriangle$, $[C_8mim][NTf_2]$; $\blacklozenge$, $[C_{10}mim][NTf_2]$.

Although the influence parameters for several $[C_nmim]$-$[Tf_2N]$ ionic liquids had been previously estimated,[20] we have refined the values using the surface tension experimental point at 298.2 K and atmospheric pressure obtained in this work. It is important to remark that it is necessary to accurately estimate the value of the pure ionic liquid to have a good calculation of the mixture and, even if the previous published values also provide reasonable agreement, the small surface tension scale of these mixtures and the slight differences from other surface tension measurements (used for previous fitting), turned into deviations of the model. In addition, when needed, the binary energy and size parameters, ξ_{ij} and η_{ij}, were fitted to the binary experimental surface tension data measured in this work. Usually, these parameters are fitted to vapor−liquid equilibrium data but, as this information was not available, the mixture surface tension data were used. The parameter β, which accounts for deviations in the crossed influence parameter of the mixture, was set to one, in order to avoid further fitting and allow the methodology to be more simple and predictive.

All of the values of the influence parameters for the pure ionic liquids are presented in Table 5 while the binary interaction parameters for each mixture are presented in Table 6. Note that when ξ_{ij} and η_{ij} are equal to 1.0 no fitting was carried out, and the model was used in a predictive manner from pure component parameters.

As depicted in Figure 1, an excellent description of the experimental data was obtained using soft-SAFT combined with DGT for interfacial properties calculations. As mentioned, only the influence parameters obtained from the pure components surface tension data were used. As it was expected, the more symmetrical mixtures (and, as a consequence, with a more ideal behavior) $[C_4mim][NTf_2]$ + $[C_5mim][NTf_2]$ and

Table 4. Molecular Weight and Optimized Molecular Parameters for the $[C_n\text{mim}][NTf_2]$ Ionic Liquids[a]

ionic liquid	M_w (g mol^{-1})	m_i	σ_{ii} (Å)	ε_{ii}/k_B (K)	$\varepsilon^{HB}_{\alpha\beta}/k_B$ (K)	$K_{\alpha\beta,ij}$ (Å^3)
$[C_1\text{mim}][NTf_2]$	377.29	5.947	3.992	391.08	3450	2250
$[C_2\text{mim}][NTf_2]$	391.32	6.023	4.069	394.60	3450	2250
$[C_4\text{mim}][NTf_2]$	419.34	6.175	4.211	399.40	3450	2250
$[C_5\text{mim}][NTf_2]$	433.35	6.247	4.277	401.80	3450	2250
$[C_6\text{mim}][NTf_2]$	447.36	6.338	4.334	404.20	3450	2250
$[C_8\text{mim}][NTf_2]$	475.48	6.489	4.450	410.00	3450	2250
$[C_{10}\text{mim}][NTf_2]$	503.50	6.653	4.551	414.00	3450	2250

[a]Values are taken from previous work.[31]

Table 5. Influence Parameters for the $[C_n\text{mim}][NTf_2]$ Ionic Liquids

ionic liquid	$10^{19}c/(\text{J m}^5\text{ mol}^{-2})$
$[C_1\text{mim}][NTf_2]$	14.67
$[C_2\text{mim}][NTf_2]$	15.93
$[C_4\text{mim}][NTf_2]$	18.05
$[C_5\text{mim}][NTf_2]$	20.28
$[C_6\text{mim}][NTf_2]$	22.50
$[C_8\text{mim}][NTf_2]$	28.04
$[C_{10}\text{mim}][NTf_2]$	34.63

Table 6. Soft-SAFT Binary Interaction Parameters for the Mixtures

binary system	ξ	η
$[C_1\text{mim}][NTf_2]$ + $[C_4\text{mim}][NTf_2]$	1.030	1.010
$[C_2\text{mim}][NTf_2]$ + $[C_4\text{mim}][NTf_2]$	1.005	1.005
$[C_5\text{mim}][NTf_2]$ + $[C_4\text{mim}][NTf_2]$	1.000	1.000
$[C_6\text{mim}][NTf_2]$ + $[C_4\text{mim}][NTf_2]$	1.000	1.000
$[C_8\text{mim}][NTf_2]$ + $[C_4\text{mim}][NTf_2]$	1.018	1.000
$[C_{10}\text{mim}][NTf_2]$ + $[C_4\text{mim}][NTf_2]$	1.065	1.010

$[C_4\text{mim}][NTf_2]$ + $[C_6\text{mim}][NTf_2]$ were predicted without using any binary parameter, being in perfect agreement with the experimental data. However, the more asymmetrical mixtures required a correction for the different dispersive energy and the different segment diameter, although the value of η_{ij} and ξ_{ij} was in all cases (with the exception of ξ for $[C_4\text{mim}][NTf_2]$ + $[C_{10}\text{mim}][NTf_2]$) very close to 1. In fact, good agreement (not shown here) could be found by adjusting only ξ_{ij}, but in this occasion, the purpose was to show the capability of soft-SAFT to correlate the new measured experimental data, and two binary parameters were used to reach better fittings. The use of binary parameters for asymmetric mixtures is very common to account for those differences in size and energy between the molecules and had been observed to model other mixtures of asymmetric compounds like, for example, n-alkanes.[55] A last remark to be noted is related to the value of the unlike energy parameter ξ_{ij} which is, in all cases, equal to or greater than 1. This indicates that the dispersive energy interactions between both compounds are slightly higher than the geometric average of the energy of each pure compound. In other words, van der Waals forces between unlike components are a bit stronger than in a hypothetical averaged one-fluid mixture, and this results in a lower surface tension value for the mixture, as is shown in Figure 1.

One of the advantages of using a theoretical tool such as a molecular-based equation of state with DGT is the possibility of studying what is happening along the interface. The calculation of the density profiles of some mixtures across the interface allows confirmation of experimental evidence concerning the

relative enrichment of the heavier ionic liquid in the interface. Figure 4 presents density profiles at 298.15 K at a mole fraction composition in the bulk liquid phase of 0.5 for the binary mixtures $[C_4\text{mim}][NTf_2]$ + $[C_2\text{mim}][NTf_2]$ (Figure 4a), $[C_4\text{mim}][NTf_2]$ + $[C_6\text{mim}][NTf_2]$ (Figure 4b), and $[C_4\text{mim}]$-$[NTf_2]$ + $[C_8\text{mim}][NTf_2]$ (Figure 4c). Starting with Figure 4a, the prevalence in the interface of the ionic liquid with the longer alkyl chain length is clearly seen, in this case the
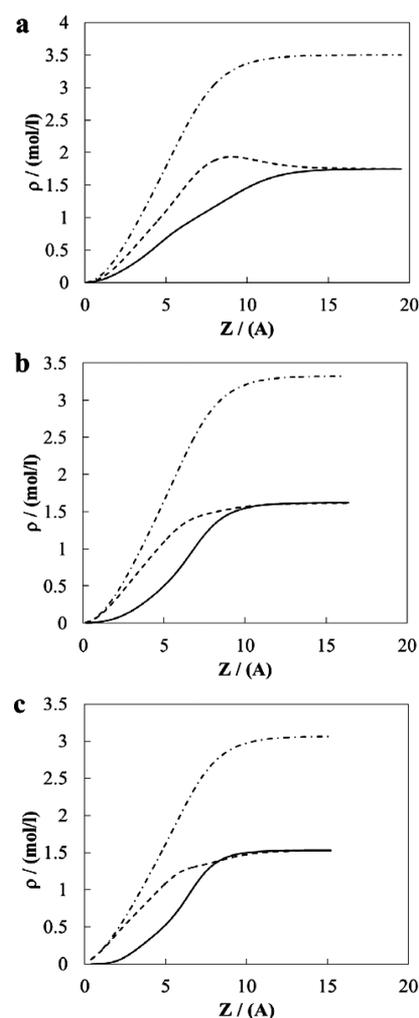

Figure 4. Density profiles across the interface at 298.15 K for (a) $[C_4\text{mim}][NTf_2]$ + $[C_2\text{mim}][NTf_2]$, (b) $[C_4\text{mim}][NTf_2]$ + $[C_6\text{mim}]$-$[NTf_2]$, and (c) $[C_4\text{mim}][NTf_2]$ + $[C_8\text{mim}][NTf_2]$ at a starting bulk liquid composition x = 0.5. The solid curve represents the density of $[C_n\text{mim}][NTf_2]$ (with n = 2, 6, or 8), the dashed curve corresponds to the density of $[C_4\text{mim}][NTf_2]$, and the dashed-dotted curve is the total density.

$[C_4mim][NTf_2]$. There is a clear enrichment of $[C_4mim]$-$[NTf_2]$ that confirms the conclusions from the experiments, where it was observed that this mixture deviated substantially from linearity. Figure 4b presents the $[C_4mim][NTf_2]$ + $[C_6mim][NTf_2]$ mixture, where no relative enrichment is observed, at least at the selected conditions. This confirms that the differences between $[C_4mim][NTf_2]$ + $[C_6mim][NTf_2]$ are less important than those between $[C_4mim][NTf_2]$ + $[C_2mim][NTf_2]$, as observed according to the deviations from linearity ($d\gamma$ in Figure 2). Finally, in Figure 4c a very minor adsorption of the ionic liquid with the longer alkyl chain length is observed. This is favored by the increase of the chain length, but still the enrichment is not so evident as it is for $[C_4mim][NTf_2]$ + $[C_2mim][NTf_2]$. This is also directly related to the difference between the surface tension values of each pure ionic liquid (the difference in surface tension between $[C_4mim][NTf_2]$ and $[C_2mim][NTf_2]$ is higher than with $[C_6mim][NTf_2]$ or even $[C_8mim][NTf_2]$).

5. CONCLUSIONS

This is the first systematic study of surface tensions of binary mixtures of ionic liquids. Mixtures composed of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, $[C_4mim][NTf_2]$, and 1-alkyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide ionic liquids, $[C_nmim][Tf_2N]$, with n = 1, 2, 5, 6, 8, and 10 were studied over the entire composition range at 298.2 K and atmospheric pressure.

The Gibbs adsorption isotherms calculated from the experimental data show 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. This trend confirms the segregation between the polar and nonpolar parts of the ionic liquid ions with the longer alkyl side chains pointing toward the vapor phase.

Finally, the surface tensions and some interfacial density profiles of these binary mixtures of ionic liquids were reproduced using the soft-SAFT equation coupled with DGT. An excellent agreement between the theoretical and experimental results is observed using influence parameters derived only from the pure component data. Binary parameters that account for differences in the size and energy of the molecules have been used for the most asymmetrical mixtures.

To our knowledge, this is the first time that a molecular-based equation of state with DGT has been used to calculate the interfacial tension of mixtures of ionic liquids and density profiles across the interface. In this context, the soft-SAFT equation coupled with a DGT approach can be envisaged as an accurate method for determining the surface tension of other ionic liquid mixtures with other cations and anions. Results indicate that soft-SAFT + DGT can be a reliable predictive tool to estimate the surface tensions of binary mixtures of ionic liquids and to describe their interface behavior with accuracy.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Information about the density values of $[C_4mim][NTf_2]$ + $[C_nmim][NTf_2]$ mixtures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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