Probing the Surface Tension of Ionic Liquids Using the Langmuir Principle

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ABSTRACT: At 298 K, the surface tension of ionic liquids (ILs) of the 1-alkyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide series, [CnC1Im][NTf2], ranges from around 35 mN m−1 for [C6C1Im][NTf2] to just below 30 mN m−1 for [C12C1Im][NTf2]. However, the decrease rate along the series is not constant: a large decrease from [C6C1Im][NTf2] to [C8C1Im][NTf2] is followed by almost constant values from [C8C1Im][NTf2] to [C12C1Im][NTf2]. Such behavior is hard to interpret from a molecular point of view without suitable information about the free-surface structure of the different ILs. In this work, we have successfully used the Langmuir principle in combination with structural data obtained from angle-resolved X-ray photoelectron spectroscopy experiments and molecular dynamics simulations, to predict the correct surface tension trend along the IL series. The concepts unveiled for this particular homologous IL family can be easily extended to other systems.

INTRODUCTION

Ionic liquids (ILs), salts that melt at temperatures not far from room temperature, are a relatively recent class of fluids with several unique structural properties.1–6 Due to their extremely low vapor pressure, large electrochemical window, high thermal stability, and structural variability, ILs are promising candidates for applications in multiphase catalysis, electrochemistry, separation technology, and many other areas.7 The nature of the IL surface layer, that is, the interface between an IL and a gas phase, becomes an important factor particularly when high surface area systems are involved. In the case of ILs, the composition of the surface layer and the structure of its gas (or vacuum) boundary is a result of different types of short- and long-range interactions related to the ILs’ complex molecular structure; the IL’s tendency to minimize its surface free energy results in its experimentally observable surface tension values.

Different ILs can exhibit quite diverse surface tension values. For instance, at 298 K, 1,3-dimethylimidazolium methylsulfate, [C3C1Im][C2SO3], exhibits a surface tension of 65.1 mN m−1, whereas 1-butyl-3-methylimidazolium octylsulfate, [C6C1Im]·[C8SO3], exhibits a surface tension of only 25.2 mN m−1 at the same temperature.8 Interestingly, many ILs fill the 40–70 mN m−1 surface tension gap that exists between most molecular solvents (with values up to 40 mN m−1 at 298 K) and water (72 mN m−1 at the same temperature).9 Molecular fluids that are exceptions to this trend and exhibit surface tensions within the 40–70 mN m−1 interval generally have a large tendency to form multiple hydrogen bonds (e.g., glycols, alkanesulfonic acids). In fact, water can be regarded as the fluid with the highest hydrogen bonding density, thus explaining its anomalous surface tension values. Conversely, in the case of ILs, the relatively high surface tension values can be rationalized in terms of electrostatic interactions between ions.

Several attempts have been made to correlate in an empirical or semiempirical way the surface tension of different ionic liquids with the characteristics of their constituting ions. Those works range from the use of quantitative structure-property relationship (QSPR) methods, to the definition of the so-called Parachor and ionic Parachor (surface-tension-weighted molar volumes) and their use in group-contribution methods.10–14 However, the development of a general framework for explaining and predicting surface tension trends across a large number of different ILs seems to be difficult, which could be related to the complex structural nature of ILs.15

As pointed out by Irving Langmuir more than 80 years ago,16 the surface tension of a fluid is related on one hand to the intermolecular interactions in the bulk (cohesive energy) and on the other to the molecular orientation at the surface. In general, high cohesive energies contribute to high surface tension values. However, this correlation is only a good approximation for liquids where surface ordering effects are negligible.

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Thus, within the framework of the so-called “Langmuir principle”, the surface tension is given by “the result of superposition over the molecule parts present at outer surface”.\textsuperscript{15}

Even as isotropic bulk liquids, ILs are known to exhibit complex structuration and nanosegregated domains which are a consequence of the balance that has to be achieved between local electroneutrality conditions among ions of opposite charge and the competition between electrostatics and other van der Waals forces that are present in different moieties of the IL ions.\textsuperscript{17,18} Such local structural anisotropy is further modified (and exacerbated) at the surface of the liquid: the 2D liquid-vacuum boundary imposes limiting conditions that induce the structural rearrangement of the ILs ions into layered arrangements parallel to the surface with different local composition.\textsuperscript{19,20}

In the present work, we will use an IL homologous series, 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonylimide), \([\text{C}_n\text{C}_1\text{Im}][\text{NTf}_2]\) (2 \(\leq n \leq 12\), to discuss the bulk cohesive energy and surface molecular orientation. These two issues are, according to the Langmuir principle, paramount to the correct evaluation and understanding of the surface tension from a molecular perspective. We have chosen this series because the experimental values for the surface tension and surface composition have been derived by the same group under identical experimental conditions.\textsuperscript{15} Despite the fact that absolute surface tension values of neat ILs deviate considerably in literature even for this series,\textsuperscript{21} in all cases the same general trend is found: surface tension of \([\text{C}_n\text{C}_1\text{Im}][\text{NTf}_2]\) ILs steeply decreases from the highest value for \(n = 2\), and with increasing chain length this decrease is reduced reaching a plateau at around \(n = 8\)–12.

Nowadays, the surface molecular orientation, or as stated originally by Langmuir, the “molecule parts present at outer surface”, can be probed by surface-sensitive experimental methods such as angle-resolved X-ray photoelectron spectroscopy (ARXPS).\textsuperscript{15} In the present work, we will match such type of data to density profiles calculated from Molecular Dynamic simulation trajectories.

### SIMULATION DETAILS

The interfacial structure of all ILs studied experimentally was probed using molecular dynamics (MD) simulations. The ILs were modeled using the CL&P atomistic force field,\textsuperscript{24} which is an extension of the AMBER and OPLS force fields\textsuperscript{25} specially designed to study ILs and their homologous series. MD simulations were carried out using the DL_POLY 2.20 package.\textsuperscript{24} The runs were performed with a 2 fs time step and a 1.6 nm cutoff distance. Ewald summation corrections were performed beyond the cutoffs. Due to the slow dynamics of this type of systems, special care was taken to ensure the attainment of true equilibrium conditions (we have performed equilibration runs under harsh temperature and charge annealing conditions). The number of ion pairs and the size of the simulation box for all studied ILs are presented in Table 1.

All simulations started from low-density configurations that were subjected to 3 ns equilibration runs under isobaric isothermal ensemble conditions at \(p = 0.1\) MPa and \(T = 298\) K, with Nosé–Hoover thermostats and barostats with relaxation time constants of 1 and 4 ps, respectively. The bulk density of each system reached constant and consistent values, indicating that equilibrium had been attained and possible ergodicity problems had been overcome. Finally, several (at least six) consecutive production stages of 1.0 ns each were performed and the combined results were used for the evaluation of relevant structural data in bulk conditions.

### Table 1. Simulation Conditions and Size of the Equilibrated Boxes

| system                  | \(N\) ion pairs | slab dimensions (nm \(\times\) nm \(\times\) nm) |
|-------------------------|-----------------|-----------------------------------------------|
| \([\text{C}_1\text{C}_1\text{Im}][\text{NTf}_2]\) | 600             | 4.0 \(\times\) 4.0 \(\times\) 16.0             |
| \([\text{C}_2\text{C}_1\text{Im}][\text{NTf}_2]\) | 600             | 4.0 \(\times\) 4.0 \(\times\) 18.0             |
| \([\text{C}_3\text{C}_1\text{Im}][\text{NTf}_2]\) | 600             | 4.0 \(\times\) 4.0 \(\times\) 20.0             |
| \([\text{C}_4\text{C}_1\text{Im}][\text{NTf}_2]\) | 600             | 4.0 \(\times\) 4.0 \(\times\) 23.5             |
| \([\text{C}_5\text{C}_1\text{Im}][\text{NTf}_2]\) | 450             | 4.0 \(\times\) 4.0 \(\times\) 18.0             |
| \([\text{C}_6\text{C}_1\text{Im}][\text{NTf}_2]\) | 450             | 4.0 \(\times\) 4.0 \(\times\) 20.0             |

To model the IL–vacuum interface, each cubic simulation box containing a pure IL was expanded to a value three times its initial size by elongating the sides of the cube along the \(z\)-axis. This generated an IL slab with two explicit liquid-vacuum interfaces and tetragonal simulation boxes with approximately 4.5 \(\times\) 4.5 \(\times\) 35.0 nm\(^3\) dimensions. A simulation run was then conducted under NVT ensemble conditions (\(T = 298\) K), with 0.5 and 2 ns equilibration and production stages, respectively; no drift in the studied properties was found from block analysis of the production stage. In order to obtain a thicker IL slab, the system was then subjected to a lateral compression (in the \(x\)- and \(y\)-axes) by running a NpT ensemble simulation for around 150 ps. This process leads to a tetragonal box with a 4.0 \(\times\) 4.0 nm\(^2\) base and a liquid layer about 16 nm thick. This configuration was then subjected to new (3 ns equilibration \(+\) 6 ns production) processes under NVT conditions that conducted to the results discussed below. Possible ergodicity problems were tested by calculating the system properties at different stages of the production runs, including comparisons between slabs of different thickness or between processes interspersed by temperature-annealing cycles.

### EXPERIMENTAL DETAILS

Surface orientation effects within the \([\text{C}_n\text{C}_1\text{Im}][\text{NTf}_2]\) \((n = 2, 4, 6, 8, 10, 12)\) IL series of this work was already investigated and published before;\textsuperscript{25} now, a re-evaluation of these data was applied to obtain more accurate values for the composition within the outermost surface layers (for more details, see Results). In particular, the absence of surface-active contaminations such as polysiloxanes or additional hydrocarbon compounds\textsuperscript{26} has been proven by angle-resolved X-ray photoelectron spectroscopy (ARXPS) as will be discussed below. It should be noted that the identical ILs have been used not only for ARXPS but for surface tension measurements as well, employing the pendant drop method.\textsuperscript{25} Experimental details of our ARXPS setup and spectra analysis are extensively described in earlier publications.\textsuperscript{25} In short, IL films with thicknesses of about 0.1 mm were spread on a planar Au foil (20 \(\times\) 15 \(\times\) 0.1 mm\(^2\)) forming a smooth coating layer and then introduced into the ultra high vacuum (UHV) system via a loadlock. The rather large sample size was chosen to avoid signal contributions from the foil edges where deviations from flat film morphology occur, particularly at the bottom part of the tilted sample holder. After at least 6 h of pumping, a base pressure of \(\sim 5 \times 10^{-10}\) mbar was eventually achieved, confirming the absence of volatile impurities such as water or nonreacted imidazole. Detailed spectra were recorded with an ESCALAB 200 VG system using nonmonochromated Al K\(\alpha\) radiation (\(h\nu = 1486.6\) eV) with an overall energy resolution of 0.9 eV. Due to the small layer thickness, the good wetting characteristics, and the relatively high viscosity of the ILs, the IL-coated Au foil could be tilted from horizontal to vertical position in order to change the polar electron detection angle for ARXPS without affecting the IL film morphology (recently, we remeasured some of the ILs of this series using a unique UHV setup with two analyzers mounted for simultaneous 0\(^\circ\) and 80\(^\circ\) electron detection with the IL sample holder fixed in horizontal geometry;\textsuperscript{27} the resulting ARXP spectra do not differ significantly from the ones obtained by sample tilting, which is a clear indication that the morphology in the center of the sample holder is not affected by sample tilting). ARXPS makes use of the dependence of XPS information depth (ID) on the electron emission angle \(\theta\) (relative to the surface normal) due to the small inelastic mean free path \(\lambda\) of the excited photoelectrons in matter; \(\lambda\) depends on kinetic
energy, that is, the core level studied, with values between 2 and 3 nm for organic materials. Due to the small acceptance angle of our electron analyzer, measurements at $\theta = 0^\circ$ probe the near-surface region with an ID of 7–9 nm (ID is the depth where 95% of the detected signal originates from, which is three times $\lambda$). This corresponds to 10–15 IL layers, estimating the mean ion pair size from the cubic root of the molecular volume for the different ILs. In contrast, measurements at 80° (ID(80°) $\approx$ ID(0°)$\cos \theta \approx$ ID(0°)/$\sqrt{3}$, $\lambda$ $\approx$ 1–1.5 nm) predominately probe the outermost surface layers. To give an example, for the C 1s level with $\theta = 0^\circ$ probe the near-surface region with an ID of 7–9 nm (ID is the depth where 95% of the detected signal originates from, which is three times $\lambda$), this uncertainty has no impact on the positioning in absolute tilt angle estimated to be $\pm 5.5^\circ$.

Table 2. Quantitative Analysis of the XP Spectra of $[\text{C}_n\text{C}_1\text{Im}]\text{[NTf}_2\text{]}$, for $n = 2$–12 (Approximate Binding Energy Positions and Atomic Sensitivity Factors, ASF, of the Core Levels Used Are Given in the First Row)$^{29}$

| Approx. Position (eV) | C 1s (hetero) | C 1s (alkyl) | N 1s (cation) | C 1s (anion) | N 1s (anion) | O 1s (anion) | S 2p (anion) | F 1s (anion) | C_{alkyl}/C_{hetero} |
|----------------------|---------------|--------------|---------------|---------------|---------------|--------------|--------------|--------------|------------------------|
| [C$_{2}$C$_{1}$Im] [NTf$_{2}$] | 286.5 | 285.0 | 401.9 | 292.8 | 399.2 | 532.5 | 167.7 | 688.8 | 0.20 |
| [C$_{3}$C$_{1}$Im] [NTf$_{2}$] | 0° | 5.0 | 1.0 | 2.0 | 2.0 | 1.0 | 4.0 | 2.0 | 6.0 | 0.20 |
| 80° | 4.4 | 1.5 | 1.8 | 2.1 | 1.0 | 3.3 | 1.8 | 7.0 | 0.34 |
| [C$_{4}$C$_{1}$Im] [NTf$_{2}$] | 0° | 5.0 | 3.0 | 2.0 | 2.0 | 1.0 | 4.0 | 2.0 | 6.0 | 0.60 |
| 80° | 4.4 | 4.1 | 1.8 | 2.0 | 0.9 | 3.3 | 1.9 | 6.6 | 0.93 |
| [C$_{5}$C$_{1}$Im] [NTf$_{2}$] | 0° | 5.0 | 5.0 | 2.0 | 2.0 | 1.0 | 4.0 | 2.0 | 6.0 | 1.00 |
| 80° | 4.4 | 6.9 | 1.7 | 1.9 | 0.9 | 3.2 | 1.8 | 6.2 | 1.57 |
| [C$_{6}$C$_{1}$Im] [NTf$_{2}$] | 0° | 5.0 | 7.0 | 2.0 | 2.0 | 1.0 | 4.0 | 2.0 | 6.0 | 1.40 |
| 80° | 4.4 | 10.3 | 1.6 | 1.7 | 0.9 | 3.1 | 1.8 | 5.8 | 2.64 |
| [C$_{7}$C$_{1}$Im] [NTf$_{2}$] | 0° | 5.0 | 9.0 | 2.0 | 2.0 | 1.0 | 4.0 | 2.0 | 6.0 | 1.80 |
| 80° | 4.4 | 14.1 | 1.4 | 1.6 | 0.8 | 2.9 | 1.7 | 4.8 | 3.71 |
| [C$_{8}$C$_{1}$Im] [NTf$_{2}$] | 0° | 5.0 | 11.0 | 2.0 | 2.0 | 1.0 | 4.0 | 2.0 | 6.0 | 2.20 |
| 80° | 4.4 | 11.8 | 2.0 | 1.9 | 1.0 | 3.9 | 1.9 | 5.5 | 2.15 |

“The nominal and the experimentally determined composition in number of atoms (bold numbers; for nomenclature, see Figure 3) are measured at 0° (bulk-sensitive) and 80° (surface-sensitive) electron emission angle as has been presented earlier; in addition to ref 25, C_{alkyl} and C_{hetero} content was corrected as described in the text taking the N 1s (cation) intensity of the imidazolium ring into account, which leads to more accurate values for the ratio C_{alkyl}/C_{hetero} (last column).”

**RESULTS AND DISCUSSION**

Figure 1 shows a snapshot of a simulation box containing 600 $[\text{C}_n\text{C}_1\text{Im}]\text{[NTf}_2\text{]}$ ion pairs. The box is a quadrangular prism with $4 \times 4 \times 35$ nm$^3$ dimensions and periodic boundary conditions in the $x$ and $y$ directions. The equilibrated system is a slab of IL, with two explicit liquid–vacuum interfaces and a thickness of around 18 nm. The figure also shows a representation of the total numerical density profile along the normal to the interfaces ($z$ axis) using the same scale of the snapshot. It was calculated taking into account equilibrated MD trajectories ca. 10 ns long. The numerical density data at a given $z$ value was calculated considering all atoms within a $4 \times 4 \times \Delta z$ nm$^3$ layer ($\Delta z = 0.058$ nm) of the simulation box, with the hydrogen atoms weighted by a 0.5 factor, and was normalized taking into account the average numerical density at the center of the slab (the 10 nm-thick central layer further away from either interface). The profiles at the interfaces have shapes which can be fitted to sigmoid functions, $S(z)=\rho(z)/\rho_{bulk}=1/(1+\exp((z-z_{1/2})/k))$, where $z_{1/2}$ is the depth where $\rho(z)/\rho_{bulk}=1/2$ (interface midpoint), and $k$ is the decay length. The $z_{1/2}$ values were used to define the origin of the $z$-axes in internal coordinates, $z_0$, relative to each interface (inset of Figure 1). The decay length of the sigmoid function, $k$, is an indication of the width of the interface: the positions of the density profile lift off, $\rho(z)/\rho_{bulk}=0.002$, is at approximately +6k and of those
of the attainment of the liquid density, $\rho(z)/\rho_{bulk}$ = 0.998, at approximately $-6k$).

The other five systems, $[C_nC_1Im][NTf_2]$ ($n = 4, 6, 8, 10, 12$), were simulated using similar conditions. Since we were interested in the comparison of the liquid-vacuum interfaces, we have decided to keep all quadrangular prisms with $4 \times 4$ nm$^2$ cross sections, thus minimizing any difference arising from finite-size effects related to the use of periodic boundary conditions in the directions parallel to the interfaces. This means that the overall width of the IL slabs increases as the corresponding molar volume of the ILs also increases along the homologous series. In the case of $[C_4C_1Im][NTf_2]$ and $[C_6C_1Im][NTf_2]$, we reduced the number ion pairs present in the system from 600 to 450 to avoid unnecessarily thick slabs.

Figure 2 compares the total number density profiles of the six systems in the region close to one of the interfaces. The graph is given in internal $z_0$ coordinates relative to that interface, with positive $z_0$ values pointing toward the vacuum region. The $\rho(z_0)/\rho_{bulk}$ values of the different profiles were offset in the graph in order to avoid superimposition of the plots. The inset shows the superimposed sigmoid functions without the offset of the profiles. The figure also shows top-view and side-view snapshots of the $[C_4C_1Im][NTf_2]$ and $[C_{12}C_1Im][NTf_2]$ interfaces.

The sigmoid profiles show that the liquid-vacuum interfaces get broader and somewhat less well-defined along the homologous series. The corresponding decay lengths of the sigmoid functions, $k$, for the six $[C_nC_1Im][NTf_2]$-ILs range from 0.071 nm for $[C_4C_1Im][NTf_2]$ over 0.087 nm ($n = 4$), 0.101 nm ($6$), 0.115 nm ($8$), 0.129 nm ($10$) to 0.134 nm for $[C_{12}C_1Im][NTf_2]$. This can be appreciated qualitatively by the side-view snapshots: shorter alkyl-chain ILs such as $[C_4C_1Im]^{-}[NTf_2]$ exhibit a sharper, more homogeneous interface than longer ones such as $[C_{12}C_1Im][NTf_2]$. In the latter case, the long alkyl chains do not cover the entire surface (one can still observe patches of the charged moieties of the IL in the top view in the upper left corner of Figure 2) and tend to form clusters, thus producing a more irregular surface. Nevertheless, by defining the zero of each interface at the sigmoid function midpoint and considering in-plane averages while calculating the numerical density profiles of the different species present in the system, it is possible to compare the different interfaces in a meaningful way, indirectly taking into account their intrinsic thickness and roughness. The definition of an origin for each interface of the slabs also allowed us to combine the simulation results from the two interfaces of each IL simulation run in order to improve the corresponding statistics. The following analyses have been performed considering such averaged data.

Figure 3 shows the numerical density profiles for all studied ILs of three selected atoms that are used as proxies for different moieties of the IL: the $[NTF_2]$ anions are represented in red by their nitrogen atom, NBT; the charged headgroups of the IL: the $[NTF_2]$ moieties of both ions, NBT/CR lines) which is depleted of CT atoms. The pro

Figure 3 shows the stratification of fluid at the IL–vacuum interface even for the IL with the shortest alkyl side chain: the $[C_4C_1Im][NTf_2]$ profiles show CT atoms at the outermost surface forming a thin alkyl layer, followed by a charged layer (containing the charged moieties of both ions, NBT/CR lines) which is depleted of CT atoms. The profiles show that the anions (red profile) tend to be slightly closer to the surface than the charged headgroup of the cations, blue profile). It must be stressed that the graphs are averages over each $4 \times 4 \times \Delta z_0$ slice used to calculate the numerical density profiles. The peaks do not represent homogeneous layers but rather the relative probability of finding an atom of a specific type at a given distance from the surface.
As the alkyl chains increase in length along the series, the profiles show a broadening of the first CT peak, and the shift of the first CR/NBT maxima further away from the surface. This broadening of the first layers is complemented by a more obvious separation of the alkyl layer and the accompanying charged layer. It also goes along with a more pronounced dip of the CT curve after the first peak, at least up to \([\text{C}10\text{C1Im}][\text{NTf}_2]\). The profiles also show less defined NBT/CR curves (double peaks, shoulders) near the surface as the series progresses toward longer alkyl side chains. Such a behavior suggests less ordered charged layers for the ILs with longer alkyl side chains.

The “molecule parts present at outer surface” issue can now be addressed by taking into account the different numerical density profiles and establishing a boundary for the “outer surface”. In order to validate the simulation results and check possible definitions for the outer surface, we have decided to match ARXPS results for the \([\text{C}_{n}\text{C1Im}][\text{NTf}_2]\) series with the present simulation data.

Figure 4 shows the ARXPS results as black circles. The surface enrichment of the alkyl chains is quantified by the intensity ratio of XPS signal of the alkyl carbon atoms, \(C_{\text{alkyl}}\), and of the carbon atoms with hetero atom (nitrogen) neighbors \(C_{\text{hetero}}\). The data show how the ratio \(I(C_{\text{alkyl}})/I(C_{\text{hetero}})\) varies along the \([\text{C}_{n}\text{C1Im}][\text{NTf}_2]\) IL series. For measurements at an angle of \(\theta = 0^\circ\) to the surface normal, the ratio is similar to the nominal \((n-1)/5\) ratio in a \([\text{C}_{n}\text{C1Im}]\) cation there are \(5\) hetero C atoms and \(n-1\) alkyl C atoms, cf. Figure 1) observed for the bulk IL, cf. dotted black line in Figure 4. For measurements at \(\theta = 80^\circ\), that is, in the surface-sensitive geometry, the ratio starts to be significantly larger at \(n = 4\) than the nominal value (dotted black line); with increasing chain length \((n > 4)\) this difference increases, as is evident from Figure 4. In other words, the surplus presence of the alkyl chains in the surface layers progressively increases along the \([\text{C}_{n}\text{C1Im}][\text{NTf}_2]\) series.

The observed enrichment of the longer alkyl chains as derived from ARXPS has been published before.\(^\text{25}\) For the quantitative comparison performed here, these results have been carefully reanalyzed with a modified procedure, which yields an even more pronounced surface enrichment as the original analysis, in particular for chain lengths with \(n = 10\) and 12. This is due to the fact that the \(C_{\text{alkyl}}\) and \(C_{\text{hetero}}\) peaks are separated only by \(\sim 1.5\) eV (285.0 and 286.5 eV, respectively),
which is just 1.7 times larger than our overall energy resolution. For long alkyl chains, the $C_{\text{alkyl}}$ signal is strongly dominating the peak shape. Additionally, the $C_{\text{hetero}}$ signal is strongly attenuated in the surface-sensitive geometry due to the surface enrichment of the alkyl chains. Both effects impose an increasing uncertainty in the fitting of both, the small $C_{\text{hetero}}$ and the large $C_{\text{alkyl}}$ signal. To overcome this difficulty and to obtain more accurate results, we have now used the $N_{\text{cation}}$ signal of the imidazolium ring nitrogen atoms as internal reference. Due to the small diameter of the imidazolium ring and the direct vicinity of the two imidazolium nitrogen atoms to the surrounding $C_{\text{hetero}}$ atoms, and due to the very similar inelastic mean free path, their intensities should change in parallel. The well-separated $N_{\text{cation}}$ signal can easily be quantified even without peak fitting. Its decrease from $0^\circ$ to $80^\circ$ (N 1s(cation))$_{\theta=0}/N$ 1s(cation)$_{\theta=80}$ was used to constrain the decrease of the $C_{\text{hetero}}$ signal in $80^\circ$ accordingly; the number of $C_{\text{alkyl}}$ atoms in $80^\circ$ was then derived by subtracting the obtained $C_{\text{hetero}}$ atoms from the total cation carbon signal in $80^\circ$. By this simple procedure, improved numbers for the surface composition in $80^\circ$ were obtained. Table 2 provides the results for the ILs' composition in $0^\circ$ and $80^\circ$ in number of atoms along with the nominal values. Note that the accuracy in absolute composition values is estimated to about ±5% as can be seen by the obtained $0^\circ$ values compared to the nominal ones. The ratio values of $C_{\text{alkyl}}$ to $C_{\text{hetero}}$ shown in Figure 4 are given in the last column with an accuracy of about ±8%.

We can now combine the MD simulation trajectories, containing the position of all atoms within the simulation box, with information about the inelastic mean free path $\lambda$ relevant for the ARXPS experiments shown here (for C 1s and N 1s: $\lambda \approx 2.8$ nm) and the corresponding signal attenuation $I(z) = I(0) \exp(-z/(\lambda \cos(\theta)))$ to calculate the $I(C_{\text{alkyl}})/I(C_{\text{hetero}})$ ratios for layers measured at $\theta = 0^\circ$ and $\theta = 80^\circ$. The red crosses in Figure 4a (expo MD) show the corresponding ratios considering that each carbon atom in the MD trajectory contributes according to the exponential decay of the ARXPS attenuation. In all cases, the exponential decay started ($z_0 = 0$) at the depth, at which half numerical density is attained (interface midpoint), and all atoms further out were counted undamped. This approach allows for defining the zero for the damping curve and is independent of the exact liftoff of the density profiles (Figure 5). The amount of undamped molecules (that is from $z_0$ to $+6k$) corresponds to an amount of a ~0.1 (C2) to 0.2 (C12) nm thick film in the bulk and thus imposes only a minor error on the analysis.

As an alternative approach, the red crosses (step MD) in Figure 4b were calculated using a step function to truncate the contribution from all atoms beyond a depth larger than $\lambda \cos(\theta)$. Such step function depths correspond to 2.8 nm for the $0^\circ$ setup and 0.5 nm for the $80^\circ$ setup. This means that if one takes into account the liftoff of the density profiles, the ARXPS experiments with the $80^\circ$ setup effectively probe a layer from $z = -0.5$ nm to $z = +6k$, i.e., 0.92 and 1.31 nm in the $[C_2\text{C}_1\text{Im}]^+[\text{NTf}_2^-]$ and $[C_{12}\text{C}_1\text{Im}]^+[\text{NTf}_2^-]$ systems, respectively.

Using either the “exponential” or the “step” approach, only the terminal methyl carbon of the alkyl chain (CT) and the carbon in C2 position (CR) from the MD simulations have been summed up for the analysis. To compare with the ARXPS data, the CT:CR ratios found for the different $[C_2\text{C}_1\text{Im}]^+[\text{NTf}_2^-]$ systems have been weighted by the factor $(n - 1)/5$ to obtain the $C_{\text{alkyl}}$: $C_{\text{hetero}}$ ratio from MD, shown in Figure 4.

The agreement in Figure 4a and b between the ARXPS intensity ratios and those obtained from the modeled interface profiles is very good, especially considering the approximations being made, namely using the CR and CT atoms to represent the position of the imidazolium ring and alkyl chain moieties. This agreement validates the trends deduced for the structure of the IL–vacuum interfaces using the present model. The two approaches applied to the analysis of the MD results (exponential vs step function) yield similar results, although the “soft” boundary imposed by the exponential decay is less affected by statistical uncertainties associated with the size of the simulation surfaces or the truncation procedure linked to the step (“hard” boundary) contributions.

Finally, it is now possible to use the ideas stated in the Langmuir principle to estimate the surface tension of the different surfaces. First, we stipulate that the surface tensions of very short and very long alkyl chains define the limiting values. In the picture, $[C_2\text{C}_1\text{Im}]^+[\text{NTf}_2^-]$ (36.3 mN m$^{-1}$) represents the contribution of the charged layer (anion and cation ring moieties without side chains) to the surface tension. On the other hand, the systems from $[C_n\text{C}_1\text{Im}]^+[\text{NTf}_2^-]$ to $[C_{12}\text{C}_1\text{Im}]^+[\text{NTf}_2^-]$ exhibit almost constant surface tension values around 29.5 mN m$^{-1}$. We thus assume that this value is the contribution to the surface tension of the alkyl side chain moieties.

Second, we used exponential and step decays to calculate the occurrence/contribution of NBT, CR, and CT atoms in layers within depth regions from $z = +k$ to $-2.8$, $-0.5$, and $-0.12$ nm, corresponding to XPS measurements at $\theta = 0^\circ$, $80^\circ$, and $87.5^\circ$ (note that no measurements for the last value exist).

Third, we calculated the volume occupied by the different moieties of the IL (anion, cation ring, alkyl side chain) present in the considered depth region. In order to do so, we weighted the occurrence probabilities of the NBT, CR and CT atoms with the molar volume occupied by the corresponding moieties (159, 82, and 17 cm$^3$ mol$^{-1}$, for $[\text{NTf}_2^-]^-$, $[C_2\text{C}_1\text{Im}]^+$ and methylene groups, respectively). For $[C_n\text{C}_1\text{Im}]^+[\text{NTf}_2^-]$ as an
Table 3. Atom, $x_i$, and Volume, $x_{V,i}$ Fractions in the Bulk, ARXPS Surfaces (0 and 80° setups) and in the Outer Surface (pseudo 87.5° Setup)*

| $n$ | 2 | 4 | 6 | 8 | 10 | 12 | 2 | 4 | 6 | 8 | 10 |
|-----|---|---|---|---|---|----|---|---|---|---|----|
| $x_{CR}$ | 0.333 | 0.333 | 0.333 | 0.333 | 0.333 | 0.333 | 0.333 | 0.333 | 0.333 | 0.333 | 0.333 |
| $x_{CT}$ | 0.333 | 0.333 | 0.333 | 0.333 | 0.333 | 0.333 | 0.333 | 0.333 | 0.333 | 0.333 | 0.333 |
| $x_{NBT}$ | 0.318 | 0.281 | 0.252 | 0.228 | 0.208 | 0.192 | 0.206 | 0.213 | 0.220 | 0.227 | 0.234 |
| $x_{V,CR}$ | 0.066 | 0.175 | 0.261 | 0.351 | 0.389 | 0.437 | 0.385 | 0.437 | 0.503 | 0.557 | 0.610 |
| $x_{V,CT}$ | 0.616 | 0.544 | 0.487 | 0.441 | 0.403 | 0.371 | 0.403 | 0.437 | 0.471 | 0.505 | 0.539 |

*Estimated (see text) surface tension values, $\sigma$.

A single example shown in Figure 3, the weighting factors for NBT, CR, and CT are 159, 82, and (4−1) × 17 = 51, respectively.

Fourth, the obtained volume fractions of each type of moiety (step 3) can be multiplied by the corresponding surface tension contribution (step 1) to yield the surface tension of the system. The values are compiled in Table 3 and plotted in Figure 6 (red crosses). The same procedure applied to the bulk stoichiometry of the CR, CT, and NBT atoms yields the dotted black line, which would represent the surface tension without alkyl enrichment.

It is obvious that the alkyl enrichment at the surface decreases the surface tension values relative to the situation of a bulk-truncated. However, the chain enrichment obtained by MD within the effective probing depth of 0.91 up to 1.31 nm, corresponds to the probing depth of ARXPS in 80° for [C$_6$C$_1$Im][NTf$_2$] and [C$_{12}$C$_1$Im][NTf$_2$], respectively, does not lead to the experimentally observed steep initial decrease in surface tension when increasing the alkyl chain; also, the saturation in surface tension above [C$_6$C$_1$Im][NTf$_2$] cannot be reproduced. The reason becomes obvious when inspecting the profiles in Figure 3: the 0.91−1.31 nm thick surface between the left-most and right-most dotted lines includes the whole alkyl layer but also a large part of the charged layer, which is not at the outermost surface. This means that the volume fraction of the charged layer as well as its contribution to the surface...
tension values will decrease too slowly from [C\textsubscript{2}C\textsubscript{1}Im][NTf\textsubscript{2}] to [C\textsubscript{1}C\textsubscript{1}Im][NTf\textsubscript{2}], and does not reach a constant value from [C\textsubscript{5}C\textsubscript{1}Im][NTf\textsubscript{2}] onward. A constant surface tension would only be achieved at much larger alkyl chain lengths (not studied here).

The important point to be made here is that the surface-sensitive ARXPS studies at 80\(^\circ\) that indeed probe the depths mentioned in the previous paragraph are not in disagreement with the surface tension data, if one simply recognizes that the "outer surface" assumed by the Langmuir principle can be thinner than the 0.91–1.31 nm probing depth of the 80\(^\circ\) ARXPS measurements.

ARXPS setups with angles larger than 80\(^\circ\) could probe such "outer surface" as envisioned by the Langmuir principle. This is, however, experimentally extremely challenging due to the required ultrahigh precision of sample positioning and emission angle, minor deviations from the flat-film geometry or surface roughness introducing shadowing effects, and additionally faces the problem of superimposed elastic scattering contributions. Nevertheless, the density profiles obtained by MD simulation can avoid the need of such much more difficult (to impossible) experiments and can be used to probe directly such "outer surface".

Since there is no experimental evidence to anchor the position of the "outer" surface, we have decided to fit a single parameter and apply it to all surfaces. Basically, we used different depths and checked what would be the trend observed for the surface tension along the series calculated using the Langmuir principle. A pseudo 87.5\(^\circ\) setup, which corresponds to probing the surface to a depth in the 0.54–0.93 range (starting at the liftoff) or a depth of just 0.12 nm after the interface midpoint, yielded the correct surface tension trend (cf. Figure 6).

Although this is an empirical fitting to experimental surface tension data, it is important to stress that the concept behind the Langmuir principle has a critical influence on the surface tension trends along the IL series: the decrease of the surface tension values between [C\textsubscript{2}C\textsubscript{1}Im][NTf\textsubscript{2}] and [C\textsubscript{5}C\textsubscript{1}Im][NTf\textsubscript{2}] can be ascribed to the receding presence of the charged layer at the so-called outer layer; the constancy of the values from [C\textsubscript{5}C\textsubscript{1}Im][NTf\textsubscript{2}] onward denotes its absence for the ILs with longer alkyl side chains.

Finally, the match between surface-sensitive experimental results and MD-generated density profiles enables on one hand the validation of the MD models and simulations that allow for obtaining density profiles, and on the other hand the scrutiny at a molecular level of the species contributing to the surface properties in such structurally complex fluids such as ILs.

**CONCLUSION**

The ideas exposed in the formulation of the Langmuir principle almost 90 years ago can be used to assist in the interpretation of surface tension data of ionic liquids and other highly structured fluids. Such use is possible nowadays due to the availability of experimental and simulation techniques that can probe the structure of the free surface of ionic liquids: the combination of angle-resolved X-ray photoelectron spectroscopy experiments and molecular dynamics simulations has allowed for the consistent determination of surface composition. Applying the Langmuir principle of group contributions at the outermost surface in a quantitative way, correct estimation of the complex surface tension trend along the [C\textsubscript{5}C\textsubscript{1}Im][NTf\textsubscript{2}] series could be derived from the molecular dynamic results. We expect that future developments in this line of research will include the renewed application of the Langmuir principle to other ionic liquid systems and their mixtures with molecular solvents.

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**Notes**

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