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Influence of Nanosegregation on the Surface Tension of Fluorinated Ionic Liquids

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Abstract

We have investigated, both theoretically and experimentally, the balance between the presence of alkyl and perfluoroalkyl side chains on the surface organization and surface tension of fluorinated ionic liquids (FILs). A series of ILs composed of 1-alkyl-3-methylimidazolium cations ($[C_nC_{1im}]$ with $n = 2, 4, 6, 8, 10$ or 12) combined with the perfluorobutanesulfonate anion was used. The surface tensions of the investigated liquid salts are considerably lower than those reported for non-fluorinated ionic liquids. The most surprising and striking feature was the identification, for the first time, of a minimum at $n = 8$ in the surface tension *versus* the length of the IL cation alkyl side chain. Supported by molecular dynamic simulations it was found that this trend is a result of the competition between the two nonpolar domains (perfluorinated and aliphatic) on pointing towards the gas-liquid interface, a phenomenon which occurs in ionic liquids with perfluorinated anions. Furthermore, these ionic liquids present the lowest surface entropy reported to date.

Introduction

Recently, fluorinated ionic liquids (FILs) have received an increasing attention in many fields due to their unique properties. They combine the best properties of ionic liquids with those of perfluorocarbons, namely high gas solubility, low surface tension, relatively low vapor pressure, generally high thermal and chemical stabilities and an easy recovery.^{1–3} Literature related to FILs has mainly focused on their synthesis and their application as reaction media.^{4–8} Other reports have mentioned their outperforming application in electrolytes for fuel and solar cells,⁹ in lithium batteries,¹⁰ as well as catalysts¹¹ or liquid crystals for optoelectronic applications.¹²

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For a thoughtful selection of an adequate IL for a particular application, their thermophysical characterization combined with their properties/chemical structures relationship is of key importance. Surface tension is one of the most important properties for the chemical industry and is of vital importance in mass-transfer operations, such as in distillation, extraction, absorption and adsorption. However, consistent and precise measurements of surface tensions of ILs are difficult due to the presence of surface active impurities.^{13–21} General trends on the IL's surface tensions according to the IL chemical structure²², alkyl chain length and cation symmetry²³ have been previously provided and discussed. These papers show that ILs surface tension decreases with the increment in the aliphatic alkyl chain length in the imidazolium cation up to alkyl chain no longer than hexyl where the surface tensions attain an almost constant value.²³

Fluorinated ionic liquids containing fluorinated alkyl chains with at least four carbon atoms can form three nanosegregated domains: one polar and two nonpolar (one aliphatic, the other perfluorinated).²⁴ These domains allow the increase of different conformations, enhancing the diversity of their surfactant behavior.²⁵ Taking into account their particular features, this work aims at expanding the knowledge and understanding of the surface properties of FILs. With this goal in mind, surface tension data of a series of ionic liquids based on the imidazolium cation in presence of a nonpolar fluorinated moiety attached to the sulfonate group ($[C_nC_1im][C_4F_9SO_3]$ with $n = 2, 4, 6, 8, 10$ or 12) at the anion were determined in the (298 to 353) K temperature range and at atmospheric pressure. Moreover, the surface thermodynamic functions were determined and the hypothetical critical temperatures were also estimated by means of the Etövos²⁶ and Guggenheim equations²⁷. Molecular dynamic simulations of these FILs were also performed in order to study the nanoscale structuring and their surface organization aiming at better understanding the uncommon behavior displayed by these compounds.

Experimental Section

Materials

Six fluorinated-based ILs were studied in this work, namely 1-ethyl-3-methylimidazolium perfluorobutanesulfonate, $[C_2C_1im][C_4F_9SO_3]$, > 0.98 mass fraction purity, halides (ion chromatography, IC) < 0.01 molar fraction; 1-hexyl-3-methylimidazolium perfluorobutanesulfonate, $[C_6C_1im][C_4F_9SO_3]$, > 0.99 mass fraction purity, halides (IC) < 0.00025 molar fraction; 1-methyl-3-octylimidazolium perfluorobutanesulfonate, $[C_8C_1im][C_4F_9SO_3]$, > 0.99 mass fraction purity, halides (IC) < 0.00025 molar fraction; and 1-dodecyl-3-methylimidazolium perfluorobutanesulfonate, $[C_{12}C_1im][C_4F_9SO_3]$, > 0.98 mass fraction purity, halides (IC) < 0.01 molar fraction. These ILs were supplied by IoLiTec GmbH and their purity checked by 1H and ^{19}F NMR. 1-Butyl-3-methylimidazolium perfluorobutanesulfonate, $[C_4C_1im][C_4F_9SO_3]$ and 1-decyl-3-methylimidazolium perfluorobutanesulfonate, $[C_{10}C_1im][C_4F_9SO_3]$ were synthesized through the ion exchange resin method. The detailed procedure is described in the Supporting Information (SI). Purity was checked by 1H and ^{19}F NMR as well as by Elemental Analysis. The quantitative integration of their characteristic 1H and ^{19}F NMR resonance peaks reveals the expected cation/anion correlations with the use of an internal standard.

Individual samples of each IL were dried at moderate temperature (~ 323 K) and moderate vacuum (~ 0.1 Pa) under constant stirring, and for a minimum period of 48 h, prior to the measurements, in order to reduce to negligible contents both water and volatile compounds. The water content of each IL, after the drying step and immediately before the measurements, was determined by Karl Fischer titration making use of a Metrohm 831 Karl Fischer coulometer. The water content was less than 100 ppm for all the studied fluorinated ionic liquids. The ILs chemical structures are depicted in Table 1.

Surface Tension

The surface tensions of each IL were determined, in the 298 K - 353 K temperature range, through the analysis of the shape of a pendant drop and measured using a Dataphysics contact angle system OCA-20. Drop volumes of (6 ± 1) μL were obtained using a Hamilton DS 500/GT syringe connected to a Teflon coated needle placed inside an aluminium chamber able to maintain the temperature control within ± 0.1 K. The temperature was attained by circulating water in a double jacketed aluminium cell by means of a Julabo F-25 water bath. The temperature inside the aluminium chamber was measured with a Pt100 probe within ± 0.02 K (placed at a distance of approximately 2 cm of the liquid drop). After reaching a specific temperature, the bubble was formed and the measurements were carried out after 30 min, to guarantee thermal stabilization. Silica gel was placed inside the aluminum closed chamber 8 hours before the surface tension measurements and the cell was kept sealed during all the measurements for a given IL to assure a dry environment. For the surface tensions determination at each temperature, and for each IL, at least six drops were formed and measured. For each drop, an average of 200 images was captured. The analysis of the drop shape was executed with the software module SCA 20 in which the gravitational acceleration and latitude were used according to the location of the assay. Density values required for the calculation of the surface tension were taken from previous works.^{3,28} Densities of the $[\text{C}_4\text{C}_1\text{im}][\text{C}_4\text{F}_9\text{SO}_3]$ and $[\text{C}_{10}\text{C}_1\text{im}][\text{C}_4\text{F}_{10}\text{SO}_3]$ were determined using an automated SVM3000 Anton Paar rotational Stabinger viscometer-densimeter in the (313.15 to 353.15) K temperature range and at atmospheric pressure (≈ 0.1 MPa) and are reported in Table S1 (in the Supporting Information). The absolute uncertainty in density is $\pm (5 \times 10^{-4})$ $\text{g}\cdot\text{cm}^{-3}$, and the relative uncertainty in temperature is within ± 0.02 K. The surface tensions of $[\text{C}_6\text{C}_1\text{im}][\text{C}_4\text{F}_9\text{SO}_3]$ were determined for temperatures above 303 K, while those of $[\text{C}_8\text{C}_1\text{im}][\text{C}_4\text{F}_9\text{SO}_3]$, $[\text{C}_{10}\text{C}_1\text{im}][\text{C}_4\text{F}_9\text{SO}_3]$ and $[\text{C}_{12}\text{C}_1\text{im}][\text{C}_4\text{F}_9\text{SO}_3]$ were determined above 313 K, since below these temperatures these ionic liquids are solid. The melting points of $[\text{C}_4\text{C}_1\text{im}][\text{C}_4\text{F}_9\text{SO}_3]$ and $[\text{C}_{10}\text{C}_1\text{im}][\text{C}_4\text{F}_9\text{SO}_3]$ were determined using a DSC Q200 Differential Scanning Calorimeter from TA Instruments following the procedure previously reported^{3,28} and are reported in Table S2 (in the Supporting Information); the melting temperatures for the remaining ILs were reported in previous works.^{3,28}

Molecular Dynamics (MD) Simulations

The interfacial structure of all ionic liquids studied experimentally was probed using Molecular Dynamics (MD) simulations. The ionic liquids were modeled using the CL&P atomistic force field,²⁹ which is an extension of the AMBER and OPLS force fields³⁰ specially designed to study ionic liquids and their homologous series. MD simulations were carried out using the DL_POLY 2.20 package.³¹ The runs were performed with a 2 fs

timestep 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. The number of ion pairs and the size of the simulation box for all studied ILs are presented in Table S3.

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 $T = 343$ 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. Then, all ionic liquids were re-equilibrated at 298 K for 1.3 ns. 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.²⁸

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 $5.0 \times 5.0 \times 20.0$ nm³ 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 4.0×4.0 nm base and a liquid layer about 10 nm thick. This configuration was then subjected to new (5.0 ns equilibration + 6 ns production at $T = 353$ K) 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. It should be stressed that, in this work, no surface tension results were calculated by MD simulation. Only the surface structure of the ILs is analyzed by MD simulation results.

Results and Discussion

Surface Tension

The surface tensions of each fluorinated-based ionic liquid are presented in Table S4 (see the Supporting Information) and depicted in Figure 1. The measured FILs' surface tension denotes a temperature dependency, commonly observed for ILs.²² The surface tensions of the studied FILs range between 19.49 and 26.35 mN.m⁻¹, presenting values substantially lower than those of other non-fluorinated imidazolium-, pyridinium-, pyrrolidinium-, ammonium- or phosphonium-based ionic liquids.^{22,32} These low values are similar to those presented by long alkyl chain size alkanes, like dodecane (25.58 mN.m⁻¹), tetradecane (26.69 mN.m⁻¹), hexadecane (27.49 mN.m⁻¹), octadecane (28.27 mN.m⁻¹) and eicosane (28.86 mN.m⁻¹)³³ or typical non-ionic organic solvents, e.g. benzene (28.88 mN.m⁻¹), tetrahydrofuran (26.40 mN.m⁻¹), dichloromethane (26.50 mN.m⁻¹), cyclohexane (24.95 mN.m⁻¹) (surface tension values given at a reference temperature of 293 K)^{34,35} and even

aromatic perfluorocarbons, like perfluorobenzene (C_6F_6 , 21.40 mN.m⁻¹) and octafluorotoluene (C_7F_8 , 21.12 mN.m⁻¹) (surface tension values given at a reference temperature of 303 K)¹⁶. On the other hand, these surface tensions are higher than those observed for linear, and cyclic non-aromatic perfluorocarbons, like perfluorohexane (C_6F_{14} , 11.70 mN.m⁻¹), perfluoroheptane (C_7F_{16} , 13.04 mN.m⁻¹), perfluorooctane (C_8F_{18} , 14.10 mN.m⁻¹), perfluorooctane (C_9F_{20} , 14.91 mN.m⁻¹), perfluoro(methylcyclohexane) (C_7F_{14} , 14.54 mN.m⁻¹) and perfluorodecalin ($C_{10}F_{18}$, 18.99 mN.m⁻¹) (surface tension values given at a reference temperature of 303 K)¹⁶. Similar to that observed for perfluorocarbons,¹⁶ the anion fluorination in FILs imposes stronger intramolecular chemical bonds (covalent bonding, the strongest single bond) and weaker van der Waals intermolecular interactions than those of hydrocarbon analogues, imposing thus an important impact on the surface tension of FILs – with FILs displaying in general lower surface tension values than most ILs.²²

For a common temperature, e.g. 313 K, the surface tension of FILs decreases in the following order: $[C_2C_1im][C_4F_9SO_3] > [C_{12}C_1im][C_4F_9SO_3] > [C_4C_1im][C_4F_9SO_3] > [C_{10}C_1im][C_4F_9SO_3] > [C_6C_1im][C_4F_9SO_3] > [C_8C_1im][C_4F_9SO_3]$. The representation of the surface tension at this temperature as a function of the IL cation alkyl side chain is shown in Figure 1b. While the increase of the cation aliphatic alkyl chain size, from ethyl up to octyl, leads to a surface tension decrease, as commonly reported for ionic liquids,^{23,36} further increase of the alkyl chain size induces a trend change, with the surface tension increasing with the increase of the alkyl chain size. The same trend was observed for other temperatures as shown in the Supporting Information (see Figure S1). In fact, a minimum occurs at $n = 8$ (for $[C_8C_1im][C_4F_9SO_3]$), here shown for the first time. This behavior is clearly uncommon, e.g. the surface tensions of R-alkyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ILs ($[C_nC_1im][NTf_2]$ with $n = 1-16$) decrease with the increase in the cation side aliphatic chain length up to $n = 6$ where it reaches a plateau (an almost constant value up to $[C_{16}C_1im][NTf_2]$).²³

Surface tension is a measure of the cohesion of liquids, depending therefore on the liquid structure and orientation of the molecules. It is well established that, for many ILs, both the cation and the anion occupy the same plane at the liquid-gas interface, typically the cations' and/or the anions' aliphatic moieties projecting towards the interface forming a top layer, while the cations' polar head groups and those of the anions form the second layer.³⁷ The ionic liquids herein studied are more complex. In particular, FILs based on the perfluorobutanesulfonate anion are known to be able to form three nanosegregated domains, polar, nonpolar aliphatic, and nonpolar fluorinated.²⁴ This segregation together with the fluorinated chains presenting lower energy than the aliphatic and the surface tensions values on the same range of the perfluorocarbons allows one to envision both the cation and the anion occupying the same plane at the gas-liquid interface but with the perfluorinated chains, instead of the aliphatic, protruding towards the gas phase. This purported surface arrangement changes as the aliphatic imidazolium chain size increases; above an octyl cation alkyl chain size the aliphatic moieties present lower energy than the perfluorobutyl chain and both the aliphatic and perfluorinated chains protrude towards the gas phase. As the aliphatic chains length further increase, and although both structure arrangements may occur at the same time, more aliphatic and less perfluorinated chains position at the gas-liquid interface,

leading to an increase of the surface tension towards non-fluorinated imidazolium ILs values. This interpretation was verified and discussed below – see Molecular Dynamic Simulations and Langmuir Principle sections.

Surface thermodynamic properties

The surface thermodynamic properties, namely the surface entropy and the surface enthalpy, were derived using the quasi-linear dependence of the surface tension with temperature. The surface entropy, S^γ , and the surface enthalpy, H^γ , can be calculated according to:³⁴

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

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

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

The values of the thermodynamic functions of all the ILs investigated are presented in Table 2 and plotted in Figure S2 of Supporting Information. In general, similarly to what was observed for the surface tensions, the studied FILs present lower surface thermodynamic properties than those of non-fluorinated ILs.²² These values reveal an extraordinary surface organization as well as a highly structured liquid phase.²⁴ In respect to the values of the surface thermodynamic properties, the FILs investigated display a similar trend as that of the surface tension with a minimum at about $n = 8$ ([C₈C₁im][C₄F₉SO₃]) (see Figure S2 of Supporting Information). Furthermore, the surface entropy of these FILs are the lowest obtained for ionic liquids (e.g. ILs based on the imidazolium cation have surface entropies of 0.0673 mJ·m⁻²·K⁻¹ for [C₄C₁im]Cl₃₈ or 0.0507 mJ·m⁻²·K⁻¹ for [C₆C₁im]BF₄₃₈, and ILs based on quaternary ammonium cations with the bis(trifluoromethylsulfonyl)imide anion present surface entropies from 0.0713 to 0.0884 mJ·m⁻²·K⁻¹)³⁹. On the other hand, the solubility capacity of an ionic liquid is also governed by its surface tension,^{40,41} and the related surface functions allow us to evaluate this solubility capacity. According to the results obtained, the FILs studied in this work favor high solubility due to their low surface entropy values.^{40,41}

Estimated Critical temperatures

Critical temperatures (T_c) are one of the most important thermophysical properties since they can be used in many corresponding states correlations regarding the equilibrium and transport properties of fluids.⁴² However, the determination of the ILs' critical temperatures is a challenging task since ILs decompose at temperatures below the critical point. Although these values are hypothetical quantities, their usefulness is unquestionable, as originally shown for ILs in a previous work.⁴³ ILs critical temperatures can typically be estimated using the Eötvös²⁶ or Guggenheim²⁷ relations:

$$\gamma \left(\frac{M}{\rho} \right)^{2/3} = K_{\text{Eot}} (T_{\text{c,Eot}} - T) \quad (3)$$

$$\gamma = K_{\text{Gug}} \left(1 - \frac{T}{T_{\text{c,Gug}}} \right)^{11/9} \quad (4)$$

where γ is the surface tension, $T_{\text{c,Eot}}$ or $T_{\text{c,Gug}}$ are the critical temperature, M is the molecular weight, ρ is the density, and K_{Eot} and K_{Gug} are fitted parameters. Both equations are in accord with the thermodynamic restriction that the surface tension becomes null at the critical point and have proven to provide reasonable estimations.^{42,44} In fact, Rai and Maggin⁴⁵ have shown that the critical temperatures extrapolated by either the Eötvös or Guggenheim methods, are in good agreement with those obtained by molecular simulation calculations and, therefore, stand as a viable and simple way of estimation. Nonetheless, since the estimation of critical temperatures uses surface tension data from a limited temperature range it should be highlighted that these critical temperature values (reported in Table 3) must be used with caution. They should be interpreted as semi-quantitative.

Molecular Dynamics (MD) Simulations

Molecular Dynamics simulations were used to probe, from a molecular point of view, the ionic-liquid-vacuum interface of the six members of the $[\text{C}_n\text{C}_{11}\text{im}][\text{C}_4\text{F}_9\text{SO}_3]$ homologous series, with $n = 2, 4, 6, 8, 10$ and 12 , studied in this work. Each system was modeled considering a 8.5 to 12.9 nm-thick slabs of pure ionic liquid limited by two explicit liquid-vacuum boundaries (cf. experimental section for further details). After the equilibration of each slab, the obtained MD trajectories were used to calculate numerical density profile functions of selected ionic liquid atoms along the direction (z) normal to the slab surfaces.

Figure 2 depicts such functions in the vicinity of the surface. The lift-off of the numerical density profiles—from their null values in the vacuum sub-phases to their values in the bulk liquid sub-phase—were used to set the zero of the z axis for each surface, with positive z -values always running towards the vacuum sub-phase. In order to improve statistics, numerical density values at the same z from the two surfaces were averaged and considered together. The four colored lines correspond to the density profiles of four selected atoms present in the ionic liquids: i) the CR carbon atom between the two nitrogen atoms of the imidazolium ring, as the representative of the charged moiety of the cation (blue lines); ii) the SBT atom of the sulfonate group of the anion representing the charged moiety of the anion (red lines); iii) the CTF terminal carbon atom of the perfluorobutyl chain of the anion representing the non-polar perfluorobutyl moiety of the anion (green lines); iv) and the CT terminal carbon atom of the longer alkyl side chain of the cation as a representative of the non-polar alkyl moiety of the cation (gray lines).

In the case of $[\text{C}_2\text{C}_1\text{im}][\text{C}_4\text{F}_9\text{SO}_3]$ (Figure 2a), the terminal CF_3 groups of the perfluorobutyl chains of the anions (green line) are the ones closer to the outer limits of the surface. One also notices huge oscillations of the numerical density profile functions in the vicinity of the surface, up to at least z -values of ca. -1.2 nm. This applies not only to the perfluorobutyl moieties (green line) but also to the polar moieties of the cation (blue line) and anion (red line). Such oscillations are a consequence of the stratification near the surface of the nano-segregated structure (polar versus non-polar domains) of the ionic liquid⁴⁶: the outer layer of the surface, which is mainly composed of perfluorobutyl chains, is followed by an inner polar layer composed of interspersed cation and anion charged moieties. The methyl groups of the very short ethyl chains of the cation (grey line) necessarily occupy positions in the vicinity of that polar layer, with some groups pointing towards the vacuum and others towards the bulk. Interestingly, the polar layer is followed by yet another inner perfluorobutyl-rich layer (conspicuous green line peak around -1 nm) before the smaller oscillations present in the bulk phase become the norm.

When one considers the other members of the $[\text{C}_n\text{C}_1\text{im}][\text{C}_4\text{F}_9\text{SO}_3]$ homologous series (Figures 2b to 2f), the most conspicuous feature is the change of the numerical density profiles of the progressively larger alkyl side chains of the cations (grey lines), with peaks closer and closer to the outer layers of the corresponding surfaces. In fact, somewhere between $[\text{C}_4\text{C}_1\text{im}][\text{C}_4\text{F}_9\text{SO}_3]$ and $[\text{C}_6\text{C}_1\text{im}][\text{C}_4\text{F}_9\text{SO}_3]$, the profile functions suggest that the outermost nonpolar layers start to be dominated by alkyl chains rather than perfluorobutyl ones. Other features also change, namely the fact that the oscillations near the surface of all curves become less pronounced for the larger members of the series. It must also be stressed that the apparent decrease in intensity of all peaks is just a consequence of the decreasing numerical density of each of the selected atoms (CR, SBT, CTF and CT) as the number of other atoms (those present in the alkyl side chains of the cations) are added to the system.

Figure 3 shows snapshots of the simulation boxes with exactly the same length scales of the graphs present in Figure 2. The different atoms were color-coded according to a scheme similar to the lines of Figure 2: red represents the charged moiety of the anion (SO_3CF_2^-); light green the non-polar moiety of the anion ($-\text{CF}_2-\text{CF}_2-\text{CF}_3$); blue the charged moiety of the cation ($\text{CH}_3\text{-im-CH}_2^-$); and gray the non-polar moiety of the cation ($-(\text{CH}_2)_{n-2}-\text{CH}_3$).

Figure 3 shows in a vivid manner the same type of information already present in Figure 2, i.e., as the alkyl side chains of the cations get bigger, the surface starts to be replaced by them, in detriment of the perfluorobutyl chains. Another fact is also discernible in the plots: the polar layer gets further away from the outer regions of the surface due to the presence of the longer alkyl chains. For instance, in $[\text{C}_{12}\text{C}_1\text{im}][\text{C}_4\text{F}_9\text{SO}_3]$ (Figure 3f) one cannot see the presence of red and blue atoms from the charged moieties of the ions in the 1nm-thick tier close to the surface.

The unexpected and non-monotonous trend of the surface tension values obtained in this work can be explained qualitatively by the MD results if one takes into account that the surface tensions of most ionic liquids (especially those without non-polar side chains) are larger than those of molecular solvents with long aliphatic chains, which in turn exhibit larger surface tension values than those of solvents with fluorinated alkyl chains.²²

For $[C_2C_1im][C_4F_9SO_3]$, the MD density profiles show that the surface is basically composed of the fluorinated and polar layers and thus the overall surface tension value can be regarded as the result of contributions from the fluorinated chains and from the polar moieties of both ions present in the ionic liquid. In the $[C_4C_1im][C_4F_9SO_3]$ system, the butyl chains start to replace the polar layer and push it further away from the outer surface. The surface becomes richer in alkyl moieties at the expense of the polar layer but not of the fluorinated one (the latter is the dominant one up to almost the $[C_6C_1im][C_4F_9SO_3]$ system). Consequently, there is a drop in the experimental surface tension values because of the replacement at the surface of groups with the largest contributions to the overall surface tension value (the polar moieties of the ionic liquid ions) by others with smaller values (the alkyl chains). As the alkyl side chains get longer, they will continue to push the polar layer away from the surface but eventually will do the same to the fluorinated moieties. At some point, for the larger members of the $[C_nC_1im][C_4F_9SO_3]$ series, the surface tension values will start to increase due to the replacement at the outer surface of the fluorinated groups (with the smallest contributions to the surface tension) by alkyl groups (with larger contributions).

The Langmuir Principle

The previous arguments can be explored in a semi-quantitative manner if one takes into account the ideas developed by Irwing Langmuir more than 80 years ago⁴⁷. The Langmuir Principle states that the surface tension is “the result of superposition over the molecule parts present at outer surface”. The “molecule parts present at outer surface” can be easily calculated from the numerical density profiles obtained from the MD trajectories, or possibly, by other surface-sensitive experimental methods such as angle-resolved photoelectron spectroscopy (ARXPS)⁴⁸. The missing part is the use of an empirical method to estimate the contributions to the surface tension from those molecule parts, which have to be “superpositioned” in order to obtain the observed surface tension values.

One possibility is to use surface tension to estimate for the different moieties and simply weight them by their composition (e.g. their volume fractions) at the outer surface. In the present case the three moieties to be considered are the ionic liquid without alkyl side chains (either aliphatic or fluorinated), the aliphatic side chains and the perfluorinated side chains.

The ionic liquid $[C_1C_1im][CF_3SO_3]$ can be considered the member of the $[C_nC_1im][C_mF_{2m+1}SO_3]$ homologous series whose side chains are so small that they still belong to the polar moieties of the ions (force-field development studies assisted by ab-initio calculations support this idea²⁹). However, to the best of our knowledge, there are no experimental data for the surface tension of $[C_1C_1im][CF_3SO_3]$. For $[C_2C_1im][CF_3SO_3]$ the value is around 39 mN.m^{-1} at 353 K⁴⁹. If one considers the difference in surface tension when the alkyl side chain in the imidazolium is decreased from C_2 - to C_1 - in other homologous series²², a reasonable value for the surface tension of $[C_1C_1im][CF_3SO_3]$ would be 40 mN.m^{-1} at 353 K. For long aliphatic and fluorinated alkyl chains at the same temperature the surface tension values tend to cluster around 23 and 12 mN.m^{-1} , respectively.⁵⁰ It must be stressed that the values estimated for the different moieties are just

educated-guesses based on available experimental data that try to capture the relative intensity of the contribution of a given moiety to the overall surface tension.

The volume fraction of each moiety at the outer surface layer is calculated in two steps. First, one integrates the numerical density profile functions for each atom representing a moiety between the limit of the surface ($z = 0$) and a stipulated point that marks the thickness of the “outer” surface layer. The representative atoms are CR for the $-C_1C_{1im}$ moiety, SBT for $-CF_2SO_3$, CT for C_{n-1} -, and CTF for C_3F_7 -. The dotted lines in Figures 2 and 3 indicate such limits and correspond to a thickness of 0.4 nm. Such value was set as half of the absolute value of the z -value (0.8 nm) at which the overall numerical density profile within the simulation box starts to deviate from the bulk average numerical density (cf. Figure 4). In other words, the thickness of the “outer” surface layer is just half of the thickness of the “whole” surface. It must also be stressed that we did not consider any additional schemes such as those that take into account the roughness of the surface, which we deem not necessary given the nature of this semi-quantitative approach and its built-in approximations. Second, the atomic numeric fractions thus obtained are converted into moiety volume fractions by taking into account the fact that each of those atoms appears just once in each moiety and that the molar volume of each moiety at 298 K is known from group contribution models^{28,51}.

Table 4 shows the results of the integration preconized in the first step (representative atomic numeric fractions at the outer surface) plus the conversion obtained in the second (moiety volume fractions at the outer surface). It also shows similar results for the bulk (where the representative atomic numeric fractions are 0.25 for each of the four types of atom). The last column of Table 4 combines the composition data with the estimated surface tension contributions of each moiety in order to estimate the overall surface tension for each system.

The results are compared in Figure 5 with the experimental surface tension data. The agreement between the experimental and “surface” sets can be considered excellent given the number of approximations and degrees of freedom inherent to the method. It must be stressed, however, that such agreement can be easily broken if one changes the estimated contributions for the surface tension of the moieties. Nevertheless, the main merit of the present model is to emphasize the fact that the experimental non-monotonous trend found for the surface tension along the $[C_nC_{1im}][C_4F_9SO_3]$ cannot be explained taking into consideration just changes in bulk composition caused by the increase of the alkyl side chains of the cation — cf. the results from the “bulk” set using the same type of approximations. In other words, the distinct and complex surface concentration patterns along the series, as highlighted by the different numerical density profiles obtained by MD, are the real reason behind the unexpected behavior observed for this particular class of ionic liquids.

Conclusions

New experimental data of the surface tension of six fluorinated ionic liquids of the $[C_nC_{1im}][C_4F_9SO_3]$ family in the temperature range from 298 to 353 K at atmospheric pressure were determined using the Pendant Drop method. The studied FILs present, on average, surface

tension values much lower than those reported for non-fluorinated ionic liquids, presenting the lowest surface tension values reported up to date for these types of compounds. FILs also present low surface entropies and surface enthalpies, lower than those of non-fluorinated ILs. This fact denotes a very high surface organization as well as a markedly structured liquid phase.

The most remarkable finding of this work is a well defined concave trend in the surface tension versus the alkyl side chain length in the $[C_nC_{1im}][C_4F_9SO_3]$ series of ILs, showing a minimum for $n = 8$. This unexpected and non-monotonous trend of the surface tension values can be rationalized if one takes into account that the surface tensions of most ionic liquids (especially those without non-polar side chains) are larger than those of molecular solvents with long aliphatic chains, which in turn exhibit larger surface tension values than those of solvents with fluorinated alkyl chains. As one moves from C_2 - to C_{12} -, first the surface is basically composed of the fluorinated and polar layers, then in C_4 - the butyl chains start to replace the polar layer, pushing it further away from the outer surface. As the alkyl side chains get longer, they will continue to push the polar layer away from the surface and they will do the same to the fluorinated moieties. Thus, for the larger members of the $[C_nC_{1im}][C_4F_9SO_3]$ series, the alkyl groups are the predominant ones at the liquid-gas interface.

The simulations results, which reveal the structure and composition of the liquid-gas interface, together with the estimations based on the Langmuir Principle, demonstrate that the competition between aliphatic and fluorinated alkyl chains towards the gas-liquid interface is responsible for the unexpectedly behavior found in these compounds.

Supporting Information

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Surface tension as a function of (a) temperature for the studied ionic liquids and (b) the imidazolium alkyl chain size for the $[\text{C}_n\text{C}_1\text{im}][\text{C}_4\text{F}_9\text{SO}_3]$ series ($n = 2, 4, 6, 8, 10$ and 12) at 313.15 K .

Figure 2.

Numerical density profile functions, ρ , along the direction normal to the slab surfaces, z , of four selected atoms of six ionic liquids of the $[C_nC_1im][C_4F_9SO_3]$ series. Green lines: terminal carbon atom of the perfluorobutyl chain of the anions; blue lines: carbon atom between the two nitrogen atoms of the imidazolium ring of the cations; red lines: sulfur atom of the anions; gray lines: terminal carbon atom of the alkyl side chain of the cations. The region between the dotted lines corresponds to the 0.4 nm-thick outer layers of each surface.

Figure 3.

Simulation snapshots of the liquid-vacuum surface of six ionic liquid slabs of the $[C_nC_1im][C_4F_9SO_3]$ series. Green atoms: non-polar moiety ($-CF_2-CF_2-CF_3$) of the perfluorobutyl chains of the anions; blue atoms: imidazolium rings and adjoining atoms of the cations ($CH_3-im-CH_2-$); red atoms: sulfonyl groups and adjoining atoms (SO_3CF_2-) of the anions; gray atoms: non-polar moiety ($-(CH_2)_{n-2}-CH_3$) of the alkyl side chains of the cations. Length scales and dotted lines as in Figure 2.

Figure 4.

Overall numerical density distribution function, $P(\rho)$, for half slab of $[\text{C}_2\text{C}_1\text{im}][\text{C}_4\text{F}_9\text{SO}_3]$.

The thickness of the surface (between the full vertical lines) is set as the distance between the takeoff of the density distribution function at $z = 0$ nm and the attainment of densities close to the average bulk values at $z = -0.8$ nm. The thickness of the outer layer of the surface (between the dotted vertical lines) was set as half of that distance, 0.4 nm.

Figure 5.

Surface tension values as a function of the alkyl side chain in the $[C_nC_1im][C_4F_9SO_3]$ ionic liquid series. Crosses represent experimental values at 353 K (extrapolated from data in Table S4 of Supporting Information); red circles represent values estimated taking into account the composition of the outer surface layer of each ionic liquid; blue squares represent estimated values taking into account the bulk composition of each ionic liquid.

Table 1

Chemical structure and acronyms of the fluorinated ionic liquids (FILs) used in this work.

FIL Designation	Purification Method	Purity ^e	Water Content ^d	Halides Content	Chemical Structure
1-Ethyl-3-methylimidazolium perfluorobutanesulfonate, [C ₂ C ₁ im][C ₄ F ₉ SO ₃] ^a	Dried under vacuum	0.98 mass fraction ^e	0.0001 mass fraction	< 0.01 molar fraction ^e
1-Butyl-3-methylimidazolium perfluorobutanesulfonate, [C ₄ C ₁ im][C ₄ F ₉ SO ₃] ^b	Rotary evaporator and dried under vacuum	0.99 molar fraction	0.0001 mass fraction	0.0001 molar fraction ^f
1-Hexyl-3-methylimidazolium perfluorobutanesulfonate, [C ₆ C ₁ im][C ₄ F ₉ SO ₃] ^a	Dried under vacuum	0.99 mass fraction ^e	0.0001 mass fraction	< 0.00025 molar fraction ^e
1-Methyl-3-octylimidazolium perfluorobutanesulfonate, [C ₈ C ₁ im][C ₄ F ₉ SO ₃] ^a	Dried under vacuum	0.99 mass fraction ^e	0.0001 mass fraction	< 0.00025 molar fraction ^e
1-Decyl-3-methylimidazolium perfluorobutanesulfonate, [C ₁₀ C ₁ im][C ₄ F ₉ SO ₃] ^b	Rotary evaporator and dried under vacuum	0.99 molar fraction	0.0001 mass fraction	0.0001 molar fraction ^f

FIL Designation	Purification Method	Purity ^c	Water Content ^d	Halides Content	Chemical Structure
1-Dodecyl-1-3-methylimidazolium perfluorobutanesulfonate, [C ₁₂ C ₁ im][C ₄ F ₉ SO ₃] ^a	Dried under vacuum	0,98 mass fraction ^e	0.0001 mass fraction	0,01 molar fraction ^e

^aSupplied by IoLiTec GmbH

^bSynthesized in our lab

^cPurity was determined by NMR

^dWater content was analyzed by Karl Fischer (KF) titration (Metrohm Ion analysis, 831 KF Coulometer)

^eAs stated by the supplier

^fNegative for AgNO₃ testing

Table 2
Surface Thermodynamic Properties of the FILs.

FIL	$10^5 \cdot (S\gamma \pm 0.2)^a / (\text{J} \cdot \text{m}^{-2} \cdot \text{K}^{-1})$	$10^2 \cdot (H\gamma \pm 0.08)^a / (\text{J} \cdot \text{m}^{-2})$
[C ₂ C ₁ im] [(C ₄ F ₉)SO ₃]	4.73	4.00
[C ₄ C ₁ im] [(C ₄ F ₉)SO ₃]	2.99	3.23
[C ₆ C ₁ im] [(C ₄ F ₉)SO ₃]	2.51	2.92
[C ₈ C ₁ im] [(C ₄ F ₉)SO ₃]	2.73	2.92
[C ₁₀ C ₁ im] [(C ₄ F ₉)SO ₃]	2.48	2.99
[C ₁₂ C ₁ im] [(C ₄ F ₉)SO ₃]	4.18	3.66

Table 3
Estimated Critical Temperatures (T_c /K) Using Both the Eötvös (Eot) and the
Guggenheim (Gug) Equations. The expanded uncertainty with an approximately 95%
level of confidence is 100 K.

FIL	$10^{-3} \cdot T_{c, Eot} / (\text{K})$	$10^{-3} \cdot T_{c, Gug} / (\text{K})$
[C ₂ C ₁ im][C ₄ F ₉ SO ₃]	1.01	0.96
[C ₄ C ₁ im][C ₄ F ₉ SO ₃]	1.51	1.25
[C ₆ C ₁ im][C ₄ F ₉ SO ₃]	1.69	1.35
[C ₈ C ₁ im][C ₄ F ₉ SO ₃]	1.44	1.23
[C ₁₀ C ₁ im][C ₄ F ₉ SO ₃]	1.78	1.40
[C ₁₂ C ₁ im][C ₄ F ₉ SO ₃]	1.06	1.00

Table 4
Surface Tension Contributions from the Different Moieties Composing the Ionic Liquid Ions, Surface and Bulk Compositions of Representative Atoms and Ionic Liquid Moieties. The Overall Surface Tensions Are Obtained by Multiplying the Different Moiety Surface Tension Contributions by the Corresponding (Surface or Bulk) Moiety Volume Fractions of Each Ionic Liquid.

[C _n ,C ₁ im][C ₄ F ₉ SO ₃]	Representative Atoms				Ionic Liquid Moieties				Overall Surface Tension
	CR	SBT	CE	CTF	-C ₁ C ₁ im	-CF ₂ SO ₃	C _{n-1} ⁻	C ₃ F ₇ ⁻	
Surface Tension Contribution (mN.m ⁻¹)									
C _n	Surface Atomic Numeric Fraction				Surface Moiety Volume Fraction				mN.m ⁻¹
	40	40	23	12	40	40	23	12	
2	0.14	0.17	0.26	0.43	0.17	0.23	0.07	0.53	24.1
4	0.05	0.10	0.38	0.47	0.06	0.13	0.28	0.54	22.4
6	0.01	0.03	0.55	0.41	0.01	0.04	0.57	0.39	19.5
8	0.00	0.00	0.63	0.37	0.00	0.00	0.72	0.28	20.5
10	0.00	0.00	0.81	0.19	0.00	0.00	0.89	0.11	21.9
12	0.00	0.00	0.88	0.12	0.00	0.00	0.95	0.05	22.4
C _n	Bulk Atomic Numeric Fraction				Bulk Moiety Volume Fraction				mN.m ⁻¹
	40	40	23	12	40	40	23	12	
2	0.25	0.25	0.25	0.25	0.31	0.33	0.06	0.30	30.7
4	0.25	0.25	0.25	0.25	0.27	0.29	0.17	0.26	29.8
6	0.25	0.25	0.25	0.25	0.25	0.26	0.25	0.23	29.1
8	0.25	0.25	0.25	0.25	0.22	0.24	0.32	0.21	28.5
10	0.25	0.25	0.25	0.25	0.20	0.22	0.38	0.20	28.1
12	0.25	0.25	0.25	0.25	0.19	0.20	0.43	0.18	27.7