Ionic Liquids



Influence of Substituents and Functional Groups on the Surface Composition of Ionic Liquids

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Abstract: We have performed a systematic study addressing the surface behavior of a variety of functionalized and nonfunctionalized ionic liquids (ILs). From angle-resolved X-ray photoelectron spectroscopy, detailed conclusions on the surface enrichment of the functional groups and the molecular orientation of the cations and anions is derived. The systems include imidazolium-based ILs methylated at the C2 position, a phenyl-functionalized IL, an alkoxysilane-functional-

Introduction

lonic liquids (ILs) are molten salts with a melting point below 100 °C. The enormous variety of cation–anion combinations (some authors speak of > 10¹⁸ possibilities^[1]) enables tuning of the physico-chemical properties of ILs over a wide range. Functional groups can be introduced into the chemical structure to adapt ILs for specific tasks, for example, the capture of CO₂ from flue gas by amine-functionalized ILs,^[2,3] or the modification of silica supports by reaction with silyl-functionalized ILs.^[4] Such functionalized ILs are known as "task-specific ionic liquids" and they are used in a variety of applications, ranging from catalysis and organic synthesis to extraction and dissolution processes.^[5]

In many applications, the interface of the IL with its environment (gas, liquid, solid) plays an important role. Therefore, knowledge about interface properties, like surface composition and surface tension, and their relation to the chemical structure is of pivotal importance for choosing the right IL for a specific application. Owing to the break in symmetry at the interface, the chemical composition of and the molecular arrange-

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ized IL, halo-functionalized ILs, thioether-functionalized ILs, and amine-functionalized ILs. The results are compared with the results for corresponding non-functionalized ILs where available. Generally, enrichment of the functional group at the surface is only observed for systems that have very weak interaction between the functional group and the ionic head groups.

ment at the interface will be different from that in the bulk. Various surface-sensitive methods under ambient pressure and under ultra-high vacuum (UHV) conditions have been employed to study the gas/IL interface (see refs. [6,7] and references therein). The majority of these studies mainly focused on non-functionalized ILs. Consequently, the knowledge about the influence of functional groups on the surface composition is still scarce.^[8-18] For non-functionalized ILs with long alkyl chains (e.g., $[C_nC_1Im]^+$ systems ($n \ge 4$, Im = imidazolium)), a common consensus has been reached concerning the molecular arrangement at the surface: the ILs are oriented with the alkyl chains sticking out towards the gas phase, forming an aliphatic overlayer above a more polar sublayer, which consists of the cationic and anionic head groups.^[6] Introducing a functional group at the terminal position of the alkyl chain leads to increased surface tension as was shown by Tariq et al. in a comprehensive review of the surface tensions of ILs. They suggested that the functional group interacts with the polar sublayer and thereby disrupts the aliphatic overlayer, an interaction that results in the observed higher surface tension.^[19] However, one should abstain from drawing general conclusions from this study alone as the nature of the functional group and of the cationic and anionic head groups strongly influence their intraand intermolecular interactions. For instance, a concomitant vibrational sum frequency spectroscopy (VSFS) and neutral impact collision ion scattering spectroscopy (NICISS) study of ethanolammonium nitrate (EtAN) showed that the hydroxy group and the ammonium head group lie below the methylene groups at the outer surface.^[10,11] However, when introducing the hydroxyethyl chain into an imidazolium-based IL, namely 1-(2-hydroxyethyl)-3-methylimidazolium tetrafluoroborate ([$(HOC_2H_4)C_1Im$][BF₄]), the hydroxy group is found at the outermost position at the surface, as was shown by molecular

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dynamic simulations (MDS)^[9] and angle-resolved X-ray photoelectron spectroscopy (ARXPS).^[8]

From these few studies, it is evident that at the moment no general conclusions can be drawn and no prediction can be made concerning the molecular arrangement of a particular cation or anion in a specific ionic liquid. Therefore, we have performed a systematic study addressing the surface behavior of a variety of functionalized and also some non-functionalized ILs. Table 1 provides an overview of the studied systems, which include imidazolium-based ILs methylated at the C2 position,

Table 1. Summary of ILs investigated in this study.				
Abbreviation	Structure	IUPAC-Name	Spectra in	
[C₄C₁lm][TfO]	$N_{\odot}^{(\odot)}N$ $F_3C-SO_3^{\Theta}$	1-butyl-3-methylimidazolium trifluoromethylsulfonate	Figure 1	
[C ₈ C ₁ Im]Br	N → N → Br ^Θ	1-methyl-3-octylimidazolium bromide	Figure 1	
[C ₈ C ₁ Im][TfO]	$N_{\odot}^{(0)}N_{\odot}$	1-methyl-3-octylimidazolium trifluoromethylsulfonate	Figure 1	
$[C_8C_1Im][Tf_2N]$	$\begin{array}{c} \overbrace{\overset{()}{\oplus}}^{F_3C, \bigcirc 0} \\ \overbrace{\overset{()}{\oplus}}^{F_3C, \bigcirc 0} \\ - \end{array} \xrightarrow{\begin{array}{c} F_3C, \bigcirc 0}^{F_3C, \bigcirc 0} \\ \overbrace{\overset{()}{\oplus}}^{F_3C, \frown 0} \\ \overbrace{\overset{()}{\oplus}}^{F_3C, \frown 0} \\ \overbrace{\overset{()}{\oplus}}^{F_3C, \frown 0} \\ \overbrace{\overset{()}{\oplus}}^{F_3C, \frown 0} \\ \overbrace{\overset{()}{\frown}}^{F_3C, \frown 0} \\ \overbrace{\overset{()}{\frown}^{F_3C, \frown 0} \\ \overbrace{\overset{()}{\frown}}^{F_3C, \frown 0} \\ \overbrace{\overset{()}{\frown}}^{F_3C, \frown 0} \\ \overbrace{\overset{()}{\frown}} \\ \overbrace{\overset{()}{\frown}}^{F_3C, \frown 0} \\ \overbrace{\overset{()}{\frown}} \\ \overbrace{\overset{()}{\frown}} \\ \overbrace{\overset{()}{\frown}} \\ \overbrace{\overbrace{\overset{()}{\frown}} \\ \odot 0} \\ \overbrace{\overbrace{\overset{()}{\frown}} \\ \overbrace{\overbrace{\overset{()}{\frown}} \\ \overbrace{\overbrace{\overset{()}{\frown}} \\ \odot 0} \\ \overbrace{\overbrace{\overset{()}{\frown}} \\ \odot 0} \\ \overbrace{\overbrace{\overbrace{\overset{()}{\frown}} \\ \odot 0} \\ \overbrace{\overbrace{\overbrace{\underset{()}{\frown}} } \\ \overbrace{\overbrace{\underset{()}{\frown}} \\ \overbrace 0} \\ \overbrace{\overbrace{\underset{()}{\frown}} \\ \overbrace{\overbrace{\underset{()}{\frown}} \\ \overbrace 0} \\ \overbrace{\overbrace{\underset{()}{\frown}} \\ \odot 0} \\ \overbrace{\overbrace{\underset{()}{\frown}} \\ \overbrace 0} \\ \overbrace{\overbrace{\underset{()}{\frown}} \\ \overbrace 0} \\ \overbrace{\underset{($	1-methyl-3-octylimidazolium bis[(trifluoromethyl)sulfonyl]imide	Figure 1	
$[C_4C_1C_1Im][TfO]$	$F_3C-SO_3^{\ominus}$	1-butyl-2,3-dimethylimidazolium trifluoromethylsulfonate	Figure 1	
[C ₈ C ₁ C ₁ Im]Br	, N, ⊕, N, → Br ^O	1,2-dimethyl-3-octylimidazolium bromide	Figure 1	
[C ₈ C ₁ C ₁ Im][TfO]	$\mathbb{N}_{\mathbb{Q}}^{\mathbb{Q}}$ $\mathbb{N}_{\mathbb{Q}}^{\mathbb{Q}}$ $\mathbb{N}_{\mathbb{Q}}^{\mathbb{Q}}$ $\mathbb{P}_{3}C-SO_{3}^{\mathbb{Q}}$	1,2-dimethyl-3-octylimidazolium trifluoromethylsulfonate	Figure 1	
$[C_8C_1C_1Im][Tf_2N]$	$\begin{array}{c} \overbrace{\begin{subarray}{c} \mathbb{N} \\ \mathbb$	1,2-dimethyl-3-octylimidazolium bis[(trifluoromethyl)sulfonyl]imide	Figure 1	
[(PhC ₃ H ₆)C ₁ Im][Tf ₂ N]	$\begin{array}{c} \overbrace{N}^{\nearrow} \\ \searrow \\ N \\ \swarrow \\ N \\ \swarrow \\ N \\ N$	1-methyl-3-(3-phenyl-propyl)imidazolium bis[(trifluoromethyl)- sulfonyl]imide	Figure 2	
$[((EtO)_3SiC_3H_6)C_1Im]CI$	N.⊕ N. OEt Si-OEt OEt_	1-methyl-3-(3-triethoxysilanepropyl)-imidazolium chloride	Figure 3	
$[(C_4F_9C_2H_4)C_1Im]I$	N N F F F F I ^Θ F F F F F	1-methyl-3-(3,3,4,4,5,5,6,6,6-nonafluorohexyl)imidazolium iodide	Figure 4	
$[C_{12}C_1Im][FC_4H_8SO_3]$	$P^{SO_3^{\Theta}}$	1-dodecyl-3-methylimidazolium 4-fluorobutylsulfonate	Figure 5	
$[C_2C_1Im][CIC_4H_8SO_3]$	N N CI SO3 [☉]	1-ethyl-3-methylimidazolium 4-chlorobutylsulfonate	Figure 6	
$[C_8C_1Im][CIC_4H_8SO_3]$		⁹ 1-methyl-3-octylimidazolium 4-chlorobutylsulfonate	Figure 6	
$[(CIC_2H_4)C_1C_1Im][TfO]$		1,2-dimethyl-3-(2-chloroethyl)imidazolium trifluoromethylsulfonate	Figure S1	
$[(BrC_2H_4)C_1Im][Tf_2N]$	$ \begin{array}{c} \overbrace{N}^{(1)} \\ \times \\ N \end{array} \\ N \end{array} \\ N \end{array} \\ Br \begin{array}{c} F_3C \\ S \\ O \end{array} \\ S \\ O \end{array} \\ \begin{array}{c} O \\ S \\ O \end{array} \\ O \\ O \end{array} \\ O \\ O \end{array} \\ O \\ O \\ O \end{array} $	1-(2-bromoethyl)-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]- imide	Figure S2	
$[(IC_2H_4)C_1Im][Tf_2N]$	$\begin{array}{c} \overbrace{N}^{\overbrace{(\bigcirc)}} N & F_3C, \overset{O}{\overset{O}} \overset{O}{\overset{O}}} \overset{O}{\overset{O}} \overset{O} \overset{O}} \overset{O} \overset{O} {\overset{O}} \overset{O}} \overset{O} {O$	1-(2-iodoethyl)-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]- imide	Figure S3	
[Me(EG) ₂ C ₁ Im][Tf ₂ N]	$N \xrightarrow{(0)}{\mathbb{N}} N \xrightarrow{(0)}{\mathbb{N}} O \xrightarrow{(0)}{\mathbb{N}} F_3 C \xrightarrow{(0)}{\mathbb{N}} \xrightarrow{(0)}{\mathbb{N}} C F_3 C \xrightarrow{(0)}{\mathbb{N}} \xrightarrow{(0)}{\mathbb{N}} O \xrightarrow{(0)}{\mathbb{N}$	1-[2-(2-methoxy-ethoxy)ethyl]-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide	in text only	
[(MeSC ₂ H ₄)C ₁ Im][Tf ₂ N]	\sim F_3C S N CF_3	1-methyl-3-(2-methylthio)-ethylimidazolium bis[(trifluoromethyl)- sulfonyl]imide	Figure 7	
[C ₂ C ₁ (MeS)Im][Tf ₂ N]	$ \begin{array}{c} & \bigwedge \\ & \bigwedge \\ & \bigwedge \\ & & \bigwedge \\ & & \\ & & \\ & \\$	1-ethyl-3-methyl-2-methylthioimidazolium bis[(trifluoromethyl)- sulfonyl]imide	Figure S4	
$[(Me_2NC_3H_6)C_1Im][TfO]$	$N_{\odot}^{(\odot)}N_{\odot}$ N_{\odot} $F_{3}C-SO_{3}^{\odot}$ Bu $C_{2}E_{2}$	1-methyl-3-(3-dimethylaminopropyl)imidazolium trifluoromethyl- sulfonate	Figure 8	
[(Me ₂ NC ₃ H ₆)PBu ₃][FAP]	$\begin{array}{c} Bu \to Bu \to Bu \to N \to Bu \to N \to Su \to \mathsf$	(3-dimethylaminopropyl)tributylphosphonium tris(pentafluoroethyl)- trifluorophosphate	Figure 8	
$[(HOC_2H_4)_2Me_2N]$ $[H_2NC_2H_4SO_3]$	$ \overset{\text{\tiny (P)}}{} \overset{\text{\tiny (OH)}}{} \overset{\text{\tiny (P)}}{} $	di(2-hydroxoethyl)-dimethyl-ammonium 2-aminoethylsulfonate	Figure 9	

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a phenyl-functionalized IL, an alkoxysilane-functionalized IL, halo-functionalized ILs, thioether-functionalized ILs, and aminefunctionalized ILs. In addition, results for corresponding nonfunctionalized ILs are recapitulated for comparison, if necessary. In each case, ARXPS is used to study the chemical composition and the molecular arrangement at the IL/vacuum interface. XP spectra of the relevant core levels are measured at two emission angles. At 0° (with respect to the surface normal), information about the first 7-9 nm of the surface is obtained, whereas at 80° only the outermost IL layers with an information depth of 1-1.5 nm are probed. Thus, a visual comparison of the 0° and 80° measurements provides direct information on orientation and/or enrichment of molecules at the surface. A preferential increase/decrease in core-level intensity with increasing emission angle indicates a higher/lower concentration of this element in the outermost layers compared with the bulk.

Results and Discussion

Methylation of C2 position of imidazolium systems $([C_nC_1Im]^+ \text{ vs. } [C_nC_1C_1Im]^+)$

One efficient way to modify the physical properties of imidazolium-based ILs is the methylation of the C2 position of imidazolium cations. Comparison with the non-methylated systems

shows that the C2 methylation increases melting point and viscosity of the IL, whereas density, conductivity, and polarity are decreased.^[21-24] The impact of C2 methylation on the surface tension was studied by Freire et al.^[25] and Yoshida et al.^[23] Both groups found lower surface tension for the non-methylated system than for the methylated one. Based on the observed change of the surface tension, we also expect a change in the chemical composition of the outer surface. To systematically study the effect of the C2 methylation on the surface composition, we used ARXPS to investigate ILs with anions of different size and ILs with the same anion, but with different alkyl chain lengths. We compare the C1s spectra of $[C_8C_1C_1Im]Br$, $[C_8C_1C_1Im][TfO]$, $[C_8C_1C_1Im][Tf_2N]$, and $[C_4C_1C_1Im][TfO]$ in 0° and 80° emission, with the C1s spectra of the respective non-methylated systems. As [C₈C₁C₁Im]Br and [C₈C₁C₁Im][TfO] are solid at room temperature, all spectra shown in Figure 1 were measured at 350 K to rule out possible temperature effects.^[26] To allow for a visual comparison of the different systems, all spectra were normalized to the N1s signal of [C₈C₁Im]Br in 0° emission and the binding energy was referenced to the $\mathsf{C}_{\mathsf{alkyl}}$ signal at 285.0 eV. The Calkyl signal stems from all carbon atoms of the alkyl (octyl or butyl) chain that are solely bound to carbon or hydrogen atoms. The carbon atoms of the imidazolium head group, atoms that are bound to at least one nitrogen atom, are combined in a signal at approximately 286.5 eV (denoted as C_{hetero}). For the [TfO]⁻- and [Tf₂N]⁻-based ILs, an additional



Figure 1. C 1s spectra of $[C_nC_1\text{Im}]X$ (black) and $[C_nC_1C_1\text{Im}]X$ (red) systems in 0° (top) and 80° (bottom) emission at 350 K. Difference spectra ($[C_nC_1\text{Im}]X - [C_nC_1\text{Im}]X$) are depicted in blue. From left to right: n=8, $X=Br^-$; n=8, $X=[TfO]^-$; n=4, $X=[TfO]^-$. To enable a visual comparison, the spectra were normalized to the N1s signal area of the imidazolium nitrogen atoms and referenced to the C_{alkyl} signal at 285.0 eV. At the top of the figure, the chemical structure of the $[C_8C_1C_1\text{Im}]^+$ cation including the atom assignment is shown.

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peak (not shown) at approximately 292.5 eV is observed, which is attributed to the CF_3 group of the anion.

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At 0° emission, all $[C_nC_1C_1Im]^+$ systems display an increased C1s signal area compared with the respective $[C_nC_1Im]^+$ systems owing to the additional carbon atom. By subtracting the C1s spectrum of the $[C_nC_1Im]^+$ system from the C1s spectrum of the $[C_nC_1C_1Im]^+$ system, difference spectra are obtained, which are also depicted in Figure 1. All difference spectra show a peak at approximately 286 eV, which is attributed to the additional methyl group of the $[C_nC_1C_1Im]^+$ cation. The areas of these peaks fit well (\pm 15%) with the intensity expected for one carbon atom. The minimum at the higher binding energy side of the difference spectra is attributed to the different electronic structure of the imidazolium ring of the $[C_nC_1C_1Im]^+$ systems compared with the $[C_nC_1Im]^+$ systems. The signal of the C2 carbon is shifted slightly towards higher binding energies, and the C1s signals of C4 and C5 carbon atoms as well as the N1s signal of the imidazolium nitrogen atom (not shown) are shifted towards lower binding energies (see also ref. [27]).

As already discussed, the alkyl chains of imidazolium cations at the surface in $[C_nC_1Im]^+$ systems ($n \ge 4$) tend to orientate themselves towards the vacuum, a trend that is reflected by an increase in the C_{alkyl} signal intensity in 80° emission. The comparison of the 80° spectra of the $[C_nC_1Im]^+$ and $[C_nC_1C_1Im]^+$ systems in Figure 1 shows a very similar increase in the Calkyl signal, suggesting a comparable alkyl enrichment for both systems. To verify that the differences in the spectra are indeed only due to the additional carbon atom in the $[C_nC_1C_1Im]^+$ systems, we also show difference spectra for 80° emission in Figure 1. The analysis of these spectra shows that the difference for each IL is a single peak at 286 eV that is due to the additional carbon atom, with only negligible changes in the position of the Calkyl peak at 285 eV. Interestingly, for all systems, the peak at 80° resulting from the additional carbon atom at approximately 286 eV is somewhat larger than that at 0°. This indicates that the methyl group at the C2 atom is preferentially orientated towards the vacuum, an observation that is in line with the ARXPS study by Lockett et al., who postulated the same surface orientation for [C₄C₁C₁Im][BF₄].^[8] This orientation effect is most distinct for $[C_8C_1C_1Im]Br$. It is attributed to the low molecular volume and the spherical shape of the bromide counterion in comparison to the bigger and more elongated $[TfO]^-$ and $[Tf_2N]^-$ anions.

Phenyl-functionalized IL

The influence of a phenyl-functionalized side chain on the surface orientation of imidazolium cations was investigated by comparing ARXPS measurements of $[(PhC_3H_6)C_1Im][Tf_2N]$ and $[C_8C_1Im][Tf_2N]$. In Figure 2 (left column), the corresponding C 1s, N 1s, and F 1s spectra at 0° emission are depicted in red ($[(PhC_3H_6)C_1Im][Tf_2N]$) and black ($[C_8C_1Im][Tf_2N]$). In the N 1s region, two peaks are observed at 402.2 and 399.6 eV, which originate from the two nitrogen atoms of the imidazolium ring (N_{Im}) and the nitrogen atom of the $[Tf_2N]^-$ anion (N_{Tf_2N}), respectively. For $[C_8C_1Im][Tf_2N]$, the peak assignment in the C 1s region has already been mentioned: the three peaks at 293.1,



Figure 2. C 1s, N 1s, and F 1s spectra of $[C_8C_1Im][Tf_2N]$ (black) and $[(PhC_3H_6)C_1Im][Tf_2N]$ (red), in 0° (left) and 80° (right) emission. Grey dashed lines are added as guides to the eye. At the top of the figure, the chemical structure of $[(PhC_3H_6)C_1Im][Tf_2N]$ is shown.

287.1, and 285.2 eV are assigned to the two carbon atoms of the $[Tf_2N]^-$ anion (C_{CF_3}) , the five carbon atoms with nitrogen atoms as their neighbor (C_{hetero}), and the seven carbon atoms of the alkyl chain (C_{alkyl}), respectively. For [(PhC_3H_6) C_1Im][Tf_2N], the C1s peak at 285.1 eV is assigned to the phenyl-functionalized side chain (labeled C_{phenyl}). Within the margin of error, this binding energy matches the value for the Calkyl signal (285.2 eV) of [C₈C₁Im][Tf₂N], a fact that indicates that the differences in C1s binding energy resulting from the different hybridization of alkyl and phenyl carbon atoms, are below the resolution of our apparatus. Interestingly, the intensity of the signal at approximately 285.1 eV is identical for both ILs, although the phenyl-functionalized side chain contains one additional carbon atom. This behavior is attributed to the fact that for phenyl rings, intensity of the main C1s peak is transferred to a $\pi \rightarrow \pi^*$ shake-up satellite at approximately 291.7 eV (denoted as C_{sat} in Figure 2).^[28] Similar shake-up satellites are also observed for the imidazolium ring, but are removed from the spectra by the subtraction of a three-point linear background. The binding energies and intensities of all other XPS signals of $[(PhC_3H_6)C_1Im][Tf_2N]$ match those of $[C_8C_1Im][Tf_2N]$, indicating that the phenyl group has no influence on the core levels of the imidazolium ring and the anion.



Information on the surface orientation can be derived from the 80° emission spectra of $[C_8C_1Im][Tf_2N]$ and $[(PhC_3H_6)C_1Im]$ -[Tf₂N] shown in Figure 2 (right column). To enable a visual comparison with the 0° emission spectra, the 80° emission spectra were multiplied by an empirical factor (see Experimental Section), and grey dashed horizontal lines were added as guides for the eye. For $[C_8C_1Im][Tf_2N]$, the increase of the C_{alkvl} intensity at 80° (compared with 0°), and the simultaneous decrease of all other XPS signals reflect the previously reported surface enrichment of alkyl chains, which form a non-polar layer above the imidazolium rings and the anions. In contrast, for $[(PhC_3H_6)C_1Im][Tf_2N]$, the C_{phenyl} signal shows only a minor increase at 80°. Despite this weak increase, the signals of the imidazolium ring (C_{hetero} and N_{Im}) decrease in the 80° emission spectra by ~10%, indicating that the phenyl groups are on average closer to the outer surface than the imidazolium rings. Analysis of the [Tf₂N]⁻ anion signals shows an increase in the F1s peak and a decrease in the O1s peak (not shown) at 80° compared with 0° , whereas the intensities of $N_{Tf,N}$, $C_{CF,\gamma}$ and S2p (not shown) stay constant. This behavior indicates that the $[Tf_2N]^-$ anion orientates itself at the surface with its CF_3 groups pointing towards the vacuum and the SO₂ groups pointing towards the bulk, an observation in agreement with conclusions based upon Rutherford backscattering experiments. $^{\mbox{\tiny [29]}}$ As both the $C_{\mbox{\tiny phenyl}}$ and the F1s signal show a similar increase in intensity (by approximately 7%) on going from 0° to 80° , we propose that the phenyl rings and the CF₃ groups lie next to each other at the outer surface; this contrasts with the situation for [C₈C₁Im][Tf₂N] where the alkyl chains lie above the CF₃ groups.

The different surface orientations of $[(PhC_3H_6)C_1lm]^+$ and $[C_8C_1lm]^+$ cations can be explained by the different interaction of alkyl and phenyl groups with the imidazolium rings and the anions. Owing to the non-polar nature of alkyl chains, $[C_nC_1lm]^+$ -based ILs with $n \ge 4$ form a heterogeneous structure in the bulk, with the alkyl chains segregating into non-polar regions, while the imidazolium rings and the anions form more polar regions.^[30,31] In contrast, the quadrupole moment of phenyl groups promotes their interaction with the anions and cationic head groups. This is concluded from molecular dynamic simulations as well as X-ray crystallography and neutron diffraction experiments on IL-benzene mixtures, the results of which showed that the anions prefer an equatorial position around benzene, whereas the imidazolium cations lie below or above the benzene ring.^[32-36]

Alkoxysilane-functionalized IL [((EtO)₃SiC₃H₆)C₁Im]Cl

In Figure 3, the XP spectra of the alkoxysilane-functionalized IL [((EtO)₃SiC₃H₆)C₁Im]Cl are depicted for both emission angles, 0° (black) and 80° (green). In the Si2p, O1s, N1s, and Cl2p regions, only one signal is observed, as expected from the structure of the IL. Note that the Si2p and the Cl2p levels are spinorbit split; for the Si2p level, the splitting is not resolved, whereas it is clearly seen for the Cl2p level, with the expected intensity ratio of 1:2 for the $2p_{1/2}$ and $2p_{3/2}$ components. In the C1s region, the signals of the different carbon environments of



Figure 3. Si2p, O1s, C1s, N1s, and Cl2p spectra of $[((EtO)_3SiC_3H_6)C_1Im]CI$ in 0° (black) and 80° emission (green), and the chemical structure of the IL.

the IL are superimposed. To simplify the analysis, the signal is treated as the superposition of two peaks, similar to the non-functionalized $[C_nC_1Im]^+$ systems. The C1s peak at 286.5 eV (C_{hetero}) contains the carbon atoms bound to nitrogen or oxygen atoms; all other carbon atoms, that is, those bound to only carbon or to silicon atoms, contribute to the peak at 284.9 eV ($C_{alk,SI}$). The quantitative analysis of the 0° emission matches the nominal atom ratio within the margin of error of $\pm 5\%$, confirming this assignment and also the purity of the IL.

Information on the orientation of the IL at the outer surface is obtained from the 80° emission spectra. The imidazolium N1s signals and the anion Cl2p signal show the most pronounced changes: both decrease when going from 0° to 80° emission, an observation that indicates a loss of atom density in these species at the outer surface compared with the bulk. The larger decrease for the N1s signal (to ~65% of the intensity at 0°) than for the Cl2p signal (to ~75%) indicates a larger mean distance from the imidazolium ring to the outer surface than from the chloride anion to the surface; in other words, the anion lies slightly above the imidazolium ring. On the other hand, the Si2p and O1s signals from the triethoxysilane group gain intensity at 80°, indicating an enrichment of the functionalized chain at the outer surface. This preferential surface orientation of the IL cation is also reflected in the C1s spectra: the Chetero signal predominantly stems from the imidazolium ring (5 out of 8 atoms), whereas the CalkSi signal originates solely from the functionalized chain. On going from 0° to 80° emission, the $C_{alk,Si}$ signal increases and the C_{hetero} signal



decreases in intensity, an observation that confirms that the functionalized chains point towards the vacuum, whereas the imidazolium rings lie below.

These observations are in line with the reported high surface activity of polysiloxanes. Marginal polysiloxane contamination can be detected at the outer surface of an IL, even for bulk concentrations below the detection limit of NMR spectroscopy.^[14, 37-39] A contamination with such surface-active substances may impose huge problems for all interface-related processes as they modify the surface properties, often in an uncontrolled way. However, we can also take advantage of the surface activity of alkoxysilanes and siloxanes. For example, catalysts and other substances could be placed preferentially at the surface/interface of an ionic liquid medium by introducing these groups into their chemical structure.

Halo-functionalized ILs

Perfluorinated alkyl compounds are known for their surface activity in aqueous^[40,41] and in IL systems.^[42–45] The very rigid and non-coordinating C-F bonds lead to very weak dispersive intermolecular interactions between the perfluorinated alkyl chains and, therefore, perfluorinated systems are energetically unfavored in the bulk.^[46] In a molecular dynamics simulation study of the perfluorinated system $[(C_nF_{2n+1}C_2H_4)C_1Im][Tf_2N]$ with n = 2-6, Smith et al. showed that the perfluorinated ILs form a heterogeneous structure in the bulk similar to that of their non-perfluorinated analogues ([C_nC₁Im][Tf₂N]).^[47] Thereby, the perfluoroalkyl chains tend to stick together in a non-polar region, whereas the surrounding polar region consists of the cationic head groups and the anions.^[47] Therefore, we expect that perfluorinated alkyl chains are also enriched at the outer surface of the IL, similar to the $[C_nC_1Im]^+$ systems. To verify this we investigated the perfluorinated assumption, IL $[(C_4F_9C_2H_4)C_1Im]I$ and the fluoro-functionalized IL $[C_{12}C_1Im]$ - $[FC_4H_8SO_3].$

In Figure 4, the ARXP spectra of $[(C_4F_9C_2H_4)C_1Im]I$ are depicted. The spectra were taken at a temperature of approximately 355 K to ensure the sample was liquid and to evaporate residual 1-iodo-1H,1H,2H,2H-perfluorohexane, which was used as a starting material in the IL synthesis. The quantitative analysis of the 0° emission spectra (black spectra in Figure 4) matches the nominal atom ratio to within the margin of error, indicating the high purity of the IL. In the C1s region, three signals are observed: the peaks at 291.7 and 294.1 eV are attributed to the CF₂ and CF₃ groups, respectively. All other carbon atoms contribute to the peak at 286.7 eV (C_{hetero}). By changing from 0° to 80°, the F1s and the C_{CF_x} signals increase in intensity, whereas the C_{hetero} , N1s, and $13d_{5/2}$ signals decrease. This behavior unequivocally demonstrates the enrichment of the perfluorinated chains at the outer surface, whereas the imidazolium ring and the iodide anion lie below. The identical decrease of the N1s and 13d_{5/2} peaks at 80° indicates that the imidazolium rings and the anions have the same mean distance to the outer surface.

In contrast to the perfluorinated IL, the surface enrichment of the fluoro-terminated chain of the fluoro-functionalized IL



Figure 4. C 1s, N 1s, F 1s, and 13d_{5/2} spectra of $[(C_4F_9C_2H_4)C_1Im]I$ in 0° (black) and 80° emission (green) taken at approximately 355 K. At the top of the figure, the chemical structure of the IL is shown.

 $[C_{12}C_1 Im][FC_4H_8SO_3]$ is not as obvious. In Figure 5, the C1s, F1s, N1s, and O1s spectra are depicted. The quantitative analysis of the 0° spectra (black) confirms the purity of the sample. Interestingly, on going from 0° to 80° emission, a slight decrease in



Figure 5. C1s, F1s, N1s, and O1s spectra of $[C_{12}C_1 \text{Im}][FC_4\text{H}_8\text{SO}_3]$ in 0° (black) and 80° emission (green). At the top of the figure, the chemical structure of the IL is shown.



the F1s intensity is observed instead of the increase expected from surface enrichment. This can be explained by the surface orientation of the [C₁₂C₁Im]⁺ cation. As already discussed, alkyl chains tend to stick out towards the vacuum. This is also the case here, as can be seen from the increase in the Calkyl signal at 80°. Because of this alkyl enrichment, all other signals are damped. The degree of damping indicates the mean distance of the species to the outer surface. At 80° emission, the imidazolium N1s signal and the O1s signal from the SO₃ group of the anion both decrease to approximately 59% of their 0° emission intensity. At the same time, the F1s signal only decreases to about 89%. This indicates that the cationic and anionic head groups have the same mean distance to the outer surface and that the fluorobutyl chain points towards the vacuum. Despite this orientation, the F1s signal experiences a slight decrease at 80° because the functionalized chain is shorter than the alkyl chain and thus the F atoms at the end of the chain are not at the outer surface. The results for $[(C_4F_9C_2H_4)C_1Im]I$ and $[C_{12}C_1Im][FC_4H_8SO_3]$ show that the preferred surface orientation of the fluorinated chains towards the vacuum is independent of the charge of the head group, that is, it occurs for both functionalized cations and functionalized anions.

As the next step, we addressed the effect of the counter ion on the degree of surface ordering. We compared two ILs with the same functionalized 4-chlorobutylsulfonate anion, but different cations, namely $[C_2C_1Im][ClC_4H_8SO_3]$ and $[C_8C_1Im]$ [ClC₄H₈SO₃], where the cations differ from each other only by the length of the alkyl chain at the imidazolium ring. In a previous study, it was shown that this anion preferentially orientates itself at the outer surface with the 4-chlorobutyl chain pointing towards the vacuum and the SO₃ group towards the bulk.^[17, 18] Evidence for this orientation can also be seen in Figure 6, which shows the C1s, N1s, Cl2p, and O1s spectra of [C₂C₁Im] $[ClC_4H_8SO_3]$ (black) and $[C_8C_1Im][ClC_4H_8SO_3]$ (red) for 0° (left column) and 80° emission (right column). To remove the effect of the different IL density and, thus, to enable a direct comparison, the XP spectra of [C₈C₁Im][ClC₄H₈SO₃] are normalized to the N1s signal of $[C_2C_1Im][ClC_4H_8SO_3]$ in 0° emission. For both ILs, the increase of the Cl2p signal and the decrease of the O and S signals at 80° confirm the proposed preferred orientation of the functionalized chain with the Cl atoms towards the vacuum and the SO_3 groups towards the bulk. For each IL, the ionic head groups have the same distance to the outer surface, as is deduced from the identical decrease of the O1s and N1s signals at 80°. When comparing the two ILs, the more pronounced decrease at 80° for $[C_8C_1Im][ClC_4H_8SO_3]$ stems from the stronger attenuation of the head group signals by the longer octyl chains compared with the ethyl chains of $[C_2C_1Im]$ $[ClC_4H_8SO_3].$

The degree of the preferred surface orientation of the functionalized anion chains can be evaluated by the ratio of Cl2p and O1s signals. For both ILs, quantitative analysis of the bulksensitive geometry (0° emission) matches the nominal value of 0.33 to within the margin of error, as is expected for clean ILs. In the surface-sensitive geometry (80°), the Cl2p/O1s signal ratio rises significantly; to 0.56 for $[C_2C_1Im][ClC_4H_8SO_3]$ and to

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Figure 6. C 1s, Cl 2p, O 1s, and N 1s spectra of $[C_2C_1Im][ClC_4H_8SO_3]$ (black) and $[C_8C_1Im][ClC_4H_8SO_3]$ (red) in 0° (left) and 80° emission (right); data partly from Ref. [18]. The XP spectra of $[C_8C_1Im][ClC_4H_8SO_3]$ are normalized to the N 1s signal intensity of $[C_2C_1Im][ClC_4H_8SO_3]$ measured at 0° emission to account for the different IL density.

0.66 for $[C_8C_1Im][CIC_4H_8SO_3]$. The larger value for the latter IL indicates that the surface orientation is more pronounced for the IL with the longer alkyl chain. This effect is attributed to the enhanced dispersive intermolecular interactions of the 4-chlorobutyl chain with the octyl chain of $[C_8C_1Im]^+$ compared with the ethyl chain of $[C_2C_1Im]^+$. The somewhat smaller absolute increase in the Cl2p signal at 80° for $[C_8C_1Im][CIC_4H_8SO_3]$ compared with $[C_2C_1Im][CIC_4H_8SO_3]$ is assigned to the fact that the functionalized chain is shorter than the octyl chain; thus, the Cl atom at the end of the functionalized chain is not at the outer surface and is therefore damped by the longer octyl chain. This effect does not occur for the IL with the shorter ethyl chain.



Comparing the Cl2p/O1s signal ratio for $[C_2C_1Im][ClC_4H_8SO_3]$ and $[C_8C_1Im][ClC_4H_8SO_3]$ (see above) to the value of 0.41 for the F1s/O1s signal ratio of $[C_{12}C_1Im][FC_4H_8SO_3]$ in 80° emission shows that the degree of surface orientation is smaller for $[C_{12}C_1Im][FC_4H_8SO_3]$ in spite of the longer alkyl chain. It is suggested that this is also due to weaker dispersive interactions of alkyl chains with C–F bonds than with C–Cl bonds, which have a greater polarizability.^[46,48]

Furthermore, we studied and compared three different ILs with a haloethyl chain attached to the imidazolium ring, namely the chloro-functionalized IL [(CIC_2H_4) C_1C_1Im][TfO], the bromo-functionalized IL [$(BrC_2H_4)C_1Im$][Tf₂N], and the iodofunctionalized IL $[(IC_2H_4)C_1Im][Tf_2N]$ (Table 1). For these three ILs, ARXPS reveals more or less isotropic behavior of the functionalized cations (i.e., no significant surface enrichment) at the outer surface (spectra are provided in the Supporting Information as Figures S1-S3). From the lack of orientation of the halogen-functionalized chain towards the vacuum (which was observed, e.g., for [ClC₄H₈SO₃]⁻ systems—see above), we conclude that the haloethyl chains are too short to form a heterogeneous structure at the outer surface. This is in line with previous investigations on [C_nC₁Im][Tf₂N] where alkyl surface enrichment was only found for $n \ge 4$, but not for shorter chains.[15,49]

Thioether-functionalized ILs

In a previous study, we showed that ether-functionalized (i.e., ethylene glycol-functionalized) cations, like [Me(EG)_nC₁Im]⁺ (n = 1,2,3), do not exhibit a preferred surface orientation owing to the formation of intra- and intermolecular hydrogen bonds between the oxygen atoms and the acidic hydrogen atoms of the imidazolium ring.^[15,49] Herein, the related thioether-functionalized IL [(CH₃SC₂H₄)C₁Im][Tf₂N] is studied. The respective XP spectra in 0° and 80° emission are depicted in Figure 7. The single peaks in the F1s and O1s spectra are assigned to the anion, the C1s, N1s, and S2p regions each contain one cation peak and one anion peak. In the C1s and S2p region, the peak at higher binding energy is attributed to the IL anion and the signal at lower binding energy to the IL cation. In the N1s region, the peak assignment is reversed. The purity of the sample is once again verified by the quantitative analysis of the 0° measurement, which matches the nominal atom ratio to within the margin of error.

We first address the surface orientation of the $[Tf_2N]^-$ anion by comparing the XP spectra at 0° and 80° emission in Figure 7. Whereas the C_{anion}, N_{anion}, and S_{anion} signals show no distinct angular dependence, the F1s signal increases and the O1s signal decreases at 80°. This indicates a preferred surface orientation of the $[Tf_2N]^-$ anion for the *cis* conformation with its CF₃ groups pointing towards the vacuum and its SO₂ groups pointing towards the bulk. This finding is in agreement with the results of the fluoro-functionalized ILs previously discussed and observed in the literature for $[C_nC_1Im][Tf_2N]$ systems.^[8,29,50-52]

For the cation, no angular dependence is observed for the thioether-functionalized chain as shown by the constant S_{cation}



Figure 7. C 1s, N 1s, S 2p, F 1s, and O 1s spectra of $[(MeSC_2H_4)C_1Im][Tf_2N]$ in 0° (black) and 80° emission (green), along with the chemical structure of the IL.

signal. However, the N_{cation} signal, which particularly probes the position of the imidazolium ring relative to the outer surface, is lower in intensity (89%) at 80° emission (note that the C_{cation} signal does not show pronounced angle dependence as the carbon atoms in the ring and in the chain cannot be distinguished by the limited energy resolution). From this behavior, we propose that the imidazolium ring lies slightly below the $[Tf_2N]^-$ anion with the thioether-functionalized chain pointing towards the vacuum. However, as the changes in the ARXP spectra are small, this preferred orientation is not very pronounced.

In addition, we also studied the thioether-functionalized IL $[C_2C_1(MeS)Im][Tf_2N]$ (Table 1). The methylthio group at the C2 position of the imidazolium ring has an effect on the electronic structure of the cation, as was shown in a previous study.^[53] The impact on the surface composition is, however, not distinct. The angle-dependent changes in the XP spectra (see Figure S4 in the Supporting Information) are only minor and show no clear tendency of the thioether chain pointing towards the vacuum.

Amine-functionalized ILs

The effect of the cationic head group on the surface enrichment of functionalized chains is investigated for a 3-dimethylaminopropyl chain substituted on the two different cationic head groups, 1-methylimidazolium and tributylphosphonium. The corresponding ILs are $[(Me_2NC_3H_6)C_1Im][TfO]$ and $[(Me_2NC_3H_6)PBu_3][FAP]$. Note that the results were partly al-



ready presented in ref. [18] and are included in this work to provide a comprehensive overview of the influence of functional groups on the surface composition of ILs. The N1s spectra of the imidazolium-based IL in Figure 8 a contain peaks



from the cation head group at 403.0 eV (N_{im}) and the tertiary

Figure 8. N 1s spectra of $[(Me_2NC_3H_6)C_1Im][TfO]$ and N 1s and P 2p spectra of $[(Me_2NC_3H_6)PBu_3][FAP]$ in 0° (black) and 80° emission (green), along with the chemical structures of the ILs; data partly from Ref. [18].

amine group of the cation at 400.3 eV (N_{amine}). The N_{amine} signal increases at 80°, whereas the N_{Im} signal slightly decreases. This behavior indicates that the amine groups tend to stick out towards the vacuum. This result is confirmed by a molecular dynamics simulation by Xing et al., who calculated the surface orientation of the IL $[(H_2NC_3H_6)C_1Im][BF_4]$. They found that the primary amine group tethered to the imidazolium cation is also preferentially orientated towards the vacuum.^[12] For the phosphonium-based IL, both the N1s and the P2p spectra have to be considered (Figure 8b and c). The N1s signal at 399.6 eV is attributed to the amine group. The two P2p signals at 133.2 and 134.9 eV are assigned to the phosphonium cation (P_{cation}) and the $[FAP]^-$ anion (P_{FAP}) , respectively (note that the spin-orbit splitting for the P2p level is not resolved). The absence of any intensity changes between 0° and 80° emission indicates an isotropic arrangement of the IL at the outer surface, contrary to the imidazolium-based IL.

As an additional amine IL, one with a primary amine functionality, we studied $[(HOC_2H_4)_2Me_2N][H_2NC_2H_4SO_3]$, which contains, next to the amine group in the anion, two hydroxy groups in the cation. The corresponding core-level spectra are depicted in Figure 9. The two N1s signals at 402.8 and 399.7 eV stem from the ammonium (N_{ammon}) and the amine nitrogen atoms (N_{amine}), respectively. The two peaks in the O1s region are attributed to the SO₃ group at 531.7 eV (O_{SO3}) and to the hydroxy groups at 533.1 eV (O_{OH}). As all carbon atoms of the IL are connected to hetero atoms, we expect only one peak in the C1s region. However, next to the C_{hetero} peak at 286.6 eV, a second signal is observed at 285.3 eV, which is a binding energy typical for carbon atoms that are only bound



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Figure 9. N1s, O1s, C1s, and S2p spectra of $[(HOC_2H_4)_2Me_2N][H_2NC_2H_4SO_3]$ in 0° (black) and 80° emission (green), along with the chemical structure of the IL. Note the small carbon contamination, which does not affect the deduced conclusions, however.

to carbon and/or hydrogen atoms. As no additional signals are observed in the XP spectra and the quantitative analysis of the IL signals matches the nominal atom ratio to within the margin of error, we attribute the C1s signal to a hydrocarbon contamination (C_{contam}). On increasing the emission angle from 0° to 80° , a strong increase in the intensity of the C_{contam} signal is observed, indicating the high surface activity of the contamination. In addition, the N_{amine} signal increases in intensity, whereas the S2p and O_{SO_3} signals of the SO₃ group decrease to approximately 73% of their 0° emission intensity. This suggests that the $[H_2NC_2H_4SO_3]^-$ anion preferentially orientates itself at the surface with the amine group pointing towards the vacuum and the negatively charged SO₃ group towards the bulk, similar to the [(Me₂NC₃H₆)C₁Im]⁺ cation. The surface orientation of the [(HOC₂H₄)₂Me₂N]⁺ cation is deduced from the behavior of the O_{OH} and the N_{ammon} signals. The N_{ammon} signal decreases at 80° emission compared with the 0° measurement, whereas the O_{OH} signal intensity stays constant within the margin of error, indicating that the mean distance from N_{ammon} to the outer surface is larger than for $O_{\mbox{\scriptsize OH}}.$ A similar preferred surface orientation of hydroxyethyl chains tethered to a cationic head group was previously reported by Lockett et al. and Pensado et al., who studied the surface orientation of the 1-(2-hydroxyethyl)-3-methylimidazolium cation by ARXPS and MDS, respectively.^[8,9] Our observations imply that for the investigated primary and tertiary amine-functionalized ILs, the neutral functional groups form the outer surface, whereas the ionic head groups lie below.

Conclusion

We have performed a systematic ARXPS study to investigate the surface behavior of a variety of functionalized and some non-functionalized ILs, including imidazolium-based ILs meth-

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ylated at the C2 position, a phenyl-functionalized IL, an alkoxysilane-functionalized IL, halo-functionalized ILs, thioether-functionalized ILs, and amine-functionalized ILs. The main results and conclusions can be summarized as follows.

Methylation at the C2 position of imidazolium systems

The influence of methylation of imidazolium cations at the C2 position was studied as a function of cation alkyl chain length $([C_nC_1C_1Im]^+ \text{ with } n=4,8)$ and anion size $(Br^-, [TfO]^-, [Tf_2N]^-)$. As for the non-methylated systems, the alkyl chains tend to orientate themselves towards the vacuum. For all the methylated systems, a preferred orientation of the methyl group at the C2 position towards the vacuum is observed, an observation that is in line with the study by Lockett et al. for $[C_4C_1C_1Im][BF_4]$.^[8]

Phenyl-functionalized ILs

The surface arrangement was studied for $[(PhC_3H_6)C_1Im][Tf_2N]$ and compared with that of imidazolium cations with non-functionalized alkyl chains of comparable length ([C₈C₁Im][Tf₂N]). In contrast to the alkyl chains, no preferential orientation towards the vacuum is found for the phenyl-functionalized chains. Nevertheless, the phenyl groups are on average closer to the outer surface than the imidazolium rings. The [Tf₂N]⁻ anion orientates itself at the surface with its CF_3 groups pointing towards the vacuum and the ${\rm SO}_2$ groups pointing towards the bulk. The phenyl rings and the CF₃ groups lie next to each other at the outer surface, in contrast to [C₈C₁Im][Tf₂N], where the alkyl chains lie above the CF₃ groups. The differences are attributed to the quadrupole moment of the phenyl group, which promotes its interaction with the anions and cationic head groups, in line with molecular dynamic simulations as well as diffraction experiments of IL-benzene mixtures.^[32-36]

Alkoxysilane-functionalized ILs

For $[((EtO)_3SiC_3H_6)C_1Im]CI$, we find that the functionalized chains point towards the vacuum, whereas the imidazolium rings lie below. The imidazolium ring is found at a larger distance from the outer surface than the chloride anion, indicating that the anion lies slightly above the cation head group. The surface enrichment of the functionalized chain is in line with the reported high surface activity of polysiloxanes.^[14,37]

Halo-functionalized ILs

Owing to their very weak dispersive intermolecular interactions, perfluorinated alkyl chains are expected to be enriched at the outer surface of the IL, similar to aqueous systems. This behavior is indeed observed for the perfluorinated chains of $[(C_4F_9C_2H_4)C_1Im]I$, with the imidazolium rings and the anions positioned underneath and at the same mean distance to the outer surface. A corresponding study of the fluoro-functionalized IL $[C_{12}C_1Im][FC_4H_8SO_3]$ demonstrates that the preferred surface orientation of the fluorinated chains towards the vacuum occurs for both functionalized cations and functionalized anions.

The effect of the counterion on the degree of surface ordering was studied for $[C_2C_1Im][ClC_4H_8SO_3]$ and $[C_8C_1Im]$ $[ClC_4H_8SO_3]$, that is, cations with different alkyl chain lengths. For both ILs, the 4-chlorobutyl chain is enriched at the outer surface, but the surface orientation is more pronounced for $[C_8C_1Im][ClC_4H_8SO_3]$, owing to the enhanced dispersive intermolecular interactions of the 4-chlorobutyl chain with the longer alkyl chain. A comparison with $[C_{12}C_1Im][FC_4H_8SO_3]$ reveals a lower degree of surface orientation despite the longer alkyl chain, an observation that is attributed to weaker dispersive interactions of the alkyl chain with C–F bonds than with C–Cl bonds, owing to the higher polarizability of the latter.^[46,48]

A comparative analysis of three halogen-functionalized ILs with short chains, namely [(CIC₂H₄)C₁C₁Im][TfO], [(BrC₂H₄)C₁Im]-[Tf₂N], and [(IC₂H₄)C₁Im][Tf₂N], revealed no specific surface enrichment. This is attributed to the fact that haloethyl chains are too short to form a heterogeneous structure at the outer surface, in line with previous investigations on [C_nC₁Im][Tf₂N] for n < 4.^[15,49]

Thioether-functionalized ILs

These studies were motivated by previous work on the ether-functionalized ILs $[Me(EG)_nC_1Im]^+$ (n = 1,2,3), which showed no preferential surface orientation owing to the formation of intra- and intermolecular hydrogen bonds between the oxygen atoms and the acidic hydrogen atoms of the imidazolium ring.^[15,49] For the related thioether-functionalized ILs $[(CH_3SC_2H_4)C_1Im][Tf_2N]$ and $[C_2C_1(MeS)Im][Tf_2N]$, the $[Tf_2N]^-$ anion shows a preferred surface orientation for the *cis* conformation, with its CF₃ groups pointing towards the vacuum and its SO₂ groups pointing towards the bulk, in agreement with the results of the ether-functionalized ILs.^[8,29,50] The imidazolium ring is found to be slightly below the $[Tf_2N]^-$ anion, with the thioether-functionalized chain of $[(CH_3SC_2H_4)C_1Im][Tf_2N]$ showing a weak preferential orientation towards the vacuum.

Amine-functionalized ILs

We studied two ILs with a 3-dimethylaminopropyl chain substituted on two different head groups, $[(Me_2NC_3H_6)C_1Im][TfO]$ and $[(Me_2NC_3H_6)PBu_3][FAP]$. Although for the imidazolium-based IL the amine groups tend to stick out towards the vacuum, for the phosphonium-based IL an isotropic surface arrangement is found. An additional amine-functionalized IL was studied, $[(HOC_2H_4)_2Me_2N][H_2NC_2H_4SO_3]$, which contains two hydroxy groups in the cation next to the amine group in the anion. The $[H_2NC_2H_4SO_3]^-$ anion preferentially orientates itself at the surface with the amine group pointing towards the vacuum and the negatively charged SO₃ group towards the bulk, similar to the $[(Me_2NC_3H_6)C_1Im]^+$ cation. The $[(HOC_2H_4)_2Me_2N]^+$ cation orients itself with the OH group closer to the surface, an observation that implies that the neutral functional groups

form the outer surface, whereas the ionic head groups lie below.

General conclusions

From the described results, we can deduce some general trends: The occurrence of surface enrichment of functional groups/chains and of non-functional alkyl chains depends on the interplay/competition between the interactions of the ionic head groups, dispersive interactions between the ionic head groups and the chains/functional units, and dispersive interactions between the chains/functional units.

1) For weak interactions between the functional units/chains and the head groups, typically, surface enrichment of the functional groups/chains is observed when the chain length is sufficient $(n \ge 4)$; examples are imidazolium-based ILs with non-functionalized, halogen-functionalized, alkoxysilane-functionalized, thioether-functionalized and amine-functionalized alkyl chains. For short chains (n < 4), that is, chloro- or iodoethyl, no such enrichment is found. These effects are found for functional groups attached to the cationic and also the anionic head groups.

2) In the case of significant interactions of the functional group with the ionic head groups, for example, through hydrogen bonding for ether groups or quadrupole interactions for phenyl groups, surface enrichment of the functional chains is suppressed, in contrast to non-functional chains of the same length.

3) In the case of surface enrichment of the functional groups/chains, the cationic and anionic head groups typically form a polar layer underneath, at equal or very similar distance to the outer surface.

4) For ILs with functionalized/non-functionalized chains on both the anion and the cation (e.g., $[C_{12}C_1Im][FC_4H_8SO_3]$), a surface arrangement is observed with both chains pointing towards the vacuum, but in the case of $[C_{12}C_1Im][FC_4H_8SO_3]$, the F atoms are not at the outer surface due to the shorter length of the functionalized chain.

5) Dispersive interactions between the functional groups/ chains on both anions and cations contribute to enhanced surface enrichment. Thus, double-functionalized ILs with short functionalized chains at the anion and the cation, for example, $[(HOC_2H_4)_2Me_2N][H_2NC_2H_4SO_3]$, show enrichment of both functional groups.

6) Independent of the occurrence of surface enrichment of the cation, for all studies with the $[Tf_2N]^-$ anion, the anion shows a preferred surface orientation for the *cis* conformation, with its CF₃ groups pointing towards the vacuum and its SO₂ groups pointing towards the bulk.

Experimental Section

Materials

A summary of all ILs studied in this paper is given in Table 1. $[C_4C_1Im][TfO]$, $[C_4C_1C_1Im][TfO]$, $[C_8C_1Im][TfO]$, and $[C_8C_1Im]Br$ were purchased from Merck, and $[C_8C_1C_1Im]Br$ and $[C_8C_1C_1Im][Tf_2N]$ were

donated to us by Merck. All other ILs were synthesized in our laboratories. Details on the synthesis are given in the Supporting Information.

ARXPS

Thin IL films (~100 μm) were prepared by deposition of the corresponding IL onto a planar Au foil (20 mm \times 15 mm). These samples were then introduced into the ultra-high vacuum (UHV) system through a loadlock. The in situ heating of the ILs was done by heating from the reverse side of the samples. A thermocouple attached near the sample gave temperature readings with an error of \pm 5 °C.

The ARXPS measurements of the ILs [((EtO)₃SiC₃H_o)C₁Im]Cl, [(C₄F₉C₂H₄)C₁Im]], and [C₁₂C₁Im][FC₄H₈SO₃] were conducted with a VG ESCALAB 200 system using non-monochromatized Al_{kα} radiation ($h\nu$ = 1486.6 eV) at a power of 150 W (U = 15 kV, I = 10 mA) and a pass energy of 20 eV. All other ILs were measured with the same chamber, but with a (newly installed) SPECS XR 50 X-ray source and a VG Scienta R3000 electron analyzer, using non-monochromatized Al_{kα} radiation at a power of 250 W (U = 12.5 kV, I = 20 mA) and a pass energy of 100 eV. For both series, the overall energy resolution was approximately 0.9 eV. Unless stated otherwise, the binding energies are denoted as measured, that is, no referencing of the binding energy scale to a particular core level was applied. In some cases, the 80° spectra were shifted by ~0.2 eV to correct for minor charging.

At the kinetic energies used (800–1300 eV), the inelastic mean free path (IMFP) of photoelectrons is approximately 3 nm in organic compounds.^[20] Therefore, the information depth (=3x IMFP) at 0° emission is 7–9 nm, whereas it is only 1–1.5 nm at 80°. To account for the overall lower intensity in 80° emission and to enable a direct visual comparison of the 0° and 80° spectra, the 80° spectra were multiplied by an empirical factor.^[14]

For the C1s spectra of $[Tf_2N]^-$ and $[TfO]^-$ -based ILs, a three-point linear background subtraction was used. For all other core-level spectra a two-point linear background subtraction was applied. All peaks were fitted by using a Gaussian–Lorentz profile with 30% Lorentz contribution. From the resulting peak areas and by taking into account the sensitivity factors for the different elements, quantitative information was obtained on the stoichiometry of the near-surface region. The atomic sensitivity factors (ASFs) were calibrated for our specific experimental setup by the process reported by Kolbeck et al.^[14] This procedure yields $\pm 5\%$ accuracy for the denoted atomic concentration values. The results of the quantitative analyses of all studied ILs are given in the Tables in the Supporting Information. Beam damage was observed for some ionic liquids after 2–3 h of X-ray exposure; all results in this paper are from experiments recorded before beam damage was detected.

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