Surfactant-Mediated Ion Exchange and Charge Reversal at Ionic Liquid Interfaces

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Room-temperature ionic liquids (ILs) exhibit a unique set of properties due to their charged character, presenting opportunities for numerous applications. Here, we show that the combination of charged surfactants with ILs leads to rich interfacial behavior due to the interplay between electrostatic and surface forces. Using traditional measures of surface activity and X-ray photoelectron spectroscopy (XPS), we find that sodium alkyl sulfates and alkyl trimethylammonium bromides are, indeed, surface-active at the air-IL interfaces of both [EMIM][EtSO$_4$] and [BHEDMA][MeSO$_3$]. XPS also reveals that surfactant counterions readily dissociate into the bulk, which when combined with the surfactant surface activity has striking consequences. We find that ion exchange occurs between surfactants and like-charged IL ions, with the greatest exchange for short surfactant alkyl chains. The initial negative surface charge of neat [EMIM][EtSO$_4$] can be switched to positive by the addition of alkyl trimethylammonium bromides, with the effect most pronounced at short chain lengths. By contrast, the surface charge of [BHEDMA][MeSO$_3$] is largely unaffected by the added surfactants, suggesting a key role for the strength of ion-pairing within the IL. The results here illustrate a simple but effective means of manipulating IL interfacial properties.

Introduction

Due to their chemical diversity, room-temperature ionic liquids (ILs) are often referred to as "designer" or "task-specific" solvents[1–4] and are already enabling new approaches in catalysis, chromatography, and even fuel cells.[4,5] The neat IL–vapor[6] and IL–solid[7] interfaces have been probed with both experimental[8–14] and modeling[15–19] approaches, revealing unique features, such as (i) the preferential orientation of cations[8–10,16,19] and (ii) the existence of surface layers.[11,14,16–18] The above two properties suggested an interesting context to explore the behavior of surface-active molecules. Although ILs have been used as bulk media for self-assembly (e.g., micelles, vesicles),[20–23] there is far less known about amphiphiles at IL interfaces.[24] In particular, by pairing charged surfactants with ILs, a wide variety of interfacial behavior should become possible due to the interplay of electrostatic and surface forces. The negligible vapor pressure of ILs also enables the use of low-pressure techniques, such as X-ray photoelectron spectroscopy (XPS), to directly probe the surface composition of the resulting interfaces.[25–31]

In this study, we have used two model ionic liquids, 1-ethyl-3-methyl imidazolium ethylsulfate, **I**, and bis(2-hydroxyethyl) dimethylammonium methyl sulfonate, **II** (see Figure 1). These ionic liquids are commonly referred to as [EMIM][EtSO$_4$] and [BHEDMA][MeSO$_3$], respectively. Importantly for our purposes, **I** and **II** are miscible with water in all proportions. Sodium alkyl sulfate and alkyl trimethylammonium bromide surfactants were deliberately chosen so as to resemble moieties in the ILs and thereby promote more complex surface interactions. With these components, we find that ion exchange and charge reversal can occur at the interface, depending on the natures of the IL and surfactant.

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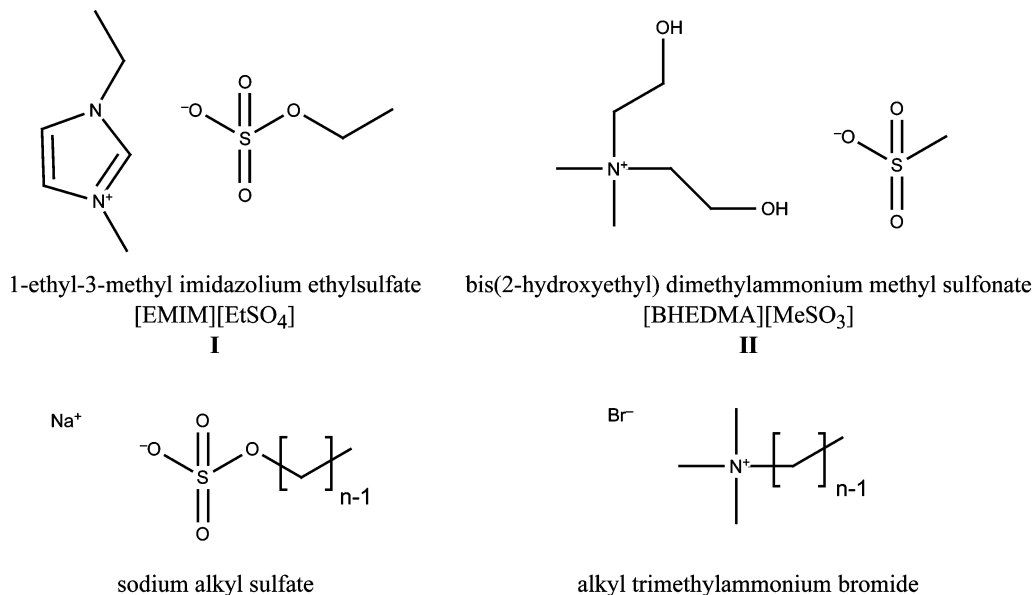## Experimental Methods

Materials. [EMIM][EtSO$_4$], **I**, was obtained from Sigma (>95%), and [BHEDMA][MeSO$_3$], **II**, was a gift from T. J. McCarthy.[32] The IL molecular weights are $M_I = 236.29$ g/mol and $M_{II} = 229.29$ g/mol, and according to the supplier, their densities are $\rho_I = 1.24$ g/mL and $\rho_{II} = 1.28$ g/mL at room temperature. Both of the ionic liquids were dried by heating at 70 °C under vacuum for 2 days. The purity of the neat ionic liquids and selected surfactants were assessed by ^{1}H NMR and did not reveal any impurities. These findings were confirmed by subsequent XPS control experiments (see Figure 2).

Sodium hexadecylsulfate, sodium dodecylsulfate, sodium hexylsulfate, Tween 20, cetyl trimethylammonium bromide (>99%) and dodecyl trimethylammonium bromide were purchased from Fisher. Sodium octylsulfate, decyl trimethylammonium bromide, tetradecyl trimethylammonium bromide, octyl trimethylammonium bromide, and polyoxyethylene(4) lauryl ether (Brij 30) were purchased from Sigma. All surfactants were used as received. The water used to dissolve the surfactants was treated with in-house reverse osmosis (RO) and additionally passed through a 0.22 μm filter. After dissolution in RO water, solutions were heated to 50 °C to make stock solutions, which were subsequently diluted to the appropriate concentrations as needed. All samples were optically transparent by visual inspection.

Tensiometry. Surface tension was measured by the Wilhelmy method with a Micro Trough X (Kibron, Inc.). At room temperature, both of the ILs have relatively high interfacial tensions with air, $\gamma_I = 48.3 \pm 0.8$ mN/m ($N = 30$) and $\gamma_{II} = 64.5 \pm 0.5$ mN/m ($N = 26$). These values are in good agreement with interfacial tensions obtained by independent laboratories using other methods.[32] Subphase volumes were ~300–500 μL of either RO water, **I**, or **II**. Each subphase was placed in Teflon-lined wells with a fixed area, in a metal alloy plate. To determine the effect of added surfactant, between 5 and 40 μL of surfactant

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Figure 1. Structures of the ionic liquids and surfactants used in this study.

1-ethyl-3-methyl imidazolium ethylsulfate
[EMIM][EtSO$_4$]
I

bis(2-hydroxyethyl) dimethylammonium methyl sulfonate
[BHEDMA][MeSO$_3$]
II

sodium alkyl sulfate
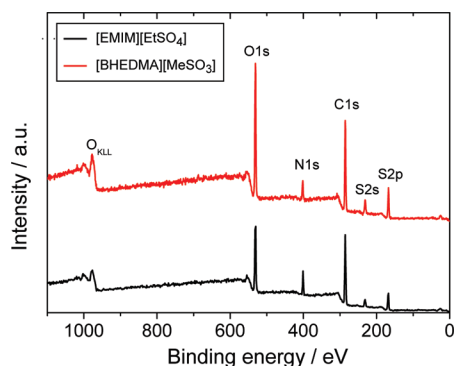
alkyl trimethylammonium bromide

Figure 2. XPS spectra of neat [EMIM][EtSO$_4$] (black) and [BHEDMA]-[MeSO$_3$] (red), recorded at $\theta = 45°$ takeoff angle.

solutions were applied to each well. Surface tensions were measured after an equilibration time of 15 min. We note that although water is introduced in the application of surfactant, it is always less than 12% by volume and does not significantly alter the bare interfacial tension ($\Delta\gamma < 3\%$ for both **I** and **II**). Finally, small amounts of water in imidazolium-based ILs have been shown both by experiment[33] and simulation[34] to be molecularly dispersed and not phase separated.

X-ray Photoelectron Spectroscopy. Five microliters of aqueous surfactant solutions were applied onto the surface of 5 μL of IL droplets using (oxygen-plasma-cleaned) silicon wafers as substrates. Samples were dried in a flowing nitrogen environment for 3 days at room temperature prior to conducting XPS measurements. Importantly, the solubility of molecular nitrogen is among the lowest for gases in ILs,[35] indicating that this is not a likely source of contaminant introduction. To be certain of the role of nitrogen drying, we measured atomic compositions of such dried samples, and the values agreed with the expected atomic ratios of the neat ILs.

XPS data were recorded using a Physical Electronics Quantum 2000 Microprobe instrument with monochromatic Al X-rays at 50 W, a 200 μm spot area, and a takeoff angle of 45°. The analyzing surface area was neutralized by an ion gun. Survey scans (3 min) were followed by regional scans ($\approx$20 min) for each atomic element of interest. Regional scans were adjusted by a two-point linear background subtraction[29] and normalized with respect to the relevant peak position for illustrative purposes

only. Atomic compositions were obtained by using known sensitivity factors for this instrument and setup (Table S1, Supporting Information). To determine molecular compositions, atomic mass balances were performed using the chemical formulas of each species (see Results and Discussion).

At a given takeoff angle θ, the exponential decay of the photoelectron intensity is given by $I/I_0 = \exp(-z/(\lambda \sin \theta))$, where z points along the inward surface normal.[36] Manipulation of the above expression leads to the fractional intensity $I/I_{tot} = 1 - \exp(-z/(\lambda \sin \theta))$, where I_{tot} is the total intensity. The depth corresponding to 95% of the signal (i.e., z at $I/I_{tot} = 0.95$) is denoted by d, and we find $d \approx 3\lambda \sin \theta$. In our experiments, the takeoff angle was kept fixed at $\theta = 45°$, and using a typical value[27,36] of the C1s electron mean free path $\lambda = 1.50$ nm gives $d = 3.2$ nm. Obviously, a different value of λ would give different results, and there is some controversy regarding the appropriate value for organic compounds.[37] In addition, there is a correction for the elemental dependence of λ: for S2p, N1s, and O1s, the 95% signal depths are 4.3, 2.2, and 0.97 nm, respectively. Because our analysis relies only on C1s, N1s, and S2p, we feel it is a reasonable approximation to simply use $d \approx 3$ nm as an average sampling depth.

We note that XPS results for both neat ILs match the expected atomic ratios, consistent with minimal impurities (Figure 2 and Supporting Information Table S1). Furthermore, treatment of neat [EMIM][EtSO$_4$] with Ar$^+$ bombardment reveals negligible change in C1s and N1s signals. Most importantly, the Si2p signal is always at the noise level, eliminating the possibility of Si contamination (Figure S1 of the Supporting Information). As still another control, experiments demonstrate that the water used to introduce the surfactant does not contain measurable contaminates because the expected atomic ratios are obtained. This control consisted of adding the appropriate volume of water, followed by nitrogen drying, as above.

Results and Discussion

The surface tension of both ILs decreased with the addition of surfactant, as might be expected.[22,38] However, the critical micelle concentrations (C_b) do not correlate with the bare air−liquid surface tensions: for both surfactant types, we find $C_{b,II} < C_{b,w} < C_{b,I}$ whereas $\gamma_I < \gamma_{II} < \gamma_w$ (see Tables 1 and 2).

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TABLE 1: Sodium Alkyl Sulfate Transition Concentrations, in mM, Determined by Tensiometry[a]

chain length	[EMIM][EtSO$_4$], I			[BHEDMA][MeSO$_3$], II			water	
	C_a	C_b	C^*	C_a	C_b	C^*	C_a	C_b
6	28	826	150	2.5	126	15	28	543
8	19	>143	20	0.19	8.5	2	2.5	123
12	1.1	14.8	5	0.012	0.53	0.05	0.49	7.7
16	0.14	2.9	1	1.2×10^{-3}	0.014	0.01	0.073	0.87

[a] XPS measurements were performed at $C^* \approx (C_a C_b)^{1/2}$.

TABLE 2: Alkyl Trimethylammonium Bromide Transition Concentrations, in mM, Determined by Tensiometry[a]

chain length	[EMIM][EtSO$_4$], I			[BHEDMA][MeSO$_3$], II			water	
	C_a	C_b	C^*	C_a	C_b	C^*	C_a	C_b
8	129	>800	300	3.1	>179	30	51.0	553
10	3.3	130	50	0.017	11.3	0.5	1.7	69.5
12	3.0	>83	20	0.036	3.0	0.2	1.1	18.4
14	0.5	>20	5	5.0×10^{-4}	0.21	0.05	0.02	3.1

[a] XPS measurements were performed at $C^* \approx (C_a C_b)^{1/2}$.
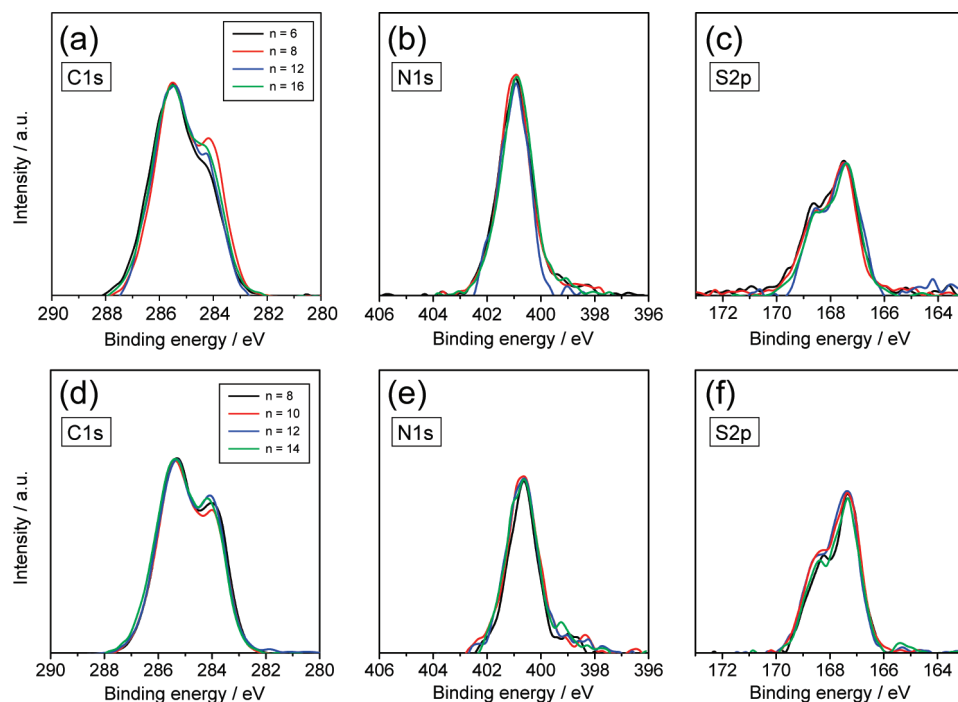
Figure 3. XPS regional spectra of (a−c) alkyl sulfate surfactants and (d−f) alkyl trimethylammonium on [EMIM][EtSO$_4$].

These results and others[20–22,38] indicate that C_b values with respect to ionic liquids are determined by several interactions, including electrostatic forces and interfacial energy. Furthermore, because the same C_b trend is observed for the neutral surfactants such as Brij-30 and Tween-20 (data not shown), it becomes apparent that the IL is playing an essential role in determining the interfacial behavior.

Due to the extremely low vapor pressure of ILs, we can use high-vacuum techniques such as XPS[25,28,31] to more closely examine the surfactant−IL interface. Survey scans of both neat ILs, [EMIM][EtSO$_4$] and [BHEDMA][MeSO$_3$], are shown in Figure 2, revealing the expected elemental signals and no indication of contamination. Introduction of surfactants is complicated by their lyotropic behavior, in particular, micellization or other aggregation states. To avoid such complications, surfactant concentrations were kept below the measured critical micelle concentration, C_b. In addition, as noted by Rayleigh,[39] the concentration C_a at the first break in surface tension marks the onset of the condensed phase (i.e., a monolayer is formed).

Thus, within the concentration range $C_a < C < C_b$, the interfacial behavior is expected to be substantially affected by the presence of surfactants. We therefore performed XPS measurements at an intermediate concentration, C^*, given by the geometric mean $(C_a C_b)^{1/2}$. Comparing the various surfactants at identical concentrations is not meaningful because the transition concentrations depend strongly on chain length (Tables 1 and 2). Finally, we note the variation in the measured transition concentrations is generally small: for $n = 12$ chain lengths, both surfactants have standard deviations <10% of the mean C_b value ($N = 3$).

Atomic composition of the interface also varies due to the presence of surfactants. In Figures 3 and 4, the C1s, N1s, and S2p regional XPS scans are shown. Due to the numerous species present, decoupling the peaks into contributions from particular elemental types is somewhat complicated. Therefore, rather than attempting to fit multiple Gaussian functions to our spectra, we analyzed the compositional data by means of atomic mass balances. Atomic mass balances can be found in standard chemical engineering textbooks[40,41] and rely on the presence of

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one or more unique atomic species (e.g., nitrogen or sulfur). As an example, we present this analysis in detail for SDS on [EMIM][EtSO$_4$]. The four ionic species present are $C_{12}SO_4^-$, Na^+, $C_6N_2^+$, and $C_2SO_4^-$, corresponding in this example to an index $i = 1-4$. Note that hydrogens are omitted in the above formulas because they are not detectable by XPS. Simply counting gives the total number of molecules $n_{tot} = \Sigma_i \, n_i$. The total number of atoms is then $w_{tot} = \Sigma_i \, w_i n_i$ where w_i is the number of atoms in the ith species, where E denotes an element and y^E denotes the atomic fraction of element E. For the example above, we obtain a set of four linearly independent equations:

$$\sum_i w_i^C n_i = y^C w_{tot} = 12n_1 + 6n_3 + 2n_4 \tag{1}$$

$$\sum_i w_i^N n_i = y^N w_{tot} = 2n_3 \tag{2}$$

$$\sum_i w_i^S n_i = y^S w_{tot} = n_1 + n_4 \tag{3}$$

$$\sum_i w_i^{Na} n_i = y^{Na} w_{tot} = n_2 \tag{4}$$

The above system is readily solved for all the n_i, since the y^E are known directly from the XPS measurement.

$$n_1 = (y^C - 2y^S - 3y^N)w_{tot}/10 \tag{5}$$

$$n_2 = y^{Na} w_{tot} \tag{6}$$

$$n_3 = y^N w_{tot}/2 \tag{7}$$

$$n_4 = y^S w_{tot} - n_1 = (12y^S - y^C + 3y^N)w_{tot}/10 \tag{8}$$

The mole fractions are then $x_i = n_i/n_{tot}$, and because these concentrations are obtained by XPS, they are hereafter denoted as x_i^{surf}. Note that the x_i^{surf} are spatial averages over the length scale $d \approx 3$ nm, which is greater than the molecular lengths of the ions and surfactants.[42,43] Using larger XPS takeoff angles is undesirable because the resultant sampling depths would be less than the size of the surfactants. We now define "surface enrichment", $\varepsilon_i = x_i^{surf}/x_i^{bulk}$, and find that both surfactant types exhibit surface enrichments $\varepsilon \gg 1$, confirming the surface activity at the IL interface (Figure 5).

We presume that the extent of surface enrichment increases with chain length due to IL solvatophobicity, similar to the hydrophobic effect in water.[42] XPS also reveals that the surfactant counterions are undetectable (below 0.1%) at the interface, indicative of nearly complete dissociation. These results are consistent with earlier studies reporting the dissociation of Br$^-$ and Cl$^-$ in ILs.[44,45] When combined with the surface enrichment of the surfactants, the counterion dissociation further contributes to a local environment of charge imbalance. That is because the counterion dissociates into the bulk, the interface largely contains only *three* types of ions, two from the IL and one from the surfactant. Ions must therefore rearrange at the interface to minimize the overall free energy, which will have contributions from both electrostatics and surface tension.

In particular, the above effects at the interface can result in ion exchange between the IL and surfactant. For the case of sulfate surfactants on [EMIM][EtSO$_4$], the IL cations exceed the IL anions: [EMIM]$^+$ > [EtSO4]$^-$ (Figure 6a). For the trimethylammonium surfactants, the situation is reversed, and
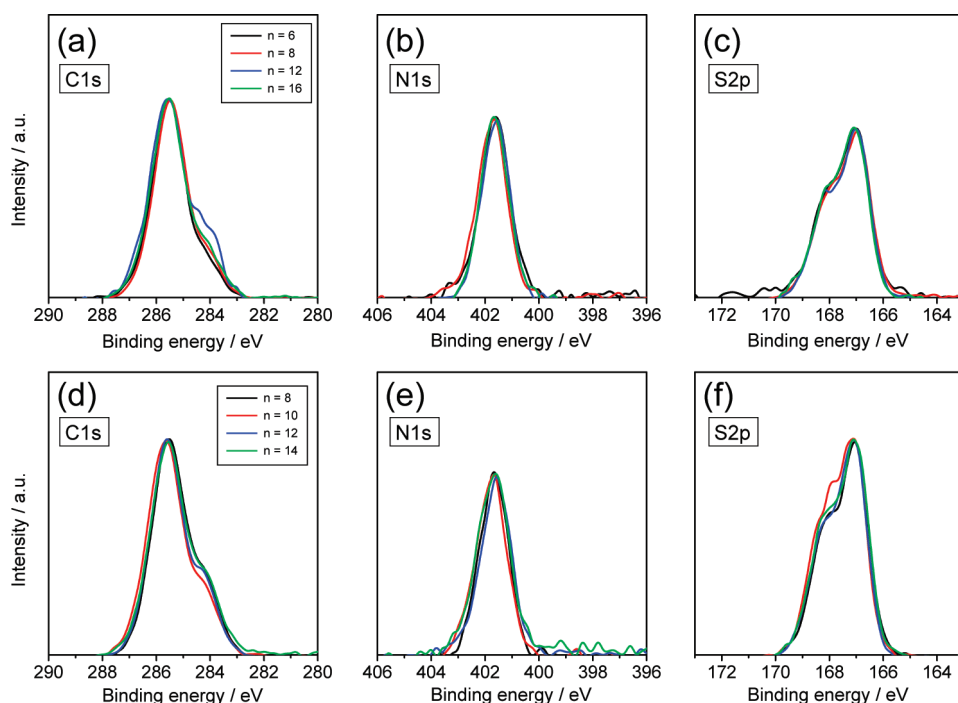

Figure 4. XPS regional spectra of (a–c) alkyl sulfate surfactants and (d–f) alkyl trimethylammonium on [BHEDMA][MeSO$_3$].
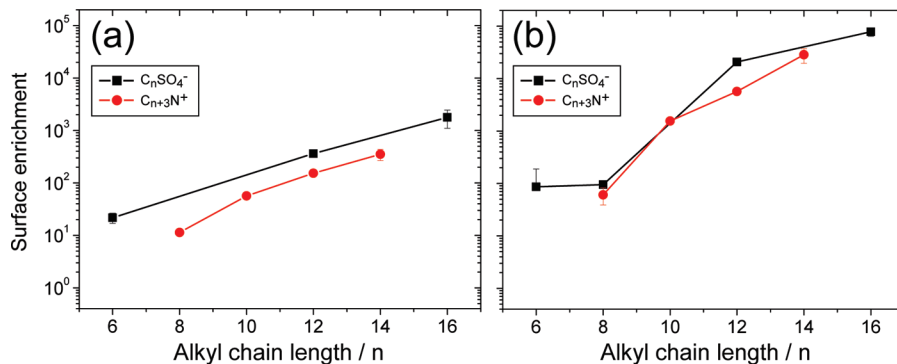
Figure 5. Surface enrichment of alkyl sulfate (squares) and alkyl trimethylammonium (circles) surfactants on (a) [EMIM][EtSO$_4$] and (b) [BHEDMA][MeSO$_3$]. Surface enrichment is defined as the ratio $\varepsilon_i = x_i^{surf}/x_i^{bulk}$, where x_i^{surf} are taken over the XPS depth $d \approx 3$ nm.
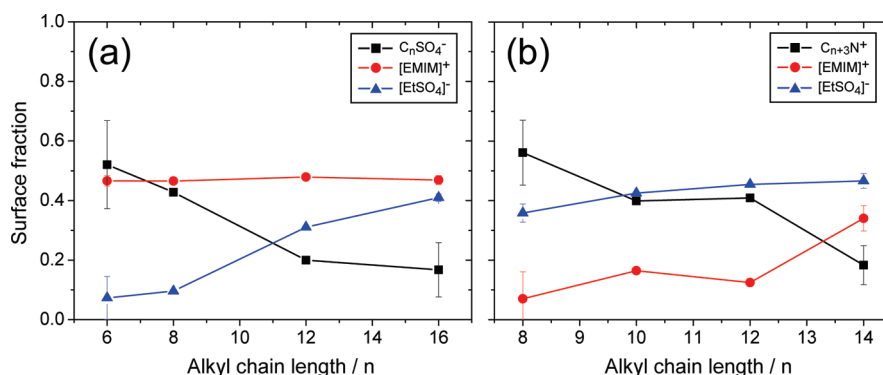

Figure 6. Surface fractions, x_i^{surf}, of (a) alkyl sulfates and (b) alkyl trimethylammoniums on [EMIM][EtSO$_4$], demonstrating ion exchange as a function of chain length. Surfactant counterions (i.e., Na$^+$, Br$^-$) are below the detection limit (<0.1%) and therefore not shown.
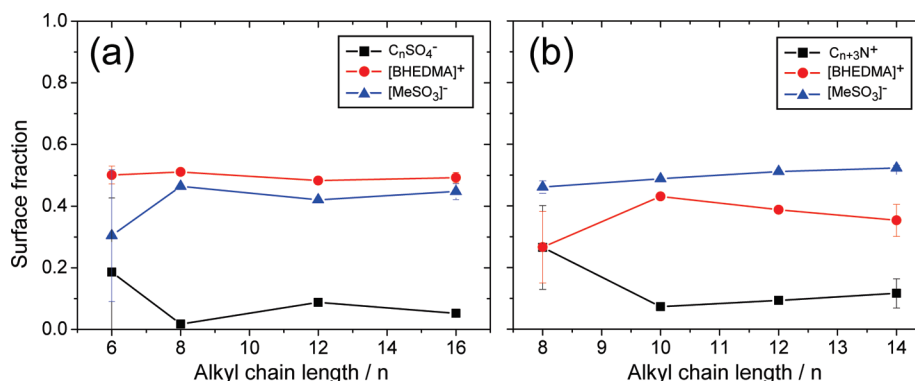

Figure 7. Surface fractions, x_i^{surf}, of (a) alkyl sulfates and (b) alkyl trimethylammoniums on [BHEDMA][MeSO$_3$], demonstrating ion exchange as a function of chain length. Surfactant counterions (i.e., Na$^+$, Br$^-$) are below the detection limit (<0.1%) and therefore not shown.

the IL anions exceed the IL cations: [EtSO4]$^-$ > [EMIM]$^+$ (Figure 6b). The surfactant always exchanges with the IL ion of the same charge, giving rise to the symmetry in Figure 6. Moreover, the extent of ion exchange increases with decreasing surfactant chain length, in agreement with the solubility trends (see Tables 1 and 2). In other words, as the surfactant alkyl chain becomes progressively smaller and presumably more soluble, the surfactant and the corresponding like-charged ion (from the IL) will exchange to a greater extent. Note that the IL ion *opposite* in charge to the surfactant has a nearly constant surface fraction x_i^{surf}, suggesting that it is minimally affected.

On [BHEDMA][MeSO$_3$], the IL cations and anions also appear to be offsetting the effect of surfactant at the interface (Figure 7). This ion exchange is most noticeable at short surfactant chain lengths ($n \leq 8$) and appears to reach a plateau

thereafter. In addition, the extent of ion exchange on [BHEDMA][MeSO$_3$] is lower than on [EMIM][EtSO$_4$] for all surfactant chain lengths, consistent with the higher interfacial energy γ_{II}. Because the IL components always remain the major surface species, this interface has a very different character from [EMIM][EtSO$_4$]. Clearly then, it will be of great interest to examine ionic liquids with different interfacial tensions and dielectric properties.

The surface charge ratio is defined here as the ratio of total surface cations to total surface anions: $\Sigma_i x_i^+/\Sigma_j x_j^-$. This ratio might be expected to be unity due to electroneutrality. However, we find that both neat ILs are slightly negative, with charge ratios 0.94 ± 0.05 for [EMIM][EtSO$_4$] ($N = 4$) and 0.95 ± 0.07 for [BHEDMA][MeSO$_3$] ($N = 5$). The above result is not unusual, given that recent XPS studies have observed excess

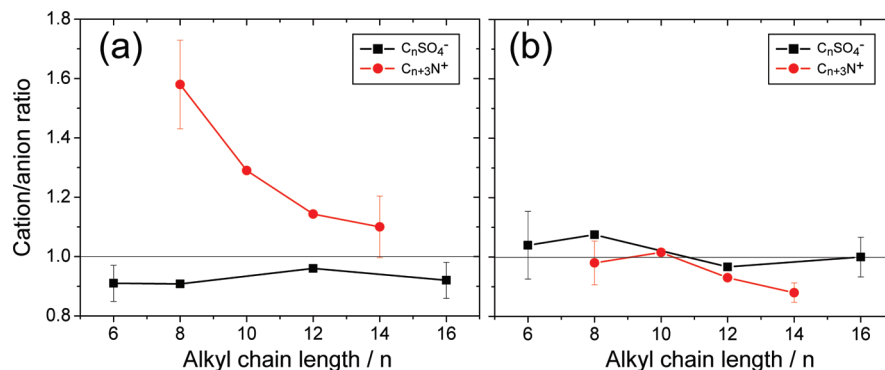Ion Exchange, Charge Reversal at IL Interfaces

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Figure 8. Overall surface charge, defined as the ratio of total surface cations to total surface anions: $\Sigma_i x_i^+ / \Sigma_j x_j^-$. Surfactants on (a) [EMIM][EtSO$_4$] and (b) [BHEDMA][MeSO$_3$]. Sodium alkyl sulfates and alkyl trimethylammonium bromides are denoted by squares and circles, respectively. Note that both neat ILs are slightly negative, with charge ratios 0.94 ± 0.05 for [EMIM][EtSO$_4$] ($N = 4$) and 0.95 ± 0.07 for [BHEDMA][MeSO$_3$] ($N = 5$).

negative charge of neat imidazolium ILs, even at a normal emission angle (i.e., $\theta = 0°$).[29,31] Furthermore, X-ray reflectivity measurements have indicated negative charge at the interface of neat [BMIM][BF$_4$].[11] This negative charge of neat ILs may be related to several factors (e.g., spontaneous symmetry-breaking, ion polarizability), but there is both experimental[46] and modeling[16] evidence for the role of (small) anion size in determining charge at the interface.

Irrespective of the underlying mechanism for the neat IL negative charge, the introduction of trimethylammonium surfactants on [EMIM][EtSO$_4$] imparts a net positive charge to the interface, in a length-dependent manner (Figure 8a). We interpret this resulting charge reversal, from negative to positive, to be due to the alkyl trimethylammonium surfactant enrichment at the air−liquid interface (Figure 5a). Indeed, the above results appear to be a direct consequence of the ion exchange occurring at the surface of [EMIM][EtSO$_4$] (Figure 6). However, sodium alkyl sulfate surfactants do not make the interface appreciably more negative, despite surface enrichment (Figure 5a) and ion exchange (Figure 6a). Thus, the interface of [EMIM][EtSO$_4$] takes on the charge characteristics of the added cationic surfactant but is affected substantially less by the added anionic surfactant. The large degree of similarity between the ethyl sulfate anion and the alkyl sulfate surfactant might, in part, minimize the impact on the net surface character.

On [BHEDMA][MeSO$_3$], the surface charge remains near zero for both surfactant types (Figure 8b). We note that the bulk concentrations in [BHEDMA][MeSO$_3$] are roughly an order of magnitude lower than in [EMIM][EtSO$_4$], due to the lower solubilities (see C_b values in Tables 1 and 2). This concentration difference indicates that despite surface enrichment, the IL ions are largely governing the interfacial behavior on [BHEDMA]-[MeSO$_3$]. Furthermore, as seen from Figure 7, the extent of ion exchange between [BHEDMA][MeSO$_3$] ions and both surfactants is quite low. Although the subject of future studies, it is quite likely that the strength of ion-pairing of the IL ions,[1,47,48] or the presence of local heterogeneities within the IL,[15,18,19,49] may be important factors in determining whether surface charge can be altered by surfactants.

Conclusions

In summary, interfacial behavior can be tuned through the judicious combination of ILs and surface-active molecules. We have shown that ion exchange and charge reversal become possible with the introduction of charged surfactants, providing a simple but effective way to control interfacial properties. The

importance of the IL is apparent and clearly dependent on the particular ion pair, although the underlying mechanisms are not yet clear. Recent simulations highlight other opportunities to modulate IL behavior; for example, through the use of external fields.[50] We expect fundamental investigations of surface thermodynamics, phase separation, kinetics, etc. to be revisited and eventually be exploited for particular applications.

Supporting Information Available: XPS regional scans following Ar$^+$ ion bombardment, table of atomic compositions, atomic sensitivity factors (ASF), and further details for atomic mass balances. This material is available free of charge via the Internet at http://pubs.acs.org/.

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