

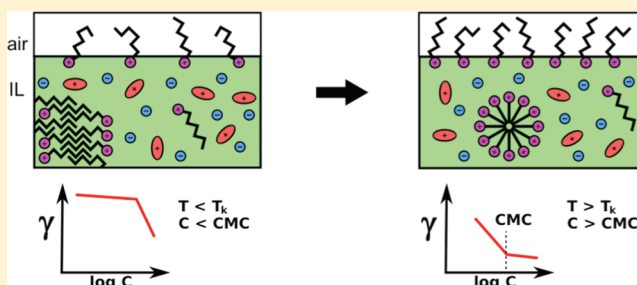
Solubility and Aggregation of Charged Surfactants in Ionic Liquids

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Supporting Information

ABSTRACT: Room-temperature ionic liquids (ILs) exhibit a unique set of properties, leading to opportunities for numerous applications. To obtain a better understanding of IL interfaces at a molecular level, we combined charged surfactants with ILs and studied their interfacial behavior. The critical micelle concentration (cmc) of each surfactant–IL pair was determined from both solubility phase diagrams and isotherms. Because the cmc is equivalent to the solubility at the Krafft temperature, a connection between the solubility of the surfactant and the physical properties of the underlying ionic liquid was established. Interfacial energy was found to be the major factor affecting the surfactant aggregation process, although its magnitude depends strongly on the IL structure. The results here give insight into explaining the nature of self-assembly of surfactants at IL interfaces and the interaction between solutes and IL solvents.



INTRODUCTION

Room-temperature ionic liquids (ILs), organic salts with a melting point below 100 °C, continue to receive intense attention as a result of their unusual and diverse properties. ILs are extremely versatile; their properties can be readily adjusted by variation of the cation and anion species.¹ As bulk solvents, ILs generally demonstrate negligible vapor pressure, high thermal stability, and a wide range of solubility for various compounds.^{2,3} For example, the bulk properties of ILs have been exploited to achieve self-assembly of micelles and vesicles.^{4,5} The interfacial properties of ILs are also of central importance in applications such as lubrication, (heterogeneous) catalysis, and chromatography.^{6–9}

Although they are sometimes referred to as “designer” solvents due to their seemingly endless diversity, achieving desired properties remains largely empirical. This state of affairs motivates the synthesis and characterization of many new IL compounds to build and validate structure–property relationships. However, simple mixing is a traditional route to bypassing the iterative procedure of synthesis and characterization. One form of such mixing (and tuning of properties) is the introduction of surfactants to an interface. Because surfactants preferentially partition to the interface, they can extend the versatility of interfacial properties, with the possibility of greater control.

It is well-established that the critical micelle concentration (cmc) for charged surfactants in aqueous solutions is reduced as the ionic strength increases.¹⁰ Intuitively, the presence of salt in water screens the electrostatic repulsion between charged headgroups, facilitating aggregation between surfactants and thereby lowering the cmc. The corresponding situation in ILs is not readily apparent, and from the argument above, it might be anticipated that cmc's in ILs are much lower than in aqueous

solutions. In contrast to this expectation, several experiments have shown that the cmc's of surfactants in ILs tend to be higher than in water,^{11–16} a result attributed to “solvatophobicity” or “solvophobicity”. We note that surveys of the literature to date are complicated by many studies where the solvent is actually a water–IL mixture. To gain further insight into solubility and aggregation behavior in ILs, here we examine a series of charged amphiphiles (alkyltrimethylammonium bromides) in four neat ionic liquids. We did not restrict ourselves to a single class of ILs (e.g., imidazolium) because our intent was to obtain information on the general behavior of surfactant–IL systems. The main factor in selecting the ILs chosen here was their relatively high bare interfacial tensions. Our results indicate that the cmc values not only vary substantially, but can be either higher or lower than that of water. These results suggest an ability to rationally tune the cmc for any given surfactant by the appropriate choice of ionic liquid.

EXPERIMENTAL SECTION

Ionic Liquids. 1-Ethyl-3-methylimidazolium ethyl sulfate, [EMIM][EtSO₄], I, and 1-butyl-3-methylimidazolium tetrafluoroborate, [BMIM][BF₄], III, were obtained from Sigma (>95% and >98%, respectively), and bis(2-hydroxyethyl)dimethylammonium methanesulfonate, [BHEDMA][MeSO₃], II, was a gift from Professor T. J. McCarthy. 1-Butyl-1-methylpyrrolidinium dicyanamide, [BMPyr][DCA], IV, was acquired from IoLiTec with mass fraction purity >98%. Their molecular weights and viscosities at room temperature, according to the suppliers, are shown in Table 1. The structures of the ILs are shown in Figure 1. All of the ionic liquids were dried by being

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Table 1. Physical Properties of the Ionic Liquids and Water at Room Temperature

	I	II	III	IV	V	H ₂ O
MW (g/mol)	236.29	229.29	226.02	208.31	108.1	18.02
viscosity (Pa·s)	0.107	2.34	0.28	0.05	0.028	0.001
surface tension (mN/m)	48.7 ± 0.5 (N = 37)	64.5 ± 0.5 (N = 28)	44.7 ± 0.5 (N = 15)	53.3 ± 0.3 (N = 7)	47.5 ¹⁹	72.8

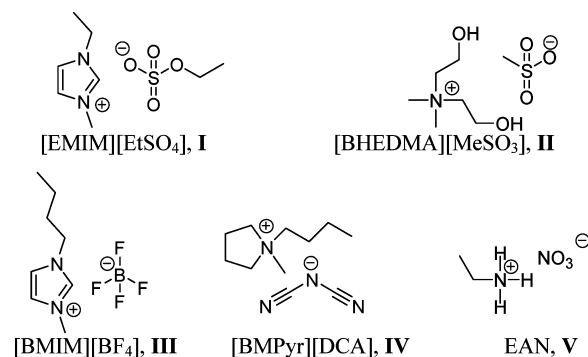


Figure 1. Structures of the ionic liquids considered in this study.

heated at 70 °C under vacuum for 2 days. IV was purified following the procedure described in Lockett et al.¹⁷ The purity of the neat ionic liquids and selected surfactants was assessed by ¹H NMR or ¹³C NMR and did not reveal any impurities. These findings were also confirmed by X-ray photoelectron spectroscopy (XPS) control experiments (see ref 18 and Table S1, Supporting Information).

Surfactants. Dodecyltrimethylammonium bromide (C₁₂TAB) (99%) and hexadecyltrimethylammonium bromide (C₁₆TAB) (>99%) were purchased from Fisher. Hexyltrimethylammonium bromide (C₆TAB) (>98%), octyltrimethylammonium bromide (C₈TAB) (>98%), decyltrimethylammonium bromide (C₁₀TAB) (>98%), and tetradecyltrimethylammonium bromide (C₁₄TAB) (>99%) were purchased from Sigma. All surfactants were used as received.

Surface Characterization. Krafft temperatures were determined by visual observation of clear glass vials containing 1 mL of IL and varying amounts of surfactant.²⁰ The IL–surfactant mixtures were slowly heated with vigorous shaking. The temperature at which the surfactant was completely dissolved was recorded. This method, while not particularly accurate, has the advantage of being simple and easy to perform.

Surface tension was measured by the Wilhelmy method using a Micro Trough XS (Kibron, Inc.) and is especially suited for high-temperature experiments as compared to pendant-drop or bubble methods. At room temperature, all four ionic liquids have relatively high interfacial tensions relative to those of traditional organic solvents but much lower than that of water (Table 1). Our experimental values are in good agreement with those of the literature, when available.^{21–24}

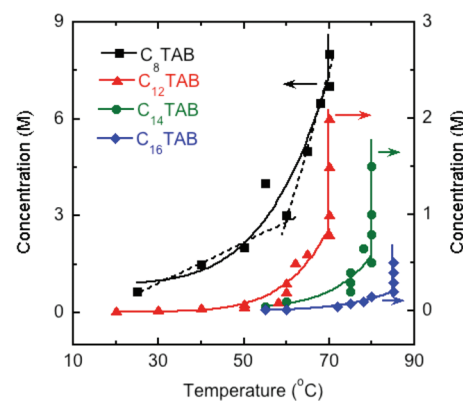
For room-temperature isotherms, in-house reverse osmosis (RO) water was passed through a 0.22 μm filter and then used to dissolve the surfactants. After dissolution, the solutions were heated to 50 °C to make stock solutions, which were subsequently diluted to the appropriate concentrations as needed. Approximately 300–500 μL of RO water, I, or II was examined as the subphase in a metal alloy plate containing Teflon-lined wells with a fixed area of 2.9 cm². To determine the effect of added surfactant, ~5–40 μL of surfactant solution was applied dropwise to the surface of the IL. Surface tensions were measured after an equilibration time of 15 min. We note that although water is introduced into the system, it is always less than 12% by volume and does not significantly alter the bare interfacial tension.^{25,26}

For high-temperature isotherms, surfactants were dissolved directly in the ILs at elevated temperature. Surfactant–IL solutions (300 μL) with different concentrations were applied on an aluminum plate with glass wells. The temperature was controlled and monitored by using a

hot plate placed underneath the multiwell plate and an Omega HH506RA multilogger thermometer probe in the well of interest.

RESULTS AND DISCUSSION

The Krafft temperature T_k corresponds to a point of phase change below which a charged surfactant remains in solidlike form, while above which its solubility rises sharply.²⁷ At the Krafft point there is an equilibrium among this ordered (but solvated) phase, dispersed monomers, and micellar structures. To obtain the cmc of the surfactants in the ionic liquids, measurements must be made above the Krafft temperature. Plots of surfactant concentration versus temperature (Figure 2

Figure 2. Solubility diagram for octyl-, dodecyl-, tetradecyl-, and hexadecyltrimethylammonium bromides in [BMIM][BF₄], III.

and Figures S1 and S2, Supporting Information) yield the Krafft temperature T_k . In the case of gradual changes in solubility, T_k is identified from the transition between linear regimes. Figure 2 shows the solubility behavior for C₈TAB, C₁₂TAB, C₁₄TAB, and C₁₆TAB in III.

Table 2 summarizes the Krafft temperature chain length dependence of C_nTAB in the ILs and water. The Krafft

Table 2. Krafft Temperature (°C) of C_nTAB in I, III, IV, V, and Water

chain length	I	III	IV	V ¹⁹	H ₂ O ²⁸
6			80 ± 2.5		
8	60 ± 2.5	60 ± 2.5			<0
12	70 ± 2.5	70 ± 1	65 ± 2	20	<0
14	75 ± 2.5	80 ± 2	65 ± 2	34	~0
16	85 ± 2.5	85 ± 2	70 ± 2	48	24

temperatures for C_nTAB in II are below room temperature for all surfactant chain lengths. I and III were found to have higher Krafft temperatures with increasing chain length of the surfactant, which is the same trend as reported in the literature for V¹⁹ and H₂O.²⁸ Interestingly, IV does not seem to obey this chain length trend.

Generally speaking, by increasing the length of the surfactant alkyl chain, van der Waals interactions are also increased. As a

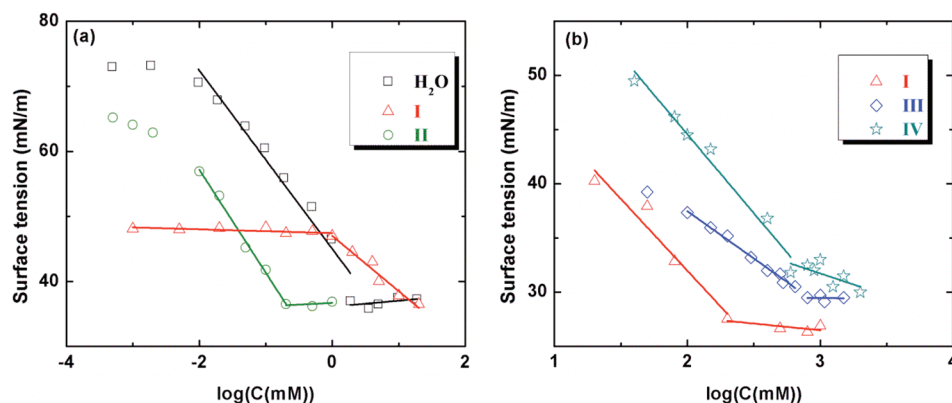


Figure 3. Isotherms of C_{14} TAB in different subphases and at different temperatures: (a) at 20 °C, H_2O , I, and II; (b) at 90 °C, I, III, and IV.

result, the Krafft temperature is shifted higher. Besides van der Waals interactions between alkyl chains, the solution conditions also affect the Krafft temperature. With increasing counterion concentration, Krafft temperatures are generally increased, irrespective of whether the counterions are introduced from the surfactant itself²⁹ or by addition of the corresponding salt.^{27,30} In other words, the increased ionic strength of the solvent phase will screen repulsive electrostatic interactions between the charged surfactants, thereby favoring an ordered (solidlike) phase and increasing T_k . The result is an inhibitory “counterion effect” on solubility/micellization²⁹ because as the surfactant concentration increases, so does the counterion concentration. If we assume that the solubility of the surfactants will be intrinsically lower for longer chains, then as the chain length increases there is a competition between the decreased counterion concentration (lowering T_k) and the increasing van der Waals interactions (raising T_k). It is possible that for trimethylammonium surfactants in IV, the counterion effect dominates and would give the observed trend in Table 2.

Another relevant example is the case of added alcohol, which has been shown to depress the Krafft temperature.³¹ It is therefore not surprising that II, with its two hydroxyl-terminated chains, displays the lowest Krafft temperatures out of the four ILs studied here. It becomes apparent that the interplay of the above effects makes it a nontrivial matter to anticipate Krafft temperatures for surfactants in ILs. However, the chemical diversity of ILs should facilitate greater control over this important interfacial property.

When a surface becomes saturated with surfactant monomers, it becomes favorable for micelles to form in the bulk solution. This process occurs in both water and IL systems. Plots of surface tension as a function of concentration for C_{14} TAB at 20 and 90 °C in different subphases are given in parts a and b, respectively, of Figure 3. As can be seen, the surface tension decreases upon addition of surfactant from the value of pure solvent to a final value which remains more or less constant. This transition is identified as the cmc of the surfactant. Note that C_{14} TAB in I at 20 °C does not show a cmc (red open triangles in Figure 3a) because its Krafft temperature is much higher than room temperature. At room temperature, the viscosity of neat IL I is roughly 100 times larger than that of water (Table 1). Moreover, at high surfactant concentration, this particular surfactant–IL solution appeared to become crystalline and was too viscous for its surface tension to be reliably measured. However, when the same experiment was performed for C_{14} TAB in I at 90 °C, a cmc could be clearly identified (red open triangles in Figure 3b). The above effects

are presented as an example of what is characteristic surfactant behavior above and below the Krafft temperature.

By maintaining a fixed isotherm temperature of 90 °C, comparisons of interfacial properties are facilitated. Figures 4

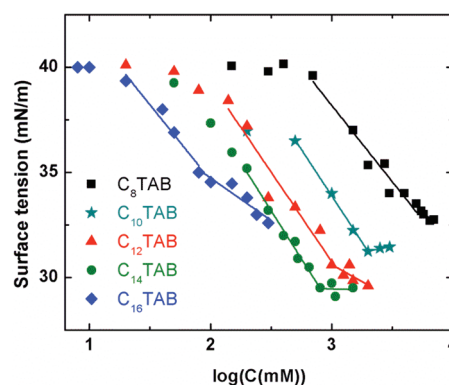


Figure 4. Isotherms of C_n TAB in $[BMIM][BF_4]$, III, at 90 °C.

and S3 and S4 (Supporting Information) summarize high-temperature (i.e., 90 °C) isotherms of alkyltrimethylammonium bromides in III, I, and IV, respectively. As the alkyl chain length of surfactants increases, there is a clear shift to the left while the surface tension is lowered (Figure 4). It is apparent that, with increasing chain length, the solution will have a lower cmc and corresponding surface tension γ_{cmc} which is similar to that of aqueous systems. From these isotherms, a series of valuable surface properties can be elucidated, such as the effectiveness of surface tension reduction Π_{cmc} , surface excess concentration at saturation Γ_1 , and surface area per molecule A_1 at the air–liquid interface (Tables 3 and S2 and S3, Supporting Information).

Table 3. Surface Properties of C_n TAB in $[BMIM][BF_4]$, III, at 90 °C

chain length	cmc ^a (mM)	cmc ^b (mM)	γ_{cmc} (mN/m)	Π_{cmc} (mN/m)	Γ_1 ($\mu\text{mol}/\text{m}^2$)	A_1 (\AA^2)
8	4000	4450	33.5	7.1	0.65	256.5
10	2500	1990	31.3	9.7	0.78	211.7
12	1000	1060	30.5	9.8	0.76	218.9
14	800	800	29.5	10.5	0.81	204.1
16	150	90	34.9	4.7	0.64	260.0

^aEstimated from Figure 2. ^bCalculated from Figure 4.

The cmc can be estimated from solubility phase diagrams (e.g., Figure 2) by identifying the first sudden and rapid rise in solubility as a function of the temperature. The cmc can also be calculated from the intersection of two linear regimes of the isotherms in Figure 4. From Table 3, it is evident that the cmc's obtained from either method are in good agreement with each other.

Π_{cmc} is defined by $\Pi_{\text{cmc}} = \gamma_0 - \gamma_{\text{cmc}}$, where γ_0 is the surface tension of the pure solvent and γ_{cmc} is the surface tension of the solution at the cmc. This parameter indicates the maximum reduction of surface tension for a pure solvent caused by the addition of surfactant and hence reflects the effectiveness of the surfactant. Because γ_0 values of the neat ILs are somewhat lower than for water, and their γ_{cmc} values are comparable, the calculated Π_{cmc} values are found to be smaller than for water.

A typical trend is that, as the chain length increases, the saturated surface tension γ_{cmc} is lowered and therefore the corresponding surface pressure at the cmc is higher. However, the surfactant with the longest chain length, C_{16}TAB , appears to disobey the trend because it has the largest γ_{cmc} and lowest Π_{cmc} . One possible reason is that the plateau in surface tension has not yet been reached (Figure 4) or that the Krafft temperature for C_{16}TAB in **III** is very near the temperature of the isotherm, resulting in a relatively unstable solution. This latter notion is supported by the good consistency with the trend for **IV** (Table S3, Supporting Information), where C_{16}TAB has a much lower Krafft temperature (Table 2) than for **I** and **III**.

The surface excess concentration Γ_1 and the interfacial area per surfactant molecule A_1 were calculated by use of the appropriate Gibbs equation.³² Γ_1 is a useful measure of the effectiveness of adsorption of the surfactant, and A_1 provides information on the degree of packing and the orientation of the adsorbed surfactant molecule.

For solutions of singly charged ionic surfactant ($m = 2$)^{32,33} in the absence of any other solutes, $\Gamma_1 = -(1/mRT)(\partial\gamma/(\partial \ln C))_T$, and $A_1 = 1/\Gamma_1$. From Table 3, we can see Γ_1 generally increases from C_8TAB to C_{14}TAB in **III** while A_1 decreases. This trend means that, with increasing chain length, more surfactant molecules are adsorbed when the surface is saturated, resulting in a higher packing density and a lower γ_{cmc} . For the same reasons discussed above, C_{16}TAB displays an atypical surface excess concentration and surface density.

Figure 5 shows the linear relationship of $\log(\text{cmc})$ versus chain length in all ILs and water. The data for ethylammonium

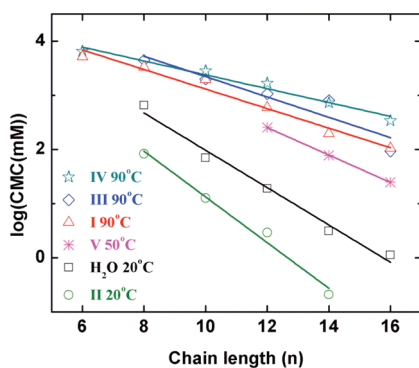


Figure 5. Dependence of the cmc on the surfactant chain length in different IL solvents (at $T > T_k$). Note that the data for **V** are taken from ref 19.

nitrate, **V**, were obtained from a previously published report.¹⁹ While many studies of aqueous solutions have already pointed out the relationship between $\log(\text{cmc})$ and chain length,^{19,34,35} in IL solvents such an analysis must be reconsidered. In addition, we aimed to understand why the cmc's of charged surfactants in ILs can be both larger (e.g., **I**) and smaller (e.g., **II**) than in water, especially when it is observed that ILs generally give higher cmc's.^{11–15,36} It would obviously be of great importance to understand the cmc and solubility behavior of the same surfactant in different solvents.

Part of the answers to the above questions can be found by a mean-field consideration of solubility.¹⁰ Considering a two-phase system where the molecular interaction energy of a particular type of molecule or particle has different values, μ_1^i and μ_2^i , if one phase ($i = 1$) is a pure liquid ($\log X_1 = 0$), from the well-known Boltzmann distribution, we have

$$\begin{aligned} X_2 &= X_1 \exp[-(\mu_2^i - \mu_1^i)/kT] \\ &= X_1 \exp(-\Delta\mu^i/kT) \end{aligned} \quad (1)$$

where X_1 and X_2 are the equilibrium concentrations of the molecules in the two phases. In general, $\Delta\mu^i$ can be any type of interaction that contributes to the chemical potential. We assume the simplest intermolecular interaction to be

$$\Delta\mu^i \approx A\gamma_i \quad (2)$$

where γ_i is the interfacial energy of the surfactant–solvent interface and A is the interfacial area per surfactant. Extending this analysis to account for other intermolecular interactions (e.g., dispersion, induction, etc.) is limited to crude estimates due to a lack of detailed IL characterization data and was therefore not pursued further. Combining the above two equations gives

$$\log X_s = -\Delta\mu^i/kT = -\frac{\gamma_{12}}{kT}A \quad (3)$$

where X_s , the quotient of X_2 and X_1 , is the solubility of the surfactant. Given the structure of the surfactants, we assume the area A is proportional to the chain length and therefore $\log X_s$ is also proportional to the chain length n .

Because the cmc is more or less independent of temperature above T_k , the cmc can be considered to be equal to the solubility under these conditions. Therefore, eq 3 can be used to explain the linear relationship between $\log(\text{cmc})$ and the chain length in Figure 5:

$$\log(\text{cmc}) \approx \log X_s \approx -\frac{\gamma_{12}}{kT}n \quad (4)$$

Here, the interfacial energy γ_{12} is expressed³⁷ as

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\Phi_{12}\sqrt{\gamma_1\gamma_2} \quad (5)$$

where γ_1 and γ_2 are the surface tensions of pure solvent and pure surfactant, respectively. The quantity Φ_{12} is a factor accounting for different types of interactions (e.g., dispersion, induction, etc.) across the interface. Because the pure surfactants used here are solids, γ_2 is estimated from the surface tension of liquid hydrocarbons with similar chain lengths.

For the interface of water with hydrocarbons, it is well-known that γ_{12} and γ_2 for the octane–water system are 50.8 and 21.8 mN/m, respectively.³⁸ We assume γ_2 for the C_nTAB series used here is similar to the surface tension of pure octane.

Therefore, the proportionality constant can be determined from eq 4, with Φ_{12} for the octane–water system being obtained from eq 5. By using the calculated constant and the slopes in Figure 5, γ_{12} and Φ_{12} for all five ILs can be calculated (Table 4).

Table 4. Summary of cmc Analysis of the Data from Figure 5

	I	II	III	IV	V	H ₂ O
γ_{12} (mN/m)	30.6	62.2	31.9	21.4	40.5	50.8 ^{37–39}
Φ_{12}	0.57	0.32	0.51	0.76	0.41	0.55

Overall, it seems that the larger the interfacial tension γ_{12} , the lower the cmc. This correlation supports the notion that interfacial energy is the major factor affecting the aggregation process for both aqueous and ionic liquid solvents. We note that such a conclusion would not be apparent from inspection of the bare interfacial tensions (Table 1). This view is also consistent with the observation that the cmc for C_nTAB surfactants in II is lower than that in water. The two hydroxyl groups in II result in a much larger interfacial tension with the C_nTAB surfactants and hence show saturation at a relatively lower concentration. At first glance, the validity of our results may seem counterintuitive, since we did not include electrostatic interactions in our mean-field model. However, increasing experimental evidence^{40,41} suggests that the extremely high ionic concentration of ILs is an exceptionally effective screen of electrostatic interactions. We note that such behavior bears a resemblance to the “ideal” behavior of polymer melts, where excluded volume effects cancel.

The Φ_{12} values reflect the *types* of interactions within each phase and across the interface,³⁹ with higher values reflecting greater similarity (and hence increased mutual solubility). Thus, the lowest Φ_{12} value for trimethylammonium surfactants in II is consistent with the lowest observed cmc. Similarly, the largest Φ_{12} value for IV is consistent with the largest observed cmc. It is obvious from eq 5 that Φ_{12} is intimately related to the interfacial tension, and equivalent arguments can be made from that perspective. We note while the general trend can be qualitatively described, there is no obvious reason why the cmc for C_nTAB in I is lower than the cmc for C_nTAB in III. Separate experiments by our group to determine IL polarity using Reichardt's dye⁴² did not indicate substantial differences between I and III (data not shown). Given the small differences between I and III and the uncertainty in each cmc determination, it is simply possible that these cmc values are not statistically distinct. Another reason for the unusual behavior of I may be related to the extent of ion pairing between the specific cation and anion of the IL.⁴³

Equation 4 suggests that directly measuring the interfacial energy between ILs and other materials (e.g., contact angle⁴⁴) would be very useful not only in confirming our results but also in predicting the aggregation and solubility of surfactants in both existing and newly available ILs. As more detailed characterization of ILs becomes available, the effects of additional intermolecular interactions may also be considered.

CONCLUSIONS

In summary, the aggregation and solubility behaviors of charged surfactants in ILs have been investigated and compared to those in water. Temperature is of great importance in both bulk aggregation and surface assembly of surfactants in ILs, as dictated by the solubility phase diagram. Isotherms at room

temperature or high temperature are measured to give a series of useful surface properties, including the chain length dependence of the cmc. These properties give us a better understanding of the surface activity of surfactants in ILs. By using a mean-field approach, we conclude that the interfacial energy is crucial in both solubility and aggregation behaviors. The role of IL chemistry is reflected in the net attractive interactions across the interface. Because interfacial energy appears to be the essential factor, our results suggest that there may be a simple method for choosing ionic liquids with desirable solvation capability and aggregation properties. Finally, we note that there is still room for even further manipulation of interfacial properties: the combination of ILs and water has already been shown to modify the aggregation behavior of particles and surfactants.^{41,45,46}

ASSOCIATED CONTENT

Supporting Information

Table of atomic compositions of neat ILs, solubility phase diagrams for I and IV, high-temperature isotherms for I and IV, and tables of surface properties for I and IV. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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