

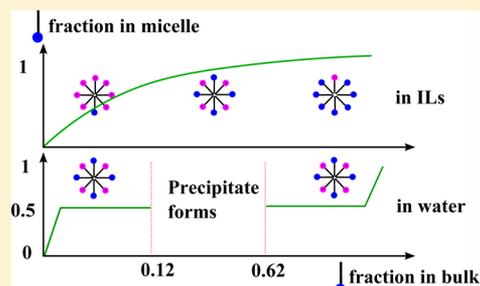
Charge Screening between Anionic and Cationic Surfactants in Ionic Liquids

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Supporting Information

ABSTRACT: The aggregation and interfacial behavior of mixtures of anionic (sodium dodecylsulfate, SDS) and cationic (dodecylammonium bromide, DTAB) surfactants were investigated. A room-temperature ionic liquid (IL) was explored as a solvent for the SDS/DTAB system and compared to water. The critical micelle concentration (cmc) and composition in mixed micelles were determined for both solvents. Our experiments showed nearly ideal mixing of SDS/DTAB over the entire composition range and suggest that charge screening is prominent in ILs. This behavior is in sharp contrast to the strong electrostatic attraction and a multiphase composition gap in water. Two models by Clint and Rubingh, which describe ideal and nonideal micellar behavior, respectively, are discussed on the basis of our results. According to Rubingh's model, the composition of mixed micelles is gradually changing with the bulk composition in ILs but tends to be a 1:1 ratio in water. The results here are further support of the strong charge screening in ionic liquids.



INTRODUCTION

Mixed surfactant systems, including their mixed micelles, exhibit striking changes in their physical properties as compared to single-component surfactants and hence are of great theoretical and practical interest. These systems are encountered in numerous applications for the purpose of separation, foam generation, dispersion, and detergency.^{1,2} On the basis of the type of headgroups in surfactants, various combinations of nonionic/cationic/anionic surfactants have been studied by a number of workers,^{1,3,4} and several models have been proposed to rationalize their behavior.^{5–9} Among them, two widely used models are those of Clint⁵ and Rubingh.⁶ The former describes ideal surfactant mixtures, and the latter uses regular solution theory to describe nonideal surfactant mixtures. Among all of the possibilities, binary mixtures of oppositely charged surfactants (i.e., cationic and anionic) are of special interest because of their strong electrostatic interaction in water and thus enhanced surface activity.

It is known that aqueous solutions of surfactant mixtures can have critical micelle concentrations (cmc) either lower⁶ or higher¹⁰ than that of each individual surfactant because of specific interactions (synergistic or antagonistic) between surfactants within micelles. These interactions as well as the surfactant composition strongly affect the phase behavior of anionic/cationic surfactant mixtures. Therefore, a better understanding of the specific interactions and the resulting micellar composition and interfacial behavior is of central importance.

Most of the previous work on mixed surfactant systems has been concerned with aqueous solutions. However, over the past few years, amphiphiles in ionic liquids (ILs) have received increasing attention.^{11–13} Ionic liquids are extraordinary

solvents with potential opportunities for numerous applications; for example, ionic liquids could be useful for contact angle probe fluids or catalysis.^{14,15} To our knowledge, excluding one study on nonionic surfactant mixtures in ILs,¹⁶ the aggregation and phase behavior of ionic surfactant mixtures in ionic liquids have not been reported. Our previous work¹⁷ as well as other reports¹⁸ has suggested that in ionic liquids the electrostatic interactions between single-component charged surfactants are negligible because of strong charge screening. Here we use the ionic liquid 1-ethyl-3-methyl imidazolium ethylsulfate [EMIM][EtSO₄] to explore its influence on anionic/cationic surfactant mixtures. [EMIM][EtSO₄] was chosen as a model ionic liquid because it has been extensively studied. A direct comparison between aqueous and ionic liquid solutions would not only help us better understand the specific interactions between surfactants but also could broaden the application range for both mixed surfactants and ionic liquids.

EXPERIMENTAL SECTION

Materials. 1-Ethyl-3-methyl imidazolium ethylsulfate [EMIM][EtSO₄] was obtained from Sigma (>95%). This ionic liquid was dried by holding at 70 °C under vacuum for 2 days. The purity of the neat ionic liquid and selected surfactants was assessed by ¹H NMR or ¹³C NMR and did not reveal any impurities. These findings were also confirmed by XPS control experiments.¹⁹ Dodecyltrimethylammonium bromide (DTAB) (99%) and sodium dodecylsulfate (SDS) (98+%) were purchased from Fisher. DTAB was purified by recrystallization from an acetone/ethanol mixture,²⁰ and SDS was used as

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received. The structures of the ionic liquid and the two surfactants are shown in Figure S1.

Methods. Surface tension was measured by means of the Wilhelmy method using a Micro Trough XS (Kibron, Inc.). For room-temperature isotherms in water, in-house reverse osmosis (RO) water was passed through a 0.22 μm filter and then used to dissolve the surfactants. For surfactant mixtures, stock solutions of cationic and anionic surfactants were mixed at certain molar ratios and kept at room temperature for over 48 h until the solution became completely clear. For high-temperature isotherms in [EMIM][EtSO₄], surfactants or surfactant mixtures were dissolved directly in [EMIM][EtSO₄] at elevated temperature. After dissolution, solutions were subsequently diluted to appropriate concentrations as needed. Surfactant solutions (300 μL) with different concentrations were applied on an aluminum plate with glass wells. Surface tensions were measured after an equilibration time of 30 min. 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. All concentrations here are presented as millimoles of surfactant per liter of solvent (mmol/L). In the case of surfactant mixtures, the concentration is based on the moles of the total surfactant alkyl chain to facilitate comparison.

RESULTS AND DISCUSSION

To obtain the cmc of the surfactants in solutions, measurements must be above the Krafft temperature, T_k .^{21,22} T_k values were determined by visual observation as described in our previous study,¹⁷ and the summary of T_k values is listed in Table S1. In general, the T_k values for surfactant–water solutions are below room temperature. However, all of the T_k values of our surfactant–IL solutions are above room temperature but below 90 °C. Therefore, isotherms were measured at 20 °C in water and at 90 °C in [EMIM][EtSO₄]. Because Shinoda²¹ and Schick²³ have pointed out that the cmc is only a weak function of temperature, a comparison of the two systems at different temperatures is reasonable. All isotherms are shown in Figures S2 and S3, and these were used to determine cmc values from the intersection of linear fits. For each isotherm, we constructed several pairs of linear fits (generally three) by using varying numbers of isotherm data points. This approach allowed us to calculate a mean value for the cmc and its standard error, and these are shown in Figure 1.

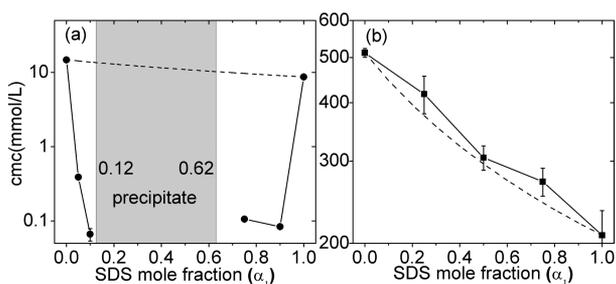


Figure 1. Critical micelle concentrations (cmc_{12}) for SDS/DTAB mixtures in (a) water (●) at 20 °C and (b) [EMIM][EtSO₄] (■) at 90 °C. The dashed lines represent $\text{cmc}_{12}^{\text{id}}$ from eq 1.

We emphasize that the gradual nature of the transition in [EMIM][EtSO₄] (Figure S3) reflects surface activity behavior that is different from that of water. Probe fluorescence (Figure S4) and ¹H NMR (Figures S5 and S6) were used as independent cmc measures of selected samples, and all of the data are in good agreement.

Clint⁵ has shown that for an ideal binary surfactant mixture the critical micelle concentration $\text{cmc}_{12}^{\text{id}}$ can be calculated from

single-component values, cmc_1 and cmc_2 , and the mole fraction of a component in the mixture, α_1 , as described by eq 1. Herein we denote SDS as component 1 and DTAB as component 2.

$$\frac{1}{\text{cmc}_{12}^{\text{id}}} = \frac{\alpha_1}{\text{cmc}_1} + \frac{(1 - \alpha_1)}{\text{cmc}_2} \quad (1)$$

When $\text{cmc}_{12}^{\text{id}}$ and the experimentally determined cmc for the mixture (cmc_{12}) are different, a nonzero interaction between the two components exists. From eq 1, ideal mixtures are predicted to have a cmc intermediate between that of the two single-component cmc values.

Figure 1 plots cmc_{12} and $\text{cmc}_{12}^{\text{id}}$ of SDS/DTAB mixtures in both water and [EMIM][EtSO₄]. We have to note that in water the range $0.12 < \alpha_1 < 0.62$ corresponds to a multiphase region;²⁴ therefore, in this concentration range, cmc_{12} is not applicable. In sharp contrast to ideal mixing behavior (Figure 1a, dashed line), the cmc_{12} values in water are much lower than those of the single components because of the strong attractive electrostatic interaction between the oppositely charged headgroups. This so-called synergistic effect²⁵ is also observed for the surface activity of mixtures in water. If we exclude the single-component data ($\alpha_1 = 0$, $\alpha_1 = 1$) in water, the trend in cmc_{12} is generally decreasing with an increasing SDS mole fraction (Figure 1a). This gradual decrease might be due to the fact that $\text{cmc}_1 < \text{cmc}_2$; that is, pure SDS has a lower cmc than does pure DTAB in water.

In contrast to the U-shaped cmc_{12} behavior of the SDS/DTAB mixtures in water, cmc_{12} values for the same mixtures in [EMIM][EtSO₄] are intermediate between the two single-component cmc values (Figure 1b). The cmc_{12} values in [EMIM][EtSO₄] are also clearly much higher than those in water because of the lower solvophobic interaction between the alkyl chain and IL as compared to the hydrophobic interaction between the alkyl chain and water.^{11,26} Furthermore, the cmc_{12} curve in [EMIM][EtSO₄] is only slightly above the ideal $\text{cmc}_{12}^{\text{id}}$ curve (dashed line) calculated from eq 1, which is due to weak repulsive interactions between the components in the mixed micelle.^{27,28} In addition, there is no multiphase composition gap in [EMIM][EtSO₄], which broadens the application of anionic/cationic surfactant mixtures. As compared to water, the different cmc behavior indicates a dramatic change in the interactions between surfactant molecules in ILs. We believe this behavior is due to the cations and anions from both the IL and the surfactant creating a “sea of ions” that screens electrostatic interactions between them.¹⁸ This charge screening, to a much lower degree, is a well-known salt effect in aqueous solution.²⁹

The Debye screening length, the distance beyond which Coulomb interactions can be essentially ignored,²⁹ lends support to highly effective charge screening in IL systems. In the case of neat [EMIM][EtSO₄], the Debye length is about 0.16 nm, which is even shorter than the radius of surfactant alkyl chains (0.2 nm). In contrast, the Debye length of a 1 mM NaCl aqueous solution is about 10 nm. Even if we recognize the limits of applicability of Debye theory,³⁰ this comparison argues that the electrostatic interaction in IL is much weaker than in water and can be largely ignored. Such a strong charge screening effect would result in the surfactant–IL solution being close to ideal, as is observed in Figure 1b.

In Figure 2, the surface tension at cmc (γ_{cmc}) of SDS/DTAB mixtures in water (20 °C) and [EMIM][EtSO₄] (90 °C) is plotted against the SDS mole fraction in surfactant mixture α_1 .

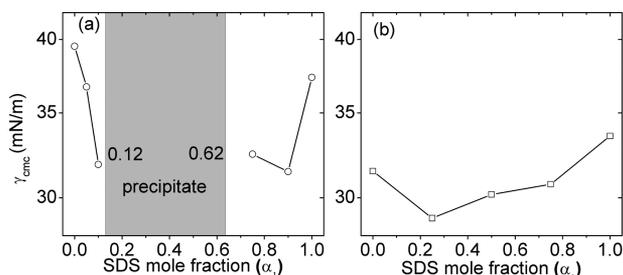


Figure 2. Surface tensions at cmc (γ_{cmc}) for SDS/DTAB mixtures in (a) water (O) at 20 °C and (b) [EMIM][EtSO₄] (□) at 90 °C.

In both water and [EMIM][EtSO₄], mixtures always show a higher surface activity than the single components as seen by the lower γ_{cmc} of the mixtures (Figure 2). We note that for [EMIM][EtSO₄], γ_{cmc} is not monotonic with α_1 as is cmc_{12} . This trend indicates different behavior at the air–liquid interface and the bulk solution. The mixed monolayers at the interface have better packing than single-component surfactants, as determined by the maximum surface excess concentration (Γ_m) (Table S2), and hence have lower γ_{cmc} values. Comparing the two solvents (Figure 2), the lower γ_{cmc} in [EMIM][EtSO₄] than in water is probably due to the higher measurement temperature.

To obtain more information on the micellar level, compositions in mixed micelles were calculated and compared to the two models for both solvents. From the Clint ideal mixing model,⁵ the SDS fraction in the mixed micelles at the cmc (x_1^{id}) can be obtained after calculating $\text{cmc}_{12}^{\text{id}}$:

$$x_1^{\text{id}} = \frac{\alpha_1 \text{cmc}_{12}^{\text{id}}}{\text{cmc}_1} \quad (2)$$

Rubingh^{6,27} extended the ideal mixing model by using regular solution theory, and this approach also permits the calculation of the SDS fraction in mixed micelles at the cmc (x_1) by numerically solving eq 3:

$$x_1^2 \ln \left[\frac{\alpha_1 \text{cmc}_{12}}{x_1 \text{cmc}_1} \right] = (1 - x_1)^2 \ln \left[\frac{(1 - \alpha_1) \text{cmc}_{12}}{(1 - x_1) \text{cmc}_2} \right] \quad (3)$$

The characteristic of this nonideal model is the net interaction parameter β for surfactants within mixed micelles:

$$\beta = \frac{\ln(\alpha_1 \text{cmc}_{12} / x_1 \text{cmc}_1)}{(1 - x_1)^2} \quad (4)$$

Values of the interaction parameter β were calculated using eq 4 for both water and [EMIM][EtSO₄] solvents. The sign and magnitude of β for water and [EMIM][EtSO₄] (Table S3) indicate strong attractive and weak repulsive interactions between surfactant molecules, respectively. The difference in the interactions is consistent with the different aggregation and surface activity behavior in water versus IL.

The calculated x_1^{id} and x_1 in water and [EMIM][EtSO₄] are plotted against α_1 in Figure 3. In water, irrespective of the SDS mole fraction in the mixture, the SDS mole fraction in the mixed micelles is always close to 0.5, with a slight ascending trend (Figure 3a). This tendency toward a 1:1 ratio in the mixed micelles is presumably due to the strong electrostatic attraction between cationic and anionic headgroups in water. On the contrary, in [EMIM][EtSO₄] x_1 is always quite close to x_1^{id} (Figure 3b). This result again agrees with the nearly ideal

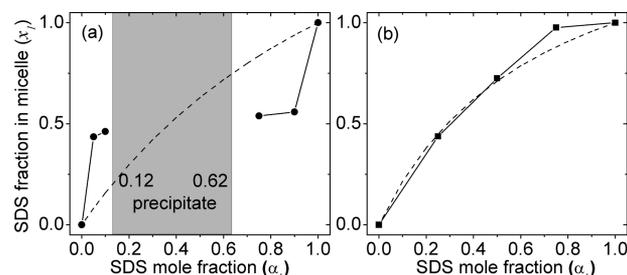


Figure 3. SDS mole fraction in micelles (x_1) from eq 3 for SDS/DTAB mixtures in (a) water (●) and (b) [EMIM][EtSO₄] (■), evaluated from eq 3 at the cmc. The dashed lines represent x_1^{id} from eq 2.

behavior of mixed surfactants in [EMIM][EtSO₄] and suggests that this system is not strongly driven by electrostatic attractions. Moreover, x_1 is always higher than α_1 , which means that SDS is more prone to form micelles than DTAB in [EMIM][EtSO₄]. This difference in micellization ability can be confirmed by the lower cmc value of pure SDS ($\alpha_1 = 1$) as compared to that of pure DTAB ($\alpha_1 = 0$) in [EMIM][EtSO₄] (Figure 1b). Cui and co-workers³¹ recently suggested that mixed surfactants do not aggregate simultaneously; rather, the component with the lower cmc aggregates first, and the second component joins these existing micelles upon reaching its own cmc, which results in mixed micelles having a composition that differs from the bulk.

CONCLUSIONS

The effect of an SDS/DTAB mixture composition on aggregation and interfacial behavior in [EMIM][EtSO₄] has been investigated and compared to that of water. In both water and [EMIM][EtSO₄], the mixtures always show higher surface activity than that of the single component because of better interfacial packing, but they have very different micellar behavior in the two solvents. In [EMIM][EtSO₄], nearly ideal mixing of the two oppositely charged surfactants was observed over the entire composition range. The behavior in [EMIM][EtSO₄] is in sharp contrast to that of water, where the strong electrostatic attraction between the two oppositely charged surfactants dominates their aggregation behavior, resulting in a composition gap because of precipitation. Our experiments suggest that charge screening in [EMIM][EtSO₄] is quite strong because of its extremely high charge density. A small deviation of cmc_{12} from ideal values indicates a weak repulsion between the surfactant molecules within micelles, supported by the model of Rubingh. This study could significantly broaden the potential application of mixed micelles in ILs where specific conditions are demanding (e.g., high temperature, low pressure, and broad composition range).

ASSOCIATED CONTENT

Supporting Information

Structures of surfactants and ionic liquid, table of Krafft temperatures, isotherms of SDS/DTAB in both water and ionic liquid, fluorescence and NMR data for cmc determinations, and tables of maximum surface excess concentrations and Rubingh interaction parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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