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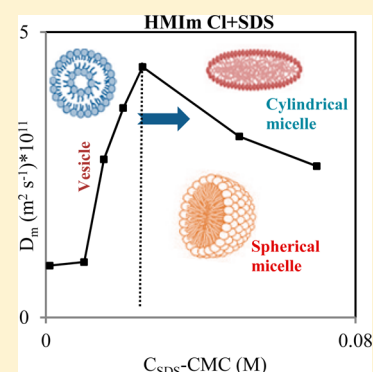
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Modifying Effect of Imidazolium-Based Ionic Liquids on Surface Activity and Self-Assembled Nanostructures of Sodium Dodecyl Sulfate

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S Supporting Information

ABSTRACT: The effect of four cationic ionic liquids (ILs), 1-butyl-3-methylimidazolium chloride (BMImCl), 1-butyl-3-methylimidazolium bromide (BMImBr), 1-hexyl-3-methylimidazolium chloride (HMImCl), and 1-hexyl-3-methylimidazolium bromide (HMImBr) on surface activity and micellization of an anionic surfactant, sodium dodecyl sulfate (SDS), is studied. The thermodynamic data on micellization and surface adsorption are obtained from tensiometry and conductometry. The applicability of UV–visible spectroscopy to study of SDS/IL systems is also investigated using Crystal Violet as the probe. Cyclic voltammetry, dynamic light scattering, and TEM imaging are employed to investigate the size and morphology of aggregates. According to the findings, addition of butyl-chained ILs to aqueous SDS results in only a slight gradual increase in average aggregate size whereas the size of SDS assemblies are dramatically increased upon addition of hexyl-chained ILs. It is proposed that BMIm⁺ cations of the IL undergo Coulombic attractive interactions with anionic headgroups adsorbed at the micellar surface in aqueous SDS whereas HMIm⁺ interact through hydrophobic chain–chain attractions as well. Thus, mixed micellization results in formation of vesicles. A micellar phase change from vesicles to micelles takes place at higher [SDS]/[IL] ratios. All of these processes are successfully tracked by the employed techniques.



1. INTRODUCTION

Surfactants are widely used in various industries such as oil industry, food and pharmaceuticals industry, textiles, ink and paint industry, cosmetics industry, agrochemicals industry, etc. as drug delivery systems, wetting agents, emulsifiers, dispersants, stabilizers, and foam makers.¹ For a better performance, modification of their properties including interfacial activity and aggregate size and morphology is of great importance to industrial applications, especially to the pharmaceuticals industry where surfactant aggregates, micelles or vesicles/liposomes, may serve as a drug delivery system.² Such modifications can be made through changing the surfactants' own structural properties^{3,4} or mixing them with each other^{5–7} as well as with additives like salts and different organic compounds.^{8–14}

Among these additives, ionic liquids (ILs) have been investigated on a larger scale because of their unique characteristics and widespread industrial use. Low toxicity, ability to dissolve many organic and inorganic compounds, low vapor pressure, and nonflammability are among their impressive characteristics which make ILs good green solvents for various purposes such as separation and extraction,^{15,16} chemical synthesis and catalysis,^{17–19} and biochemical and biological researches.^{20–22} On this basis, numerous studies have been carried out to understand the behavior of surfactants in various IL solvents.^{23–26} On the other hand, ILs (especially

those with long hydrophobic chains) have been reported to show amphiphilic properties in aqueous solution.^{27–29} Aside from the electrostatic interaction of charged head groups, ILs' hydrophobic chains may effectively interact with surfactants and modify their aggregation behavior. Thus, the attitude of IL molecules toward surfactants is expected to be quite different from that for organic and inorganic salts.^{30,31} Many researchers have studied the effect of ILs as additives on aqueous solutions of various surfactants.^{32–34} Although simple salts usually enhance surfactants' surface adsorption and micellization, IL molecules have been observed to act as either a cosolvent or a cosurfactant additive. A specific surfactant may even show such a dual behavior in different concentration ranges.^{34,35} Generally, the overall behavior of ILs toward surfactants is determined by their electrostatic and hydrophobic interactions which are, in turn, controlled by the structural properties of IL molecules including headgroup and counterion type and hydrophobic chain length.^{30,36–38} Besides, some ionic liquids like imidazolium-based ILs (IBILs) are well-known for forming hydrogen bonding with water as well as with counterions^{39,40} and this can also influence IL's interaction with surfactants considerably^{30,41} and make it even more complicated. Thus, it is so difficult to

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make a generalization and prediction about the effect of ILs on interfacial and aggregation properties of surfactants that any IL/surfactant mixture should be studied separately as a specific case. Because of this complexity, the effect of IL additives on surfactant solutions is still studied by many to shed light on the unknown aspects of such systems.

The present work aims to comprehensively study the effect of four imidazolium-based ionic liquids (IBILs) with different chain lengths and anion types (Figure 1) on the surface activity, self-aggregation behavior, and aggregate morphology of the anionic surfactant, sodium dodecyl sulfate (SDS), in aqueous solution. A few researchers have previously studied the surface activity and micellization in some aqueous SDS/IBIL mixtures from the viewpoint of thermodynamics,^{29,37,42,43} but the effect of IBILs on SDS micelles size and morphology has not been investigated sufficiently so far. In this paper, tensiometry and conductometry techniques are employed to obtain the thermodynamic data on surface adsorption and micellization of the SDS/IL systems. The applicability of UV–visible spectroscopy to SDS/IL systems using a cationic dye probe is also investigated. Finally, the sizes of aggregates are measured by cyclic voltammetry using an electroactive probe as well as by dynamic light scattering. The morphology of aggregates is then investigated by means of transmission electron microscopy. This study is expected to provide a comprehensive view of the interaction of imidazolium-based ionic liquids with SDS as well as of similar systems.

2. EXPERIMENTAL SECTION

2.1. Materials. 1-Butyl-3-methylimidazolium chloride (BMImCl), 1-butyl-3-methylimidazolium bromide (BMImBr), 1-hexyl-3-methylimidazolium chloride (HMImCl), and 1-hexyl-3-methylimidazolium bromide (HMImBr) were prepared using the method described in the literature.⁴⁴ The characterization data for the synthesized ILs are reported in our previous works.^{30,45} For synthesis, all manipulations were performed in a nitrogen atmosphere under standard conditions and all of the used solvents were obtained commercially. Sodium dodecyl sulfate (SDS) with a purity of 99%, ferrocene (bis(η^5 -cyclopentadienyl)iron), NaCl, and NaBr were all obtained from Merck. Crystal Violet (tris(4-(dimethylamino)phenyl)-methylum chloride) was obtained from Fluka. The molecular structures of all materials are shown in Figure 1. Ferrocene was used without further recrystallization. Doubly distilled water

was used for sample preparation and dilution. The stock solutions of ILs with the concentrations of 0.05, 0.1, 0.5, and 1% (w/w) were prepared and also used for preparation of concentrated SDS solutions. All titrations were carried out using Hamilton syringes.

2.2. Methods. **2.2.1. Specific Conductivity Measurements.** the electrical conductivity of solutions was measured using a Jenway 4510 conductometer at 298 ± 1 K. After any injection of concentrated SDS solution, the solution was stirred and allowed to equilibrate for 10 min, and then three successive measurements of specific conductivity were performed. The uncertainty of the measurements was $\pm 0.01 \mu\text{S cm}^{-1}$.

2.2.2. Tensiometry. Surface tension measurements were made with a Krüss K12 tensiometer through the Du-Nouüy ring method under atmospheric pressure at 298 ± 1 K. The platinum ring was thoroughly cleaned by acetone and water and then flamed until glowing temperature before each measurement. Here again, the solution was stirred and allowed to equilibrate for 10 min after any injection of the concentrated SDS solutions. In all cases more than three successive measurements were carried out and the standard deviation did not exceed 0.08 mN m^{-1} . The uncertainty of the measurements was $\pm 0.1 \text{ mN m}^{-1}$.

2.2.3. UV–Vis Spectroscopy. Visible absorption spectra were recorded using a Shimadzu 2100 UV–visible spectrometer. A matched pair of glass cuvette with the optical path length of 1 cm was used for control and sample solutions. Solutions were prepared and allowed to equilibrate for 10 min before measurements and their temperature was kept constant at 298 K using a thermostated water bath. The concentration of Crystal Violet was constant at $6.17 \times 10^{-6} \text{ M}$ for all aqueous solutions but $6.17 \times 10^{-5} \text{ M}$ in ethanol. PeakFit v4.12 software was employed for separation of the absorption peaks.

2.2.4. Cyclic Voltammetry. Cyclic voltammetry was performed using a SAMA 500 electrochemical analyzer at 298 ± 1 K. A three-electrode system consisted of a platinum disk electrode (0.0314 cm^2) as the working electrode, a saturated Ag/AgCl reference electrode, and a Pt wire as the counter electrode. All solutions contained 0.05 M NaCl as the supporting electrode. Ferrocene was used as the electroactive probe. A concentrated 50 mM solution of ferrocene was prepared in ethanol (because of its low solubility in water) and then a very small volume of it was added to the sample solutions to obtain a constant final ferrocene concentration of 0.05 mM. It is worth mentioning that the concentration of ferrocene used does not significantly affect the micellization of the surfactants and their mixtures. Electrodes were plunged in solutions for 10 min and then voltammograms were recorded for each solution with a scan rate of 100 mV s^{-1} and the fifth cycles were saved. After each measurement, the surfaces of the working and counter electrodes were cleaned carefully by polishing and washing with nitric acid, acetone, and water.

2.2.5. TEM, DLS, and ζ Potential Measurements. For all techniques, the solutions with certain concentrations were prepared and delivered to the operator. Transmission electron micrographs were recorded on an electron microscope (Zeiss, Model EM-10C) operating at 100 kV. Samples were placed on carbon-coated grids and kept waiting for the solvent to evaporate, and then the micrographs were acquired. Zetasizer Nano (Malvern, MRK825-02, UK) was also employed for dynamic light scattering and zeta potential measurements.

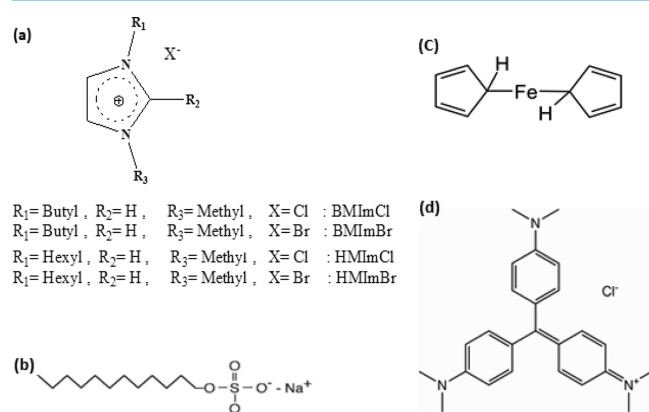


Figure 1. Molecular structure of (a) different imidazolium-based ionic liquids, (b) sodium dodecyl sulfate (SDS), (c) ferrocene, and (d) Crystal Violet (CV).

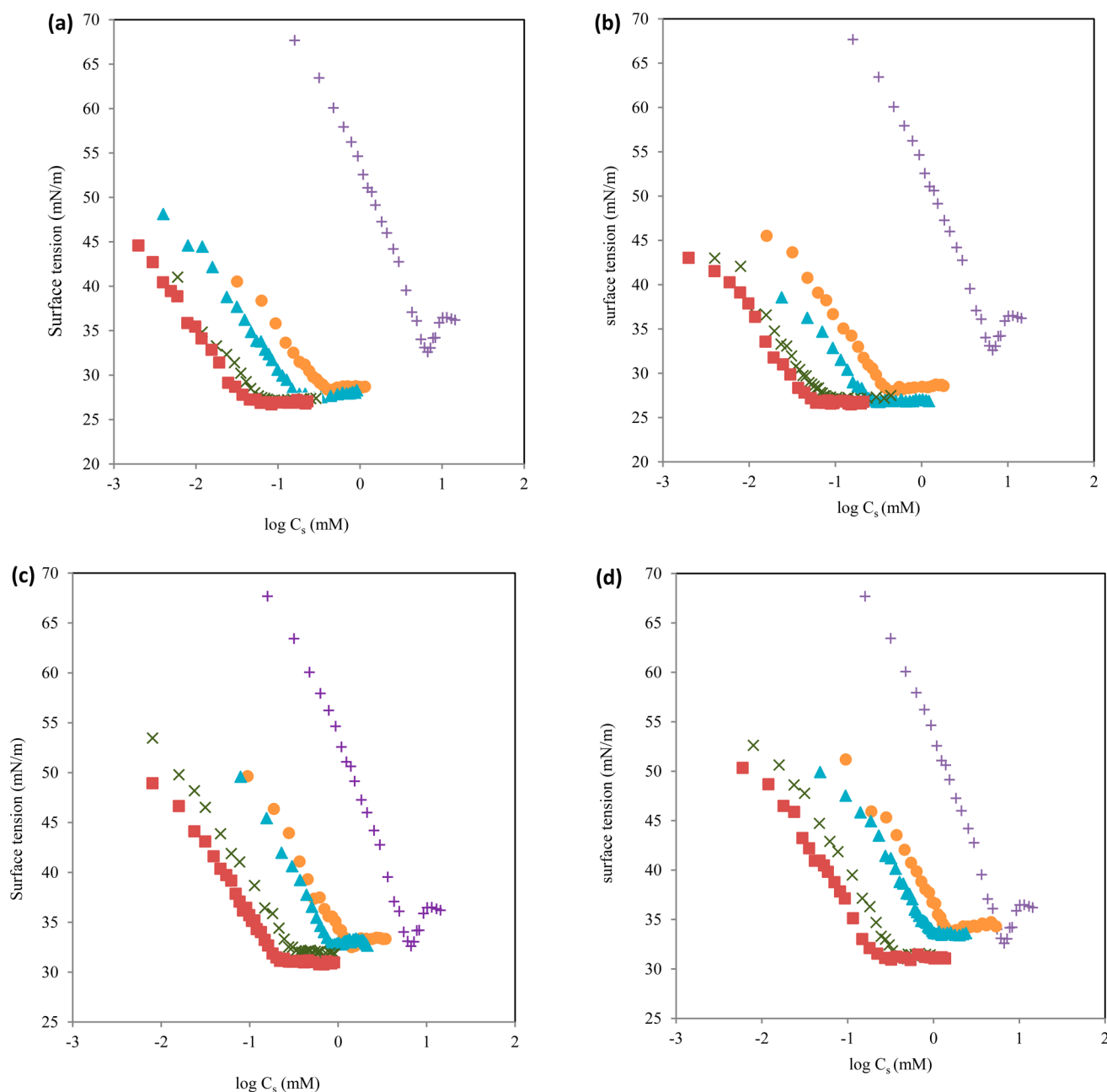


Figure 2. Tensiometry plots for (a) the SDS/HMImCl system, (b) SDS/HMImBr, (c) SDS/BMImCl, and (d) SDS/BMImBr in (+) 0% w/w, (●) 0.05% w/w, (▲) 0.1% w/w, (×) 0.5% w/w, and (■) 1% w/w solutions of ionic liquids at 298 K.

3. RESULTS AND DISCUSSION

3.1. Effect of Ionic Liquids on CMC and Interfacial Properties of SDS.

The variation of surface tension for pure SDS solution and its mixtures with 0.05, 0.1, 0.5, and 1% w/w solutions of various ionic liquids was obtained using tensiometry. It is obvious from Figure 2 that the initial surface tension of IL solutions is almost $15\text{--}20\text{ mN m}^{-1}$ lower than pure water's. This confirms a moderate surface activity for the studied ILs (Supporting Information). It is also seen that the CMC of SDS well decreases in the presence of even a small amount of ILs. Table 1 lists the CMC values. This decreasing effect of ILs on surfactants' CMC is generally observed at lower IL concentrations and attributed to their electrolyte effect.^{35,46} At lower concentrations, ILs act as simple salts and shield the electrostatic repulsion between anionic heads of SDS

molecules, resulting in the CMC decrease through the electrostatic stabilization of micelles' polar shell. As the concentration of ILs increases from 0.05 to 1% w/w, the CMC decreases even more as a result of further electrostatic stabilization of the micelles. Figure 3a shows the conductometry plots for SDS solutions in the presence of NaCl and NaBr salts and the extracted CMC values are shown in Table 1. Although these salts considerably decrease the CMC of SDS, the amount of decrease is quite smaller compared to that caused by the equivalent concentrations of ILs. Thus, the CMC decreases not only under the influence of electrolyte effect but also as a consequence of hydrophobic interactions between alkyl chains of IL and SDS.⁴⁷

The contribution of hydrophobic interactions becomes even more pronounced as the alkyl chain of the IL changes from

Table 1. Data Extracted from Tensiometry and Conductometry Plots for SDS/IBIL Aqueous Solutions at 298 K

w/w % of ILs	equivalent concn of ILs and salts (mM)	CMC ^a (mM)	CMC ^b (mM)	CMC ^c (mM)	α	$\Gamma_m \times 10^6$ (mol·m ⁻²)	A_{min} (nm ² /molecule)
No ILs							
		9.23	7.73	2	0.45	2.02	0.82
BMImBr							
0.05	2.28	1.58	1.96		0.64	1.41	1.18
0.1	4.56	1.10	1.19	0.9	0.61	1.32	1.26
0.5	22.81	0.36				1.22	1.36
1	45.64	0.27				1.19	1.39
BMImCl							
0.05	2.86	1.61	1.72		0.64	1.29	1.22
0.1	5.72	0.86	1.06	0.8	0.56	1.27	1.25
0.5	28.62	0.33				1.20	1.38
1	57.25	0.22				1.16	1.43
HMImBr							
0.05	2.02	0.41	0.48		0.59	1.16	1.43
0.1	4.04	0.24	0.34	0.3	0.55	1.05	1.58
0.5	20.23	0.09				1.03	1.61
1	40.46	0.06				1.02	1.63
HMImCl							
0.05	2.47	0.43	0.46		0.62	1.10	1.51
0.1	4.93	0.27	0.37	0.25	0.62	1.07	1.55
0.5	24.66	0.06				1.00	1.66
1	49.32	0.04				0.98	1.69
NaBr							
	4.56		6.27		0.48		
NaCl							
	5.72		6.04		0.50		

^aThe values obtained from tensiometry. ^bThe values obtained from conductometry. ^cThe values obtained from UV–vis spectroscopy.

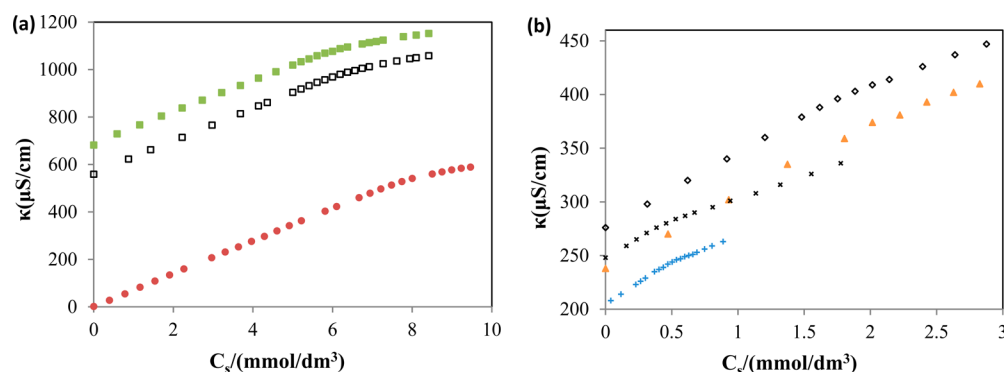


Figure 3. Conductivity plots of (a) SDS solutions (●) in the absence of salts and ILs, (□) in the presence of 4.56 mM NaBr, and (■) in the presence of 5.72 mM NaCl. (b) SDS in 0.05% w/w solutions of (▲) BMImBr, (◇) BMImCl, (×) HMImCl, and (+) HMImBr at 298 K.

butyl to hexyl. Comparing the CMC values of BMImCl and BMImBr to those of HMImCl and HMImBr, we find the decrease in the CMC of SDS is greater for longer-chained ILs. Depending upon conditions, ILs may act as either a cosolvent or a cosurfactant agent. Their overall effect on surfactants is a combination of factors such as electrolyte effect, electrostatic and hydrophobic interaction, and hydrogen bonding with solvent, counterions, and surfactants. We recently studied the effect of IBILs on micellization behavior of the cationic surfactant, cetyltrimethylammonium bromide (CTAB).³⁰ We observed that as the IL's chain length varied from butyl to hexyl, the amount of reduction in the CMC of CTAB decreased. We discussed that the similar charges of surfactant and IBIL molecules along with the IBILs' ability to disturb water structure through hydrogen bonding and steric effect results in an overall cosolvent effect which partially, but not

completely, compensates for the cosurfactant factors of electrolyte effect and hydrophobic interaction. This partial cosolvent effect gets stronger as the chain length increases. But here, there is no electrostatic repulsion between SDS and IBIL molecules. Instead, the electrostatic attraction between them in conjunction with the ILs' electrolyte effect and the hydrophobic interactions of alkyl chains yields a considerable cosurfactant effect. This cosurfactant effect intensifies as the chain length of ILs increases, resulting in the facilitation of mixed micellization at a lower CMC (see section 3.3). It seems short-chained ILs (BMImCl and BMImBr) chiefly act as simple electrolytes with a minor contribution of mixed micellization whereas both electrolyte effect and mixed micellization play important roles in the case of longer-chained ones (HMImCl and HMImBr).²⁹ When micelles are formed in solution, counterions bind with the micelle surface. The degree of micelle ionization (α) is a

measure of counterion binding to the micelle surface. The smaller the value of α is, the more bonded the counterions are to the micelle surface. The α values extracted from conductometry plots using Frahm's method⁴⁸ are listed in Table 1. It is observed that α increases in the presence of electrolytes, but this increase is more considerable for ILs than for inorganic salts. This happens because part of the micelle surface charge is partially neutralized through the contribution of oppositely charged ILs to the micelles' polar shell. Furthermore, the probable formation of hydrogen bonding between hydrogen atoms of the imidazolium ring and oxygen atoms of the SDS headgroup may also contribute to the observed increase in α through redistribution of the negative charge density at micelle surface. ζ potential measurements for SDS aggregates confirm this partial charge neutralization once again (Table 2).

Table 2. ζ Potentials (mV) Measured for SDS Aggregates in the Presence of ILs at 298 K

SDS (15 mM)	SDS (15 mM) + BMImBr (0.5% w/w)	SDS (15 mM) + BMImBr (1% w/w)	SDS (5 mM) + HMImBr (0.5% w/w)	SDS (15 mM) + HMImBr (0.5% w/w)
−96.4	−79.7	−51.8	−19.8	−37.9

According to the extracted data, the anion type of ILs (Cl^- , Br^-) has no considerable effect on the CMC of SDS. In fact, anionic Br^- and Cl^- are not expected to have any electrostatic shielding effect on the similarly charged SDS head groups. The repulsion between them and micelles' negative surface charge, especially at lower IL concentrations, may diminish their contribution to the polar shell of SDS micelles unless the mole fraction of ILs in micelles is so high that these counterions can effectively interact with micelles through the electrostatic attraction and hydrogen bonding with the inserted IL cations. Anyway, the effect of IL counterions on electrostatic stabilization of micelle surfaces and surface monolayer is not pronounced for oppositely charged surfactant/IL systems.⁴⁷

In addition to the micellar phase, it is important to investigate the effect of ILs on the surface adsorption of SDS. A quantitative measure of the surfactant adsorption at the solution surface is usually obtained by the surface excess concentration (Γ_{max}), which can be determined using the Gibb adsorption equation for dilute solutions:⁴⁹

$$\Delta\gamma = -2RT \int_{\ln C_1}^{\ln C_2} \Gamma_{\text{max}} d \ln C f_{\pm} \quad (1)$$

$$\Gamma_{\text{max}} \left(\frac{\text{mol}}{\text{cm}^2} \right) = \frac{-1}{nRT} \left[\frac{d\gamma}{d \ln C f_{\pm}} \right]_{T,P} \quad (2)$$

Here, R is the gas constant, T is the temperature, γ is the surface tension, C is the surfactant concentration, n is the number of species formed in solution during monomer dissociation, and f_{\pm} is the mean activity coefficient for a mixture of ionic surfactant and ionic liquid:

$$\Delta\gamma = -2RT \left[\int_{\ln C_1}^{\ln C_2} \Gamma_s d \ln C f_{\pm} + \int_{\ln C_1}^{\ln C_2} \Gamma_i d \ln C f_{\pm} \right] \quad (3)$$

where s and i refer to the anionic surfactant and ionic liquid, respectively. In the studied system, the concentration of ionic liquid is constant and then the second part of the above

equation will be eliminated. Because of this, we used the single-component Gibbs equation.

The minimum area per surfactant headgroup (A_{min}) at the CMC point was also calculated using the following equation:⁴⁹

$$A_{\text{min}} (\text{nm}^2/\text{molecule}) = \frac{10^{18}}{N_A \Gamma_{\text{max}}} \quad (4)$$

where N_A is Avogadro's number. To calculate Γ_{max} , tensiometry plots were fitted to a polynomial equation ($y = ax^2 + bx + C$) and then the slope of the tangent at CMC point was considered as $(d\gamma/d \log C)$.⁵⁰ Thomas et al. have shown that, if adsorption reaches a plateau before the CMC, then the analysis is straightforward and can be reasonably accurate. However, both direct measurements at higher concentrations and less direct measurements using added electrolyte indicate that adsorption of anionic surfactants has generally not reached a packing limit at the CMC; i.e., it is necessary to fit a polynomial to the data below the CMC and, because this is abruptly terminated at the CMC, there are no effective objective criteria for the choice of that polynomial.⁵¹ Menger et al. have also argued that the interface is, in fact, not saturated in the pre-CMC region.^{52,53} Nonlinear curve fitting to linear pre-CMC region slightly improves the calculated molecular areas. Recently, Phan has successfully modeled CTAB adsorption at the air/water interface without the Gibbs adsorption isotherm.⁵⁴

Inorganic salts are known to increase Γ_{max} by reducing the electrostatic repulsion between surfactant head groups. Table 1 shows the calculated values of Γ_{max} and A_{min} . It is obvious that the surface excess concentration of SDS has decreased in the presence of ILs. The amount of decrease is slightly greater in the presence of HMImCl and HMImBr than in the presence of BMImCl and BMImBr. Despite ILs' electrolyte effect, their moderate surface activity results in their tendency toward solution surface (as mentioned above). Hexyl-chained ILs show even a greater tendency for surface adsorption because of their greater surface activity. Because the solution surface is partly occupied by IL molecules, the total number of SDS molecules at the air/water interface decreases and A_{min} rises. As the concentration of IL increases, fewer sites become available for SDS molecules and a further decrease in Γ_{max} is observed. Another possibility is the formation and adsorption of bulkier SDS–IL ion pairs, which are expected to be more hydrophobic than both components. Thus, it is likely that the solution surface is simultaneously occupied with individual surfactant and IL molecules as well as with their ion pairs. Anyway, it is not sensible to have a discussion about these ion pairs and their orientation at the surface without performing further investigations.

3.2. Applicability of UV–Visible Spectroscopy in Investigation of IL–Surfactant Interactions. It is a well-known fact that ionic surfactants show a totally different aggregation behavior in the presence of even a very small amount of oppositely charged organic dye molecules. Thus, oppositely charged dyes are not a good probe at all for spectroscopic investigation of ionic surfactant micellization. We have here investigated the applicability of positively charged Crystal Violet to spectroscopic study of SDS/IL system. Figure 4 shows the obtained visible spectrum for aqueous solution of Crystal Violet (spectrum no. 1). Two absorption peaks appear at $\lambda_{\text{max}} = 590 \text{ nm}$ and $\lambda_{\text{shoulder}} = 530 \text{ nm}$. The shoulder peak has been assigned to the dimer form of Crystal Violet.⁵⁵ The interaction of Crystal Violet with SDS has comprehensively

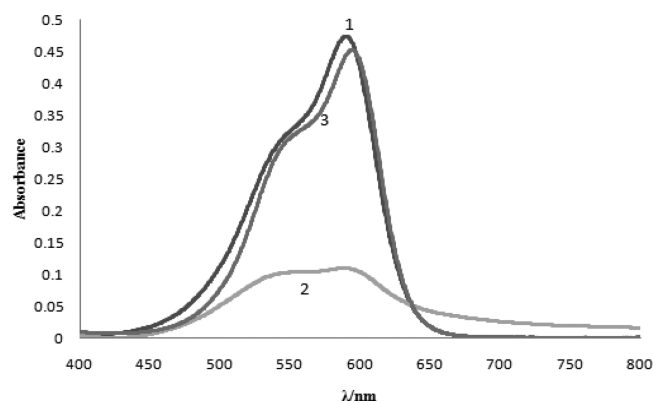


Figure 4. Effect of SDS concentration on the visible spectrum of Crystal Violet: (1) [SDS] = 0 mM, (2) [SDS] = 1 mM, (3) [SDS] = 100 mM. [Crystal Violet] = 6.17×10^{-3} mM and $T = 298$ K.

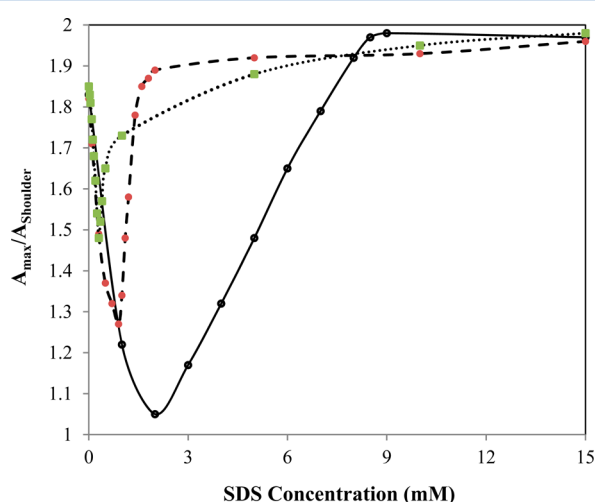


Figure 5. Variation of absorbance ratio for Crystal Violet peaks versus SDS concentration (○) in the absence of ILs and in the presence of 0.1% w/w of (●) BMImBr and (■) HmImBr.

been studied by Garcia-Rio. He has reported that addition of small amounts of SDS tremendously changes the absorption spectrum of Crystal Violet.⁵⁶

Figure 5 shows the change in the ratio of absorbance at 590 and 530 nm. As the initial amounts of SDS are added, the ratio ($A_{\max}/A_{\text{shoulder}}$) starts to decrease sharply. This phenomenon also appears in the spectrum as a band widening (spectrum no. 2 in Figure 4). Such changes in the Crystal Violet spectrum are

attributed to formation of SDS–dye ion pairs. These ion pairs are also surface active and adsorbed at the solution surface. The absorbance ratio reaches a minimum value at SDS concentration of 2 mM. At this point the surface is saturated with ion pairs and further addition of SDS results in the aggregation of ion pairs in the form of dye–surfactant premicelles or dye-rich micelles.⁵⁶ Our previous studies on some similar dye/surfactant systems showed these ion pair premicelles or dye-rich micelles are then transformed into surfactant micelles with solubilized dye molecules as the concentration of surfactant reaches the CMC of pure surfactant.^{57,58} Therefore, further addition of SDS beyond the minimum point results in solubilization of SDS–dye ion pairs into premicelles and micelles, which is reflected as the increase of absorbance ratio up to its initial value for pure Crystal Violet solution (spectrum no. 3 in Figure 4). Such a reduction in absorbance ratio is also observed in the presence of ILs (Figure 5), but the ratio reaches its minimum value at a lower SDS concentration (0.9 mM for BMImBr and 0.3 mM for HmImBr) compared to that in the absence of ILs (2 mM). The tensiometry and conductometry results revealed SDS micelles/mixed micelles are formed in the presence of ILs at concentrations well below the CMC of pure SDS. These CMCs (Table 1) are even smaller than the CMC of SDS–dye ion pairs (2 mM).

As a result, IL molecules do not allow SDS–dye ion pairs to form aggregates of their own and compete with dye molecules for SDS molecules. In other words, as the initial amounts of SDS are added to dye/IL solutions, both SDS–dye and SDS–IL ion pairs are formed but when the concentration reaches the CMC of SDS/IL micelles, all ion pairs (including SDS–dye and SDS–IL ones) decompose into SDS/IL micelles/mixed micelles with solubilized dye molecules. Table 1 shows the CMCs obtained from spectroscopy are in good accordance with the values obtained from other techniques. Therefore, the presence of the dye probe in SDS/IL solution did not affect the aggregation behavior of the system and successfully revealed the micellization process.

On the other hand, contribution of Crystal Violet into SDS micelles results in the partial red shift of λ_{\max} from 590 to 595 nm (plot has been provided as Supporting Information). The spectral changes of dye molecules in the presence of oppositely charged micelles have been suggested to be caused by the electrostatic interaction between oppositely charged molecules,⁵⁹ formation of molecular complexes with oppositely charged micelles,⁶⁰ and changes in the microenvironment of dye chromophore.^{61,57} Ghanadzadeh et al. have reported a blue shift in λ_{\max} of Crystal Violet through the reduction of solvent

Table 3. Variation in Maximum Absorbance Wavelength of Crystal Violet for Different SDS/IL Solutions at 298 K^a

% w/w of ILs	BMImBr	BMImCl	HmImBr	HmImCl
0	589.94	589.94	589.94	589.94
0.05	595.40 (590.23)	595.27 (590.11)	594.94 (590.09)	595.36 (589.90)
0.1	595.94 (590.12)	596.19 (590.23)	596.25 (590.03)	596.70 (590.20)
0.2	595.74	597.12	600.12	600.77
0.3	597.05	597.37	601.27	601.42
0.4	597.53	597.61	601.48	601.62
0.5	597.91 (590.21)	597.55 (590.18)	601.57 (590.29)	601.71 (590.37)
1	598.21 (590.44)	597.74 (590.24)	601.30 (590.29)	601.77 (590.72)
2	598.50	599.12	601.46	601.97

^aThe SDS and Crystal Violet concentrations for all solutions are constant at 8 M and 6.17×10^{-3} mM, respectively. The values in parentheses are in the absence of SDS.

polarity.⁶² We also recorded a λ_{\max} of 587.73 nm for 6.17×10^{-2} mM solution of Crystal Violet in ethanol. Therefore, the observed red shift in the micellar region may be caused by an increase in microenvironment polarity of the Crystal Violet chromophore; that is, the incorporation of dye molecules into hydrophobic core of SDS micelles is rejected and they can only interact with the micelles' polar shell. Table 3 lists the values of λ_{\max} for Crystal Violet solutions in the presence of 8 mM SDS and various weight percentages of ILs. In the absence of SDS, no change in maximum absorbance is observed, showing the lack of effective interaction between Crystal Violet and ILs. But as the concentrations of ILs increase from 0 to 2% w/w, the polarity of the micelle surface increases and a red shift is observed (9 nm for butyl-chained and 12 nm for hexyl-chained ILs). The observed red shifts in the presence of ILs are a little greater than that observed for SDS/Crystal Violet solution (5 nm) showing a more polar micellar surface for SDS/IL micelles/mixed micelles. The polarity of the micelle surface for SDS/HMImBr and SDS/HMImCl mixed micelles is even expected to be greater in comparison with the polarities of SDS/BMImBr and SDS/BMImCl micelles. This polarity difference may be caused by a difference in aggregation number, size, or morphology of these aggregates. Section 3.4 investigates such a probability.

3.3. Interaction Parameters of IL and SDS Molecules at the Solution Surface and in the Micellar Phase.

Imidazolium-based ILs with alkyl chains longer than four carbon atoms are generally known to behave as amphiphilic compounds with surface activity.²⁸ We have previously reported CMC values of 312 and 358 mM for HMImBr and HMImCl, respectively.³⁰ This moderate surface activity of hexyl-chained ILs promises a strong interaction with SDS molecules at the adsorbed surface monolayer as well as in the micellar phase. The aim of this section is to quantitatively investigate this interaction. To achieve this, we employ the Rubingh's regular solution model for surfactant mixtures.⁶³ On the basis of this model, the interaction parameter (β^M) in micellar phase, which is a measure of interaction strength, can be calculated using the following equations:³⁴

$$\frac{(X_1^M)^2 \ln(\alpha_1 C_{12}^M / X_1^M C_1^M)}{(1 - X_1^M)^2 \ln[(1 - \alpha_1) C_{12}^M / (1 - X_1^M) C_2^M]} = 1 \quad (5)$$

$$\beta^M = \frac{\ln(\alpha_1 C_{12}^M / X_1^M C_1^M)}{(1 - X_1^M)^2} \quad (6)$$

where X_1^M is the mole fraction of surfactant in mixed micelles, α_1 is the total mole fraction of surfactant in solution, C_1^M is the CMC of the pure surfactant, C_2^M is the CMC of the pure IL, and C_{12}^M is the CMC of their mixture. Similarly, the interaction parameter for a mixed monolayer (β^σ) is calculated using the following equations:^{64,65}

$$\frac{Z_1^2 \ln(\alpha_1 C_{12} / Z_1 C_1^0)}{(1 - Z_1)^2 \ln[(1 - \alpha_1) C_{12} / (1 - Z_1) C_2^0]} = 1 \quad (7)$$

$$\beta^\sigma = \frac{\ln(\alpha_1 C_{12} / Z_1 C_1^0)}{(1 - Z_1)^2} \quad (8)$$

Here again, Z_1 is the mole fraction of surfactant in the mixed monolayer, α_1 is the total mole fraction of surfactant at the concentration required to produce a certain value of γ before CMC point, and C_1^0 , C_2^0 , and C_{12} are the molar concentrations

of surfactant, IL, and their mixture, respectively. A negative value of β means that there is either greater attraction or smaller repulsion between SDS and IL than between the molecules of the same type.

The calculated results are shown in Table 4. β has a considerably negative value for both of the ILs at any

Table 4. Interaction Parameters for SDS/IL Systems in the Micellar Phase and at the Surface Monolayer Calculated at 298 K

% w/w of ILs	β^M	X_1^M	f_1^M	β^σ	Z_1	f_1^σ
HMImBr						
0.05	-12.89	0.57	0.09	-15.27	0.52	0.03
0.1	-12.81	0.53	0.06	-15.62	0.48	0.02
0.5	-11.38	0.43	0.03	-13.96	0.39	0.01
1	-10.39	0.39	0.02	-13.20	0.35	0.004
HMImCl						
0.05	-12.66	0.57	0.10	-15.85	0.52	0.02
0.1	-12.45	0.52	0.04	-16.82	0.47	0.01
0.5	-11.95	0.42	0.02	-14.97	0.38	0.003
1	-10.53	0.38	0.01	-13.06	0.34	0.004

concentration. This strong synergism is an indisputable result of the strong electrostatic and hydrophobic attractions between SDS and IL molecules. Here again, the effect of ILs' counterions type (Br^- and Cl^-) on micellization and surface adsorption of surfactant is not pronounced. It is also seen that the mole fraction of components at 0.05% w/w of ILs is nearly 0.5 (1 IL molecule per SDS molecule) but as the concentration of ILs rises to 1% w/w, the mole fraction of SDS at the surface monolayer and in micelles drops to nearly 0.35 (2 IL molecules per SDS molecule).

This is why β becomes less negative as the concentration of ILs increases. The electrostatic repulsion between IL molecules increases gradually at the surface monolayer and in micelles, but the attraction between SDS and IL molecules is still strong enough to give an overall negative value for β . Under the influence of such a strong synergism, it is expected that the mixed micellization will modify to a large extent the size and morphology of SDS micelles (see section 3.4).

3.4. Size and Morphology of IL/SDS Aggregates. Size modification of SDS micelles by ILs can be investigated using a hydrophobic electroactive probe. Such a probe can enter the micelle core. In this case, the diffusion coefficient of the probe corresponds to that of the aggregates. Diffusion coefficients can be determined through cyclic voltammetry measurements. Ferrocene is a very suitable probe for this purpose because it is completely hydrophobic and undergoes a reversible oxidation through the following reaction:



The peak current ($i_{p,a}$) of the voltammogram is related to the diffusion coefficient through the Randles–Sevcik equation:⁶⁶

$$i_{p,a} = 0.4463 F A C n \left(\frac{n F v D_m}{RT} \right)^{1/2} \quad (10)$$

where n is the number of electrons involved in redox reaction, A is the area of the electrode, F is the Faraday constant, R is the gas constant, T is the absolute temperature, D_m is the diffusion coefficient of ferrocene (it here corresponds to that of the aggregates), C is the probe concentration in the solution, and v is the scan rate.

At concentrations slightly above the CMC, aggregates mutually interact, which leads the calculated D_m values to be lower than the real values at the CMC point. Therefore, linear interaction theory was used for the calculation of interparticle interaction parameters:⁶⁷

$$D_m = D_m^0[1 - k_d(C_{\text{SDS}} - \text{CMC})] \quad (11)$$

where k_d is the interparticle interaction parameter, D_m^0 is the self-diffusion coefficient in the absence of interparticle interaction, and C_{SDS} is the surfactant concentration. Plotting D_m versus $(C_{\text{SDS}} - \text{CMC})$, the values of k_d and D_m^0 can be obtained from line slope and intercept, respectively. Having the value of D_m^0 and assuming a spherical shape for the aggregates, we can calculate the mean hydrodynamic radius (R_h) of the aggregates with the Stokes–Einstein equation:⁶⁸

$$D_m^0 = \frac{kT}{6\pi\eta_0 R_h^m} \quad (12)$$

k is the Boltzmann constant, T is the absolute temperature, and η_0 is the solution viscosity. Once the value of R_h^m is obtained, aggregation number (N_{agg}) can also be calculated by the following equation:

$$N_{\text{agg}} = \frac{\frac{4}{3}\pi R_h^3}{X_{\text{SDS}}V_{\text{SDS}} + X_{\text{IL}}V_{\text{IL}}} \quad (13)$$

V_{SDS} and V_{IL} are the volumes of SDS and IL molecules, respectively. The molecular volumes can be calculated using Gaussian software. X_{SDS} and X_{IL} are the mole fractions of SDS and IL in aggregates. For SDS/BMImBr systems, we do not expect any mixed micellization, thus in this system $X_{\text{SDS}} = 1$ and $X_{\text{IL}} = 0$. But for SDS/HMImBr mixed micelles, these values can be obtained using the method described in section 3.3. It is worth mentioning that cyclic voltammetry does not provide a size distribution range and all of the calculated parameters are in fact the mean values.

Figure 6 shows the variation of aggregates' diffusion coefficient with SDS concentration (voltammograms have

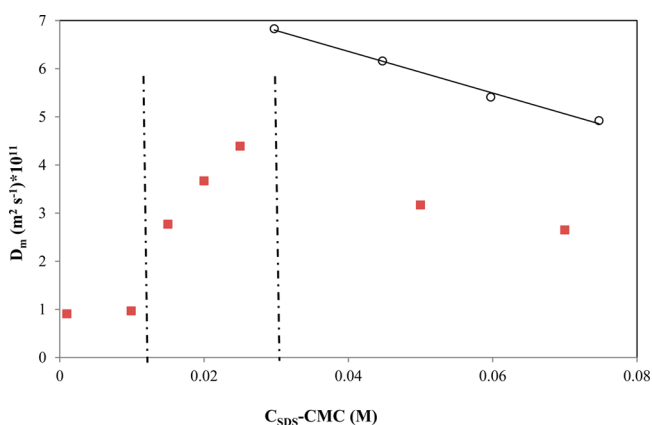


Figure 6. D_m versus $(C_{\text{SDS}} - \text{CMC})$ in the presence of 1% w/w of (○) BMImBr and (■) HMImBr at 298 K.

been provided as Supporting Information). For the SDS/BMImBr system, the diffusion coefficient decreases linearly as SDS concentration rises. Such a linear decrease is representative of a micelle size growth without any micellar transformation. However, the case for SDS/HMImBr is different because the corresponding plot is composed of three separate regions. The

considerable increase in diffusion coefficient through region II implies that a phase transition from larger particles (region I) to smaller ones (region III) takes place. TEM images prove this hypothesis. Figure 7 shows that vesicles formed at region I (Figure 7a) transform to micelles at region III (Figure 7b). This is conceivable, because the mole fraction of SDS to HMImBr increases considerably by going from region I to region III.

The data obtained from cyclic voltammetry are listed in Table 5. According to the data, addition of ILs to SDS solution results in a notable increase in N_{agg} , interparticle interaction parameter (k_d), and aggregate size. The efficiency of oppositely charged IL molecules in reducing electrostatic repulsion between SDS head groups is the main cause of the increase in micelles' aggregation number for SDS/IL systems. In addition, the strong hydrophobic interaction between components in the SDS/HMImBr mixture has a key role in formation of the vesicles and mixed micelles with huge aggregation numbers. The variation in k_d can be interpreted from the viewpoints of the aggregate's surface charge density and phase transition/micellar growth.^{69,70}

From ζ potential measurements (Table 2), it was found that the addition of ILs to SDS solution generally reduces the micelles' surface charge density as a result of partial SDS charge neutralization. Furthermore, although this charge density reduction was shown (Table 2) to be larger for SDS/HMImBr than for SDS/BMImBr, k_d has a greater value for the former system. Thus, the observed increase in k_d is likely to be caused by the growth in aggregate size, or in other words, by the growth in the micelles' surface area.

Before putting an interpretation on particle size changes, we also employed dynamic light scattering technique to evaluate the accuracy of cyclic voltammetry in measuring the aggregates size. Although the value calculated for pure SDS micelles is a little smaller than that measured by DLS, there is a good accordance between the results obtained for the SDS/BMImBr system. These two techniques suggest a micelle size of about 5 nm for SDS micelles in the presence of BMImBr. The wide DLS peak suggests a large size distribution range for these micelles, which is also obvious from the TEM image (Figure 7c), but the majority of micelles, however, have sizes larger than 5 nm. Analysis of the TEM images of the SDS/HMImBr system reveals a great accordance between the sizes obtained by cyclic voltammetry and electron microscopy. From TEM images analysis, it was found that the vesicles of region I have sizes from 30 to 60 nm with 52% being between 40 and 50 nm (Figure 7a). The large negative value of the interaction parameter shows a considerable synergism between surfactant and ionic liquid molecules. As a result, surfactant molecules can preferentially mixed with them to form mixed micelles or vesicles instead of stabilizing their droplets.

In region III, the mixed micelles are distributed in the range 5–25 nm with 73% of them being between 10 and 20 nm (size distribution plots have been provided as Supporting Information). In other words, cyclic voltammetry has successfully measured the size of vesicles and mixed micelles for the SDS/HMImBr system. It is seen that the micellar transformation from mixed vesicles to mixed micelles decreases the size, aggregation number, and intermicellar interaction parameter. Therefore, as the concentration of long-chained ILs increases, the probability rises for phase transition from pure surfactant micelles to larger surfactant/IL aggregates such as vesicle or wormlike micelles.

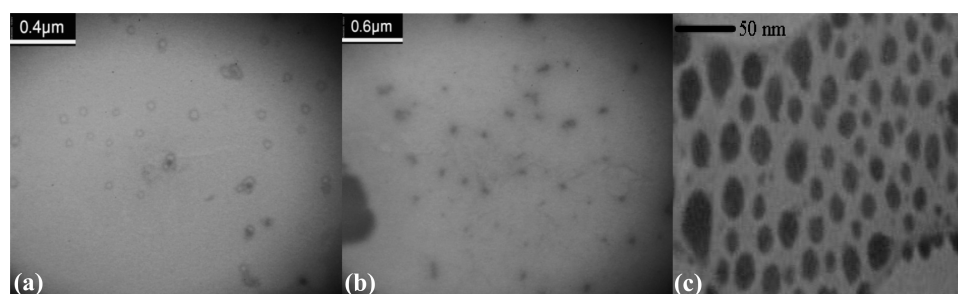


Figure 7. TEM micrographs for 1% w/w solutions of (a) HMIImBr + SDS 7 mM, (b) HMIImBr + SDS 70 mM, and (c) BMImBr + SDS 15 mM.

Table 5. Structural Parameters of SDS/IL Aggregates Obtained from Cyclic Voltammetry Measurements at 298 K

% w/w of ILs	$D_m^0 \times 10^{-11}$ ($\text{m}^2 \text{s}^{-1}$)	k_d ($\text{dm}^3 \text{mol}^{-1}$)	R_h^m (nm)	N_{agg}	diameters from DLS ^a (nm)
No ILs					
0	50.00	3.93	0.43	69	2.5 (21.4) ^b
BMImBr					
0.5	7.55	6.36	2.86	280	3.5 (6.3) ^b
1	8.08	5.34	2.67	228	4.1 (56.1) ^b
HMIImBr					
0.5	0.41 ^c		49.37 ^c	224102 ^c	
	2.55 ^d		8.47 ^d	9830 ^d	
1	0.91 ^c	8.14 ^c	20.41 ^c	46638 ^c	
	3.40 ^d	7.38 ^d	6.35 ^d	4308 ^d	

^a[SDS] = 15 mM. ^bThe values in parentheses show peak width. ^cRegion I. ^dRegion III.

4. CONCLUSION

The findings of the present study show that even small amounts of ILs can notably change the surface activity and micellization behavior of oppositely charged ionic surfactants. The ILs with shorter alkyl chains generally act as simple salts and enhance surfactant micellization through electrostatic stabilization of their micelle surface, whereas longer-chained ILs interact also through hydrophobic chain–chain attractions. Thus, mixed micellization should be considered for the mixtures of surfactants and oppositely charged ILs with chains longer than hexyl. Such a mixed micellization may completely modify the size and morphology of aggregates so that larger aggregate-like vesicles or wormlike micelles rather than spherical micelles can form. However, micellar growth is a well-known fact even in the presence of short-chained ILs. This study also shows that all aggregation processes can be successfully tracked using cyclic voltammetry. Aggregate size is also obtainable from voltammetry measurements with an acceptable accuracy. Finally, although oppositely charged dye molecules are not considered as a suitable spectroscopy probe for ionic surfactant systems, we showed here that they can appropriately be used as a UV–visible probe for spectroscopic study of surfactant/IL system under the following conditions: (i) there should be trivial interaction between IL and dye probe, (ii) the concentration of dye probe should be well below the concentrations of surfactant and IL, and (iii) surfactant should have a greater tendency for IL than for dye probe (in other words, the CMC for surfactant/IL aggregation should be well below the CMC for surfactant/dye aggregation).

■ ASSOCIATED CONTENT

Supporting Information

Tensiometric plot of pure ILs (S.1), variation of Crystal Violet maximum absorbance wavelength with SDS concentration in the absence of ILs (S.2), voltammograms for various SDS concentrations in the presence of ILs (S.3, S.4, S.5 and S.6), and size distribution of the aggregates extracted from the TEM image (S.7 and S.8) are available in supporting file. This information 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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