Interfacial and Aggregation Behaviour of Sodium Dodecyl Sulphate Induced by Ionic Liquids

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Abstract: Aggregation studies of anionic surfactant sodium dodecyl sulphate (SDS) was investigated in aqueous 1-butyl-3-methylimidazolium chloride [bmim]Cl and *N*-butyl-*N*-methyl pyrrolidinium tetrafluoroborate [bmp]BF₄ ionic liquid (IL) solutions respectively. Systems were studied by surface tension, conductance, UV-VIS absorption/emission spectroscopy and dynamic light scattering. Critical micelle concentration (CMC) values gradually decreased with increasing IL concentration which indicates synergistic interaction between ILs and SDS. Gibbs free energy change results demonstrated spontaneous micellization induced by ILs; however the effect of ILs were not similar to the corresponding regular salts (NaCl and NaBF₄). Aggregation number (*n*) of micelles, determined by fluorescence quenching method, indicate that the 'n' values increase with increasing ILs concentration, induced by the oppositely charged IL cation. Size of the micelles, determined by dynamic light scattering studies, increased with increasing ILs concentration, which were due to the formation of larger aggregates; the aggregates are considered to be comprised of the anionic surfactant with a substantial proportion of ILs cation as the bound counter ions. Such studies are considered to shed further light in the fundamentals of IL induced micellization as well as in different practical applications.

Key words: ionic liquid, surfactant, SDS, micelle, aggregation, spectroscopy

1 Introduction

Surfactants exhibit amphiphilic natures that alter the surface tension at air-liquid interface. Self aggregation behaviour of surfactant depends on different physicochemical parameters, *viz.*, temperature, pH, additives, salinity and ionic strength¹⁻⁴. An ionic liquid (ILs) usually contains one cationic organic component and also consists of short lived ion pair, that facilitates interfacial adsorption and aggregation of conventional surfactants⁵⁻⁷. Ionic liquids not only have emerged as alternatives to the conventional solvents, but it can also significantly alter surfactant aggregation⁸⁻¹⁰. In case of ILs having melting point below 100°C, mutual interfacial adsorption and aggregation take place along with the surfactants⁷. ILs can easily interact with surfactant molecules leading to the formation of mixed micelles¹¹. Electrostatic interaction between two oppositely charged head groups can demonstrate different hydration energy for the surfactant molecules in presence of ionic liquid, especially for anionic surfactants^{12, 13}. Oppositely charged IL

+ surfactant mixtures exhibit strong synergistic interaction which are capable to exhibit superior interfacial properties, *viz.*, higher surface activity, lower CMC, formation of a variety of aggregates⁵⁻⁷. Charge on such micellar aggregates, induced by IL are mainly governed by two parameters: i) extent of charge neutralization and ii) presence of counter ions^{14, 15}. In general, IL + surfactant mixtures are capable to form various complex phases¹⁶, like coacervates¹⁷, micelles¹⁸, aggregates¹⁹, and vesicles²⁰ that arise at different ILs concentration, as well as other environmental factors.

Having the ability of self organisation as micelle, certain ILs carrying long hydrocarbon chain possessing the amphiphilicity with distinct hydrophobic tail and hydrophilic head groups are called surface-active ionic liquids (SAILs)²¹. In SAIL, either the surface active part or the counter ion can have an ionic liquid like component. SAILs possess the dual benefits of surfactant as well as ionic liquids.

The main aim of the present work is to understand the

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physicochemistry of SAILs. Towards the endeavour, initially it is considered worthy to replace the common cations in anionic surfactants with a cationic moiety of ionic liquids (*e.g.*, 1-alkyl-3-methylimidazolium, 1-alkylpyridinium ion). Aggregation behavior of conventional surfactants in IL + Water mixture need to be investigated in order to understand the aggregation behaviour of the aforementioned systems. For this reason, aggregation behavior of SDS was studied in aqueous solutions of two different ionic liquids, 1-butyl-3-methylimidazolium chloride ([bmim]Cl) and *N*-butyl-*N*-methyl pyrrolidinium tetrafluoroborate ([bmp]BF₄). These two ILs find applications in different fields that include enzymatic hydrolysis²², adsorbents for gas separation²³, energy storage²⁴ and high power electric storage²⁵, to mention a few.

Physicochemical investigation on the surface adsorption and aggregation behaviour of anionic surfactant sodium dodecyl sulphate (SDS) in aqueous-IL (IL + W) mixed solvent systems were carried out in presence of two ILs, 1-butyl-3-methylimidazolium chloride [bmim]Cl, and *N*-butyl-*N*-methyl pyrrolidinium tetrafluoroborate [bmp]BF₄. The choices of the two ILs are specific as the two ILs mainly favour solvating properties differently due to their differences in the charge densities in their cationic moieties⁵. Both SDS based SAILs and SDS in water form micelles which were reported to be useful in drug delivery. Micelles of surfactant having lower CMC value, in the presence of IL, than that of only SDS in water are more suitable for practical applications^{12, 13}. As the CMC values of SDS based SAILs and IL + surfactant mixtures were found to be comparable. IL + surfactant mixed micelles are thermodynamically and kinetically as stable as the micelles of SDS based SAILs. Moreover, simply mixing aqueous SDS with IL we get the desired mixed micelles. SDS finds to be suitable in a variety of applications, *viz.*, fabrication of nanomaterials²⁶, tooth paste²⁷, detergents²⁸, and microemulsion formulation²⁹, to mention a few. On the other hand, ILs find applications as lubricant³⁰, cleaning³¹, in food industries³², microemulsion³³ and preparation of pharmaceutical products, *etc.*,³⁴. Hence, IL + SDS mixed systems are considered to exhibit a wide range of applications, *viz.*, biochemical research³⁵, textile wetting³², synthesis of nanoparticle²⁶, drug delivery³⁶, molecular separation^{37, 38}, and cosmetics³⁹. Micelles can incorporate the bulky organic ions of ionic liquids by inciting the hydrophobic part of surfactant through electrostatic and hydrophobic interactions^{40, 41}. ILs in water do not show micellization properties, staying in ionised condition like electrolytes therefore, starting from minimum range of ILs concentrations used in mixed micelles and looking for stable, leak proof micelles with lower CMC. Higher hydrophilicity of imidazolium or pyrrolidinium groups with SDS are quite different than that of the aggregation of mixed micelles, so using such surfactant with multitude of such ionic liquids are considered to be very

important⁴². Studies were carried out by surface tension, electrical conductance, UV-VIS absorption and emission spectroscopy, and dynamic light scattering (DLS) studies^{6, 40, 43}. Critical micelle concentration (CMC), surface pressure at CMC (π_{CMC}) and Gibbs free energy change for micellization (ΔG^0_{mic}) values were obtained from surface tension data⁷. Degree of dissociation (α) values of the micellar aggregates were determined by analyzing the conductance data. Aggregation number of the micellar aggregates (*n*) in presence of varying concentration of ILs were determined by fluorescence quenching method using pyrene (Py) as the probe and hexadecylpyridinium chloride (HPC) as the quencher. Hydrodynamic diameter (d_h), polydispersity index (PDI) values were evaluated from the dynamic light scattering studies. Formation of aggregates leading the much more favourable usefulness towards human being as contributing different types of master's roles in medicinal purpose industrial purpose as well as in daily uses also^{5, 10, 40}. The aggregation behaviour and thermodynamics of the micellization processes have been studied to develop suitable drug delivery systems having high drug loading properties⁸, and templates/media for the synthesis of nanoparticles. Micellization behavior of IL + SDS mixtures exhibits new insight, would be eventually help to study the aggregation⁴⁴. Present research group is in a process to study the aggregation behaviour of counter ion free ionic liquid based surfactant. Prior to that, in order to understand the effect of the IL on the aggregation behaviour, such a set of studies have been undertaken.

2 Experimental section

2.1 Materials

Sodium dodecyl sulphate (SDS), 1-butyl-3-methylimidazolium chloride [bmim]Cl, *N*-butyl-*N*-methyl pyrrolidinium tetrafluoroborate [bmp]BF₄ were the products from Sigma-Aldrich Chemicals Pvt. Ltd. (St. Louis, MO, USA). AR grade pyrene, hexadecylpyridinium chloride (HPC), ethanol were purchased from Acros Organics Pvt. Ltd (Mumbai, India). 99% pure chemicals were used as received; the chemicals were purified using the standard procedure. Double distilled water with specific conductance 2-4 $\mu\text{S cm}^{-1}$ at 298 K was used in preparing the different experimental solutions. Structure of surfactant and ionic liquids are shown in Scheme 1.

2.2 Methods

2.2.1 Determination of critical micelle concentration (CMC)

CMC values of SDS in water and IL + W mixtures were determined by surface tension, conductance, UV-VIS absorption/emission spectroscopy studies^{5-7, 10}.

Scheme 1 Chemical structure of SDS, [bmim]Cl and [bmp]BF₄.

2.2.2 Surface tension measurements

Surfactant stock solutions (twenty times stronger than the anticipated CMC values) was prepared in pure water or corresponding ionic liquid + water (IL + W) mixed solvent systems at different ionic liquid concentration in water in the range of 0.025–2.5 mM. 20 mL of double distilled water or (IL + W) was taken in a container; temperature was controlled by circulation water bath (Hahntech Corporation, South Korea). Quantitative amount of surfactant mixture, dissolved in water or in water + IL mixed solvent systems, were progressively added using a Hamilton (USA) microsyringe to the respective solvent and were homogenized using a magnetic stirrer. Surface tension data was recorded by du Noüy tensiometer with a stated error of $\pm 0.1 \text{ mNm}^{-1}$ (Jencon, Kolkata, India)^{45–47}. CMC value was determined from the breakpoint of surface tension (γ) vs. $\log[S]$ plots ($[S]$ being the surfactant concentration).

2.2.3 Conductance studies

Conductance studies were also carried out using the same protocol as adopted in the surface tension measurement. Specific conductance (κ) of solution was measured by a direct reading conductivity meter, Cyber Scan CON510 (Eutech Instruments, Singapore) with an accuracy of $\pm 0.1 \mu\text{Scm}^{-1}$. Conductance (κ) vs. $[S]$ plots, at a particular break point indicates CMC⁴⁸.

2.2.4 UV-VIS absorption/emission spectroscopic studies

Initially, 1 mM pyrene solution was prepared in dehydrated ethanol. A 10^{-4} M Py solution in ethanol was prepared by dilution; afterwards 2.5 μM Py in water was prepared by proper dilution and sonication technique. UV-VIS spectrophotometer (UVD-2950, Labomed Inc., USA) instrument was used in recording the absorption spectra⁴⁹. Py displays four major absorption peaks at 241, 274, 337 and 345 nm and two weak bands at 263 and 321 nm (panel A, Fig. S1, supplementary section)⁵⁰. The sum of the absorbance (A_T) vs. surfactant concentration $[S]$ followed sigmoidal profiles; CMC values were determined from the plot using the following expression^{46, 50}:

$$A_T = \frac{(a_i - a_f)}{\left[1 + \exp \frac{(x - x_0)}{\Delta x}\right]} + a_f \quad (1)$$

where, x_0 is centre of the sigmoid (herein the CMC), x is the surfactant concentration, a_i and a_f is initial and final asymptotes of the sigmoidal curve respectively, and Δx is

the interval of the independent variable. Fluorescence spectroscopic studies were also performed (Hitachi High Technologies Fluorescence Spectrophotometer Corporation, F-7100, Tokyo, Japan) to determine the CMC value of SDS under varied concentration of ILs. First vibronic emission peak at 375 nm (I_1) and the third vibronic emission peak at 385 nm (I_3) of Py were considered for emission studies. (panel B, Fig. S1)⁵⁰. Py was excited at 337 nm and the emission spectra were recorded in the range 350 to 450 nm. From the midpoint of the sigmoidal profile of the I_1/I_3 vs. $[S]$ plot, CMC values were determined⁴⁶.

2.2.5 Dynamic light scattering (DLS) studies

A Zetasizer Nano ZS-90 (Malvern Instruments, U.K.) dynamic light scattering spectrometer was used to determine the size and polydispersity index (*PDI*) of micellar aggregates⁵¹. He-Ne laser operating light (632.8 nm) was used for DLS measurements and the data were collected at a scattering angle of 90°. Ten times concentrated surfactant solutions (than its CMC value) were used for DLS studies. Surfactant mixtures were filtered through 0.45 μm Millipore cellulose acetate membrane filter prior to recording the data. Viscosity of the medium was measured by a DV II-Pro roto viscometer (Brookfield, USA) with a stated accuracy of $\pm 0.01 \text{ cP}$ ⁵². Viscosity coefficient was measured at different shear rate and extra plotted the zero shear viscosity was evaluated from the plot of viscosity vs. shear rate. Refractive index of the medium was measured by an Abbe type refractometer⁵³. Experimental value of the viscosity coefficient and refractive index of the solution under investigation, as measured above were taken into account while performing the DLS studies.

All experiments were carried out at 298 K.

3 Results and Discussion

3.1 Critical Micelle Concentration (CMC)

CMC value of SDS at different concentration of ILs in water were evaluated by analyzing the surface tension, conductance, UV-visible absorption and emission spectroscopic data at different concentration of SDS. Representative profiles for determining the CMC values of SDS are shown in Fig. 1^{5, 6, 40}. CMC values (reported herein as the average CMC determined by all the aforementioned

Fig. 1 Variation of surface tension (γ , A), specific conductance (κ , B), sum of the peak absorbance (A_T , C), and I_1/I_3 ratio (D) with SDS concentration ($[S]$) at 298 K. $[Py] = 2.5 \mu\text{M}$. $\lambda_{\text{ex}} = 337 \text{ nm}$. Systems: $\square$, water; $\circ$, $[\text{bmim}]\text{Cl} + \text{W}$ and Δ , $[\text{bmp}]\text{BF}_4 + \text{W}$. Concentration of ionic liquid in water, $[\text{IL}] = 0.25 \text{ mM}$.

Table 1 Variation of CMC , surface pressure at CMC (π_{CMC}), Gibbs free energy of micellization (ΔG_{mic}^0), fraction of counter ion binding (β) and aggregation number (n) of SDS with the variation of ionic liquid concentration in water at 298 K.

[IL]/mM	CMC/mM					$\pi_{CMC}/\text{mNm}^{-1}$	$(-)\Delta G_{mic}^0/\text{kJ mol}^{-1}$	$\beta = (1 - S_2/S_1)$	n
	Surface tension	Conductance	UV-vis abs.	Fluorescence	Average				
0 (water)	8.0	8.1	7.6	7.8	7.7	37.0	17.7	0.42	73
[bmim]Cl									
0.025	3.6	4.0	3.9	4.0	3.72	36.4	18.5	0.40	90
0.225	3.1	3.9	3.5	3.7	3.38	36.8	19.4	0.41	130
0.250	2.7	3.5	3.2	3.5	3.02	37.7	21.0	0.57	133
1.375	2.5	2.7	2.5	2.4	2.44	39.0	22.9	0.43	134
2.250	2.2	2.6	2.4	2.1	2.24	38.8	23.6	0.60	148
2.500	2.0	2.4	2.1	2.0	2.06	39.2	24.4	0.63	161
[bmp]BF ₄									
0.025	3.8	4.3	4.1	4.1	3.90	34.7	18.1	0.37	78
0.225	3.4	3.9	3.5	3.9	3.48	34.4	19.0	0.38	80
0.250	3.0	3.7	3.3	3.6	3.18	34.6	20.2	0.42	102
1.375	2.6	3.1	3.1	2.7	2.74	36.3	21.3	0.49	134
2.250	2.4	2.9	2.7	2.3	2.46	36.4	22.7	0.57	166
2.500	2.2	2.7	2.3	2.2	2.26	37.6	23.5	0.60	170

methods) of SDS gradually decreases with increasing ILs concentration in water (Table 1).

CMC of SDS in water as well as in IL + W is one of the

important parameters primarily in understanding the aggregation behaviour of mixed micelles. CMC value of SDS in water is 7.7 mM close to literature value⁽⁴⁵⁾. CMC value of

Fig. 2 Variation of surface pressure at the CMC (π_{cmc} , A), fraction of counter ion binding (β , B) and Gibbs free energy of micellization (ΔG_{mic}^0 , C) with the concentration of ionic liquid [IL] in water at 298 K. Systems: $\circ$, [bmim]Cl and Δ , [bmp]BF₄.

SDS in 2.5 mM [bmim]Cl and [bmp]BF₄ were 2.06 mM and 2.26 mM respectively. The effect of [bmim]⁺ on the CMC value of SDS is more profound than [bmp]⁺ due to higher the polarizability/charge density on the imidazolium ring than the pyrrolidinium moiety, that stabilizes/neutralizes the charge of the anionic surfactant promoting the micellization at lower concentration. Besides, the presences of a butyl side chain in both the ionic liquids are expected to form some sort of mixed micelles^{12, 13}.

3.2 Interfacial behaviour

Interfacial behaviour of SDS in IL + W mixed solvent systems were investigated, which were then compared with that of SDS in water.

Surface pressure at CMC (π_{cmc}) values were determined for both the imidazolium and pyrrolidinium based IL + W mixed solvent systems at different concentrations by using the following equation^{5, 6, 40, 45, 55}:

$$\pi_{\text{cmc}} = \gamma_{\text{S}} - \gamma_{\text{cmc}} \quad (2)$$

where, the γ_{S} and γ_{cmc} are the surface tension of pure solvent (either pure water or IL + water mixture) and the same for a surfactant solution at the CMC value of surfactant solution. For both the ionic liquids with increasing concentration, π_{cmc} values progressively passed through minima which was graphically shown in Fig. 2 (panel A). Results suggest that the ILs initially increases the hydrophobicity of the medium, thus assisting adsolubilization of surfactant, beyond a certain concentration, the ILs tender

similar effects as that of the normal salts. The π_{cmc} values vary in the range 36.4 - 39.2 mN m⁻¹ and 34.7 - 37.6 mN m⁻¹ for imidazolium and pyrrolidinium based IL respectively (Table 1). Due to higher polarizability of imidazolium ring the effect was more pronounced than the pyrrolidinium based IL.

3.3 Conductance studies

Conductance measurements were carried out to determine the CMC values and the fraction of counter-ion dissociation (α) of the SDS in IL + W mixed solvent systems. The slope of post (S_2)- and pre (S_1)-micellar regions can effectively be used in evaluating the fraction of counter ion dissociation (α) values vide the following equation^{45, 56}:

$$\alpha = \frac{S_2}{S_1} \quad (3)$$

The α values of SDS in both the IL + W mixed systems initially increases and passes through maxima which then decrease monotonously with increasing IL concentration, as shown in Fig. 2 (panel B). The α value of SDS only in water is found to be 0.58, that was comparable with the literature values^{45, 54}. For both the ILs, the α values pass through maxima further supporting the proposition that initially the ILs help in the adsolubilization of SDS, beyond a certain concentration the effects of ILs become similar to the conventional salts in water; the only major difference lies in the fact that unlike the conventional salts, IL cations can form mixed micelles with the SDS where the IL cations also act as counter ions^{12, 13}. While describing the fraction

of counter ion binding, evaluated by analyzing the conductance data, it is proposed that a substantial fraction of ionic liquid cations can act as the counter ions to the anionic micelles. The fraction of counter ion binding (β , as presented in Table 1) increased from 0.4 in water to ~ 0.6 in presence of 2.5 mM aqueous ILs in water. It is proposed that the increased β value is due to the incorporation of ionic liquid cations onto the anionic micelles as the counter ion. This proposition was further supported by the DLS data, as discussed later. However further investigations involving the structural parameters are warranted in order to confirm the proposition.

3.4 Thermodynamics of micellization

Gibbs free energy of micellization (ΔG_{mic}^0) values were evaluated using the following expressions^{46, 57–61}:

$$\Delta G_{\text{mic}}^0 = (2 - \alpha)RT \ln X_{\text{cmc}} \quad (4)$$

where, X_{cmc} is the mole fraction of surfactant (the other component being the solvent) at the CMC, R and T have their usual significances. Negative values of ΔG_{mic}^0 indicate spontaneity of micellization processes, shown in Fig. 2 (panel C). The ΔG_{mic}^0 value for SDS in water is found to be $-17.7 \text{ kJ mol}^{-1}$ similar to the earlier reported values^{45, 54}. With increasing IL concentration in water the magnitude of the ΔG_{mic}^0 values increase is more prominent in case of [bmim]Cl (-18.5 to $-24.4 \text{ kJ mol}^{-1}$) than the [bmp]BF₄ + W system (-18.1 to $-23.5 \text{ kJ mol}^{-1}$) further supporting the earlier proposition. From the β values of SDS in mixed solvent systems, it can be concluded that the extent of dissociation of surfactant molecules occur more spontaneous with increasing polarity of the medium.

3.5 Micellar aggregation number

Aggregation number of SDS (n) in water and as well as in IL + W mixed solvent systems were determined using Py as probe and HPC as quencher (Q) using the following equation^{43, 46, 60, 61}:

$$\ln \frac{I_0}{I} = n \frac{[Q]}{[S] - \text{CMC}} \quad (5)$$

where, I_0 and I are the fluorescence intensity of pyrene in the absence and presence of Q respectively, in the presence of a particular surfactant concentration $[S]$. The third vibronic emission peak of Py (385 nm) was taken into account to determine the aggregation number (n) of SDS. Some representative $\ln I_0/I$ vs. quencher concentration $[Q]$ plots have been shown in Fig. S2 (supplementary section). Aggregation number of SDS in pure water is 73, similar to the literature value⁴⁵. Micellar aggregation number of SDS gradually increases with increasing concentration of IL; in case of [bmim]Cl the values increase in the range of 90 to 161 while for [bmp]BF₄ it ranged in between 78 to 170 (Fig. 3, panel A (also summarized in Table 1, along with other results)). Increased aggregation number of SDS in IL + W

Fig. 3 Variation of aggregation number (n , A) and hydrodynamic diameter (d_h , B), of SDS micelles with the concentration of ionic liquid [IL] in water at 298 K. Systems: ○, [bmim]Cl and Δ, [bmp]BF₄.

mixed solvent systems compared to pure water are due to the presence of ionic liquid molecules in water which increases the polarity of the mixed systems; also it is known that the micellar aggregation number increases with increasing salt concentration^{43, 46, 60, 61}. Almost two fold increases in micellar aggregation number in presence of ionic liquids are due to the formation of mixed micelles between the dodecyl sulphate anion and ionic liquid cations that interact favourably through electrostatic attraction. Besides, the butyl moieties of the ionic liquid cations can easily get anchored on to the palisade layer of the anionic micelles, as also evidenced by a 1.5 times increase in the fraction of counter ion binding in presence of ILs, obtained from the conductance data. The proposition was further supported by the DLS data as discussed below.

3.6 Dynamic light scattering (DLS) studies

Hydrodynamic diameter (d_h) and polydispersity index (PDI) values of SDS micelles in different IL + W media were measured by DLS studies. Size of SDS in pure water is

found to be 3.8 nm, close to literature value^{45, 55}. Size of SDS micelles increased sigmoidally with increasing IL concentration in water (Fig. 3, along with other data). d_h varied in the range 92-161 nm for [bmim]Cl + W while for [bmp]BF₄ it varied in the range 89-169 nm. Increase in micellar size with increasing IL concentration is driven by the strong electrostatic interaction between the IL cation and the anionic surfactant; the charge neutralization eventually increases the hydrophobicity of the medium that effectively increases the micellar size⁵¹. Besides, after a threshold concentration, the effect of IL becomes similar to the conventional electrolytes, as already mentioned earlier. The charge density in imidazolium is higher than that of pyrrolidinium ring; hence it imparts higher polarity to SDS. The hydrophobic interaction into the micelles as well as dominant of SDS in micelles is the main factor for formation of larger aggregates. From the surface tension measurements it was observed that with increasing IL concentration the molecular cross sectional area increases. Hence it is quite expected that the micellar size of SDS (partly the ionic liquid molecules also take part in the micellization process). Thus the observations from the surface tension data, aggregation number and dynamic light scattering data could be correlated in explaining the variation of different physicochemical parameters of SDS aggregates in varying concentration of IL in water. Size and aggregation number of mixed micelles at the certain concentration of ILs were maximum, i.e., aggregate tendency higher has been shown up to certain concentration of ILs (almost about at 1 mM conc.). It is believed that the increases in micellar size in presence of ILs are due to the incorporation/coadsorption of ionic liquid cations to the anionic micellar surface.

Polydispersity index (*PDI*) value of SDS in water was found to be greater than 0.4 although count rate of photon was comparatively low. In presence of ILs, heterogeneous aggregates were formed, as reflected through the nonsystematic variation of *PDI* values with the variation of ILs concentration (data not shown). As together the equilibrium area per surfactant molecule and surfactant tail length were higher in value than that of surfactant tail volume at aggregate interface occurring the resultant mixed micelles were spherical in shape, the results could be well correlated with aggregation number. However, further studies like, rheology measurements, small angle X-ray scattering, small angle neutron scattering, cryo-electron microscopy are warranted to envisage the structure of the aggregates.

4 Conclusion

In this work a bunch of experiments have been carried out to understand the interfacial and micellar aggregation behaviour of SDS in water as well as in [bmim]Cl + W and

[bmp]BF₄ + W mixed solvent systems at different concentration of IL. Also the comparative studies have been done between imidazolium and pyrrolidinium based ionic liquid in water as mixed solvent systems. The lower *CMC* values of those mixed micelles indicate hydrophobic interaction between SDS and cationic head groups of ILs. *CMC* values of SDS in presence of imidazolium based IL are lower than pyrrolidinium based IL that is contributed by the high polarity of ionic liquid head group^{12, 13}. The change in conductance value in different mixed micelle systems, leading to the negative values of ΔG_{mic}^0 indicate spontaneity of the aggregation process. Combined hydrogen bonding and electrostatic interaction between SDS and ILs in water, π_{cmc} of mixed micelle systems pass through minima which lead to the associative interaction at the micellar surface. Dissociation of SDS molecules lead the high charge density at the micelle surface, as reflected from the fraction of counter ion dissociation values. Larger size of micelles are the results of the formation of larger aggregates induced by the cationic moieties of ILs that form some sort of mixed micelles with the anionic surfactant^{12, 13}. Interfacial and aggregation behavior of SDS in aqueous-ionic liquid mixed solvent systems are considered to be important in electrostatic differentiation in molecular level of the particles as well as in nanoparticle synthesis; such systems can also be used as drug delivery systems. In order to explicitly understand the effect of two different ionic liquids, studying the micellization of a surfactant with two ionic liquids comprising similar counter anion is considered to be worthy. Besides the effect of ionic liquids' counter anions should also be investigated by studying the micellization in presence of corresponding conventional salts; these are considered as the future perspectives.

Conflict of Interest

Authors declare that there is no conflict of interests.

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Supporting Information

This material is available free of charge via the Internet at <http://dx.doi.org/jos.70.10.5650/jos.ess20303>

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