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ORIGINAL ARTICLE

Interaction Between Ionic Liquids and Gemini Surfactant: A Detailed Investigation into the Role of Ionic Liquids in Modifying Properties of Aqueous Gemini Surfactant

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Abstract Tuning physicochemical properties of aqueous surfactant solutions comprised of normal or reverse micelles by external additives is of utmost importance due to the enormous application potential of surfactant-based systems. Unusual and interesting properties of environmentally benign ionic liquids (IL) make them suitable candidates for this purpose. To understand and establish the role of IL in modifying properties of aqueous gemini surfactants, we studied the effect of the IL, 1-hexyl-3-methylimidazolium bromide ([Hmim][Br]) and 1-octyl-3-methylimidazolium bromide ([Omim][Br]) on the properties of the aqueous cationic gemini surfactant 1,6-hexanediyl-α,ω-bis(dimethyltetradecyl)ammonium bromide (14-6-14,2Br$^-$). The behavioral changes were investigated by measuring the critical micelle concentration (CMC) using electrical conductance, surface tension, dye solubilization and fluorescence probe measurements at 298.15 K. It was observed that the CMC of 14-6-14,2Br$^-$ gemini surfactant decreases with addition of IL, thus favoring the micellization process. An increase in micellar size was observed at lower IL concentration using dynamic light scattering, with a decrease in aggregation number (N_{agg}) determined from fluorescence probe quenching measurements. It is noteworthy that the extent of modulation of the micellar properties is different for both the IL due to their structural differences. IL behave like electrolytes at lower concentrations and cosurfactants at higher concentrations and form mixed micelles with the cationic gemini surfactant showing an increase in N_{agg}.

Keywords Ionic liquids · Gemini surfactants · Fluorescence quenching · Dynamic light scattering · Aggregation number

Abbreviations

ANS	8-Anilino-1-naphthalenesulfonic acid
CMC	Critical micelle concentration
CPC	Cetylpyridinium chloride
DLS	Dynamic light scattering measurements
EG	Ethylene glycol
[Hmim][Br]	1-Hexyl 3-methyl imidazolium bromide
IL	Ionic liquids
N_{agg}	Aggregation numbers
[Omim][Br]	1-Octyl 3-methyl imidazolium bromide
SANS	Small angle neutron scattering
14-6-14,2Br$^-$	1,6-Hexanediyl-α,ω-bis(dimethyltetradecyl)ammonium bromide
PIL	Protic ionic liquids

List of symbols

β	Counter ion binding
ΔG_m^0	Standard free energy of micelle formation
γ	Surface tension
A_{min}	Area per molecule at the air–water interface
Γ_{max}	Maximum surface excess concentration

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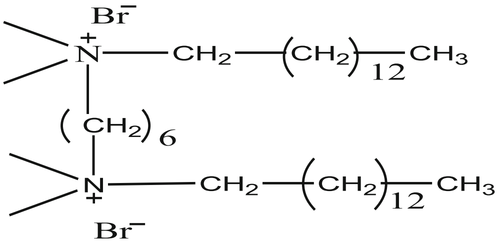
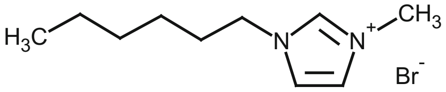
R	Universal gas constant
N_A	Avogadro's number
Π_{CMC}	Surface pressure at the CMC

Introduction

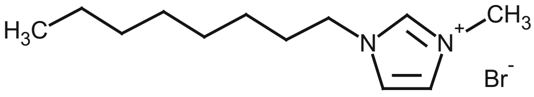
Due to their immense application potential, surfactant-based systems are a topic of major research interest in both academia and industry. Surface-active molecules self-assemble in aqueous media to form nano-sized aggregates called micelles. Recently, dimeric or gemini surfactants having two identical or different hydrophobic chains and two ionic/polar head groups covalently connected by a spacer group (Scheme 1) have been investigated [1–6]. The superiority of gemini surfactants over conventional monomeric surfactants includes, remarkably low critical micelle concentration (CMC), high surface activity, low Krafft temperature, unusual rheological properties, antimicrobial activity, better wetting ability and multifarious aggregate structures [7–9], to name a few. Such unique properties encouraged their applications in various field of study, such as gene transfection, drug formulations and drug delivery, food industry, cosmetics, catalytic reaction, oil recovery and polymerization, etc. [10–12]. In aqueous solution, gemini surfactants behave differently than conventional monomeric surfactants. The aggregation behavior in monomeric conventional surfactants is mainly controlled by intermolecular interactions, whereas in gemini surfactants it is controlled by the co-operativity of both inter-molecular and intra-molecular interactions. The properties of gemini surfactants in aqueous solution significantly depend upon concentration, temperature, nature of hydrophobic tails, spacer properties, hydrophobic tails asymmetry and salt concentration [13–16].



Hexamethylene 1, 6-bis (N-tetradecyl-N, N-dimethylammonium bromide) (14-6-14 2 Br^-)



1-Hexyl 3-methylimidazolium bromide ([Hmim][Br])



1-Octyl 3-methylimidazolium bromide ([Omim][Br])

Scheme 1 Structures of the cationic gemini surfactant (14-6-14,$2Br^-$), Ionic liquids [Hmim][Br] and [Omim][Br]

If conditions are unchanged, aqueous gemini surfactant solutions have more or less fixed physicochemical properties that are difficult to modify. One possible way to modify the solution properties is to use some external means such as temperature/pressure and/or addition of a variety of modifiers such as organic salts, organic solvents, hydrotropic salt, cosurfactants, electrolytes, polymers, nonpolar organics, inorganic salts, biomolecules, conventional surfactants or polyelectrolytes [17–24] to name a few.

Under ambient condition, judicious selection of environmentally benign substances, such as ionic liquids (IL) can play a major role in modifying the properties of gemini surfactants. IL, composed entirely of cations and anions are known to be effective green solvents due to their negligible vapor pressure and ability to recycle. The other fascinating properties of IL, which draws the attention of academic as well as industrial researchers includes, wide liquid ranges, good thermal stabilities, electrolytic conductivity, wide range of viscosities, adjustable miscibility, nonflammability, etc. Long alkyl chain IL can also show surfactant like properties [25–30]. Comprehensive studies on the interactions between mixtures of gemini and conventional single chain surfactants of different charge classes to form mixed micellar aggregates have been reported [31–34]. In recent decades, studies on the interactions between single chain surfactants and IL have been reported and the results obtained are discussed at length [35–46]. Pandey *et al.* [35–38] reported the dual behavior of IL in aqueous solutions of single chain surfactants. However interactions between gemini surfactants and IL are hardly studied.

Recently, Chai *et al.* [47] studied the composition and structural parameters of W/O microemulsions containing the gemini imidazolium surfactant and its monomeric form of IL using the dilution method. Li *et al.* [48] has studied the aggregation behavior of a cationic gemini surfactant with methylene spacers in two different protic IL (PIL), propylammonium nitrate (PAN) and butylammonium nitrate (BAN), by small and wide-angle X-ray scattering, polarized optical microscopy and rheology measurements. The study reveals that changing from PAN to BAN, phase transition of the aggregate was observed from the reversed to normal hexagonal phase due to the attractive interaction between the IL and cationic gemini surfactants. Wang *et al.* [49] studied the aggregation behavior of dissymmetric cationic gemini surfactants in PIL and observed that structure dissymmetry plays an important role in aggregation process. Shang *et al.* [50] have investigated the mixed micellization of binary mixtures containing cationic gemini surfactant, trimethylene-1,3-bis(dodecyl ammonium bromide) (12-3-12) with the conventional cationic surfactant dodecyltrimethyl-ammonium bromide (DTAB) and with IL, [C$_n$mim]Br ($n = 4, 6, 8$). The concentration-dependent dual role of the IL is well documented [6, 37].

Jn a lower concentration range, IL behave like common electrolytes, however, in a higher concentration range they behave like polar co-solvents [6, 37]. Shang *et al.* studied the effect of [C$_n$mim][Br] (where $n = 4$, 6 and 8) IL and NaBr on the aggregation behavior of cationic gemini surfactants. IL plays the role of inorganic electrolyte at lower concentration whereas at higher concentration it acts like cosurfactant and cosolvent [50]. The influence of the long chain IL (1-tetradecyl-3-methylimidazolium bromide) on the micellar properties of single and double chain cationic surfactants was investigated [51]. The results showed an attractive interaction between the IL and the gemini surfactant with a short spacer and promoted micellization due to the more hydrophilic character [51].

The concentration dependent dual role of IL as inorganic electrolytes (at lower concentration) or as cosurfactants (at higher concentrations) encouraged us to study the effect of IL on the aggregation behavior of cationic gemini surfactants. The IL used in the current report were chosen based on their relatively high interfacial tensions. Mixtures of IL with gemini surfactants have better surface properties, can show remarkable physicochemical properties and are more cost effective than single chain surfactants [31–33]. Additionally, studying the complex molecular interactions in these systems can help us to better understand biological systems and functions [10–12, 34].

In the present investigation, the IL, 1-hexyl 3-methyl imidazolium bromide ([Hmim][Br]) and 1-octyl 3-methyl imidazolium bromide ([Omim][Br]) were added in fixed concentrations to an aqueous solution of the cationic gemini surfactant 1,6-hexanediyl-α,ω-bis(dimethyltetradecyl)ammonium bromide (14-6-14,2Br$^-$) with varied concentrations. The physicochemical properties of aqueous 14-6-14,2Br$^-$ with and without addition of IL were characterized by conductance, surface tension, UV–visible and steady state fluorescence and dynamic light scattering (DLS) techniques.

Experimental Section

Materials

1,6-Dibromohexane (98 %), 1-methylimidazole (99 %), 1-bromooctane (98 %) and 1-bromohexane (98 %) were purchased from Spectrochem PVT Ltd (Mumbai, India). *N*,*N*-dimethyltetradecylamine was purchased from Aldrich Ltd and used as received. Ethyl acetate (Merck, 99 %), *n*-hexane (Finar, 95 %), acetone (Merck, ≥99 %), ethyl alcohol (J.H.I.T. Co. Ltd. 99.9 %), acetonitrile (R.F.C. Ltd. 99 %). Water, double distilled over $KMnO_4$ and deionized, with a conductivity of 6.1–6.4 $\mu S\ cm^{-1}$ was used throughout the experiments. 8-Anilino-1-naphthalenesulfonic acid (ANS) (used as a chromophore) was obtained from Aldrich and used as received. Stock solutions of IL and chromophore (1 mM) were prepared using distilled water. All of the IL were dried under vacuum at 343 K for a few days to remove any trace amounts of water. Karl–Fisher analysis of the samples indicated that the water content was reduced to <100 ppm in all the IL.

Synthesis of 14-6-14,2Br$^-$

14-6-14,2Br$^-$ was synthesized [52, 53] by the reaction of 1,6-dibromohexane with *N*,*N*-dimethyltetradecylamine in dry ethanol. A 1:2.1 reaction mixture (slight excess of 1,6-dibromohexane ensured complete bis-quaternization) was refluxed (at 80 °C) for 48 h. After completion (the reaction progress was monitored by TLC), solvent was removed under vacuum from the reaction mixture and the solid was recrystallized five times from a mixture of hexane and ethyl acetate to obtain the compound in pure form. The overall yield of the surfactant was 80 %. Purity of the surfactant was checked on the basis of C, H, N analysis, which was further characterized by ^{1}H-NMR [53] spectroscopy (M.P. 221 °C).

The ^{1}H-NMR of 14-6-14,2Br$^-$ is as follow: (200 MHz, $CDCl_3$, δ ppm): 0.88 (t, 6H, 2× $–CH_3$), 1.26–1.36 (m, 44H, 2× $–\mathbf{(CH_2)_{11}}–CH_3$), 1.79 (s, 2H, $\mathbf{–CH_2–}(CH_2)_{11}–CH_3$), 2.41 (s, 2H, $–N–\mathbf{CH_2}–CH_2–(CH_2)_{11}–CH_3$), 3.39 (s, 12H, 2× $–N–(\mathbf{CH_3})_2$, 3.51 (m, 8H, 2× $–N–\mathbf{CH_2}$ from spacer and 2× $–N–\mathbf{CH_2}$ from alkyl chain, 3.86 (s, 8H, 2× $–N–CH_2–\mathbf{CH_2}–\mathbf{CH_2}–$ from spacer).

Synthesis of IL

IL reported here were prepared according to the procedure reported in the literature [54–56]. Briefly, the reaction of 1-methylimidazole and excess molar amount of appropriate alkyl bromide was performed in 1,1,1-trichloroethane under reflux at ca. 343 K for 48 h. The 1,1,1-trichloroethane was then removed using a rotary evaporator under reduced pressure. The product was purified by recrystallization from ethyl acetate/acetonitrile (3:2 by volume) at least four times, to remove any unreacted reagent. Any residual solvents were removed by heating at 343 K under vacuum. The water content was measured using Karl–Fisher titration (Metrohm, 890 Titrando) and was lower than 100 × 10^{-6} mass%. The DSC thermograms (Mettler Toledo, DSC-1) for both the IL samples showed a sharp single endothermic peak supporting the high purity of both IL samples. The IL was also analyzed by ^{1}H NMR and ^{13}C NMR (Advance DPX 200 Bruker, CSMCRI) to confirm the absence of any major impurities.

The ^{1}H NMR of [Hmim][Br] is as follows: (200 MHz, DMSO-d_6, δ ppm):0.86 (3H,t, N–$(CH_2)_5$–CH_3), 1.27 (br. S, 6H, N–CH_2– CH_2– **$(CH_2)_3$**–CH_3), 1.78 (2H, quintet, N–CH_2–**CH_2**–$(CH_2)_3$–CH_3), 3.85 (3H, singlet, N–CH_3), 4.15 (t, 2H, N–**CH_2**–CH_2–$(CH_2)_3$–CH_3), 7.70 (s, 1H), 7.77 (s, 1H), 9.10 (s, 1H). ^{13}C NMR (200 MHz, 16.14,24.18, 27.43, 31.69, 38.10, 41.85, 51.02, 124.56, 125.86, 136.82).

The ^{1}H NMR of [Omim][Br] is as follows: (200 MHz, DMSO-d_6, δ ppm): 0.86 (3H, t, N–$(CH_2)_5$–**CH_3**), 1.25 (br. S, 10H, N–CH_2– CH_2– **$(CH_2)_5$**–CH_3), 1.78 (2H, quintet, N–CH_2–**CH_2**–$(CH_2)_5$–CH_3), 3.85 (3H, singlet, N–**CH_3**), 4.15 (t, 2H, N–**CH_2**–CH_2–$(CH_2)_5$–CH_3), 7.70 (s, 1H), 7.77 (s, 1H), 9.10 (s, 1H). ^{13}C NMR (200 MHz, 16.13, 24.14, 27.83, 30.59, 33.27, 38.37, 51.57, 79.13, 121.21, 123.82, 125.65, 138.13).

Electrical Conductivity Measurements

Aqueous solutions of IL were prepared by weight using an analytical balance with a precision of ±0.0001 g (B 204-S, Mettler Toledo, Switzerland, operated in a dry box) in Millipore grade deionized double distilled water. The calculated amount of 14-6-14,$2Br^{-}$ solution was added from the stock solution to the IL solutions. Electrical conductivities were measured at 298.15 ± 0.1 K by a EUTECH PC 6000 digital conductivity meter (Eutech Instruments, Singapore) having a sensitivity of 0.1 μS cm^{-1} with an accuracy of 0.5 %. The temperature was maintained within 0.1 K using a constant temperature bath. The dip type conductivity probe (EC-CONSEN 21B) provided with the instrument has an inbuilt temperature probe. Prior to measurements, the probe was calibrated with aqueous KCl solutions in the concentration range of 0.01–1.0 mol kg^{-1}. At least three repetitive measurements were made for each concentration and only the mean values were taken into consideration. The standard uncertainty of the measurements was <0.3 %.

Surface Tension Measurements

Surface tension measurements were made using a K9 tensiometer (Krüss Instruments, Germany) using a platinum ring by the ring detachment method at 298.15 ± 0.1 K. The temperature was maintained constant within 0.1 K using a constant temperature bath. The surface tension of deionized double distilled water having surface tension of 72.2 mNm^{-1} at 298.15 ± 0.1 K was used for the calibration purpose. Surfactant concentration was varied by adding concentrated surfactant solution in small installments, and the readings were noted after thorough mixing and temperature equilibration. The measured surface tension values were corrected according to the procedure of Harkins and Jordan using the instrument software. The accuracy of γ measurements was within 0.1 mNm^{-1}. The CMC values were determined by noting inflections in the γ *versus* the logarithm of surfactant concentration isotherms.

UV–Vis Absorbance Measurements

UV–Vis absorption spectra were measured using a Carry 50 spectrophotometer (Varian, Switzerland) equipped with a thermostated cell compartment. The absorption spectrum of the aqueous solution of gemini surfactant + ANS + IL mixture was collected against the reference solution containing the ANS + IL at 298.15 ± 0. 1 K temperatures, using a quartz cuvette with a path length of 1 cm. ANS was used as the probe with a concentration of 1.6 × 10^{-6} mol dm^{-3} in all experiments to avoid any interference in the micelle formation.

Steady-State Fluorescence Measurements

Steady-state fluorescence measurements were performed using a Fluorolog spectrofluorometer (Horiba Jobin Yvon) using a 1-cm path length quartz cuvette. Pyrene was used as the polarity probe with a concentration of 1.0 × 10^{-6} mol dm^{-3} in all experiments to avoid any interference in micelle formation. The emission spectra of pyrene were recorded in the wavelength range 350–500 nm at an excitation wavelength of 334 nm using 1 nm excitation and emission slit widths. The first (I_1) and third (I_3) vibronic peaks of pyrene appeared at 373 and 384 nm, respectively. CMC values were determined by the I_1/I_3 of pyrene spectrum as a function of surfactant concentration. The fluorescence spectra were corrected for the instrumental response. To determine surfactant aggregation numbers, steady-state fluorescence quenching measurements were performed using pyrene and cetylpyridinium chloride (CPC) as the probe and static quencher, respectively. All the measurements were performed at 298.15 ± 0.1 K using a constant temperature control bath.

Dynamic Light Scattering Measurements

Dynamic light scattering measurements were performed at 298.15 ± 0.1 K on a Spectro Size 300 (Malvern Instruments, UK) with a He–Ne laser (633 nm, 4 M_w). An appropriate amount of IL was added by weight to the 14-6-14,$2Br^{-}$ solution (2 mL) taken in a cylindrical quartz cuvette. The aqueous solution of gemini 14-6-14,2Br$^-$ were prepared above the CMC. The temperature of the measurements was controlled within an accuracy of ±0.1 K.

All the solutions were prepared in deionized double distilled water on a weight basis. The concentrations of individual surfactants were kept higher than CMC values and then mixed with appropriate volumes of IL to obtain different bulk concentrations of the binary systems. All the measurements were taken in triplicate and averaged. All the data were analyzed using Microsoft Excel and OriginPro 8.0 softwares.

Results and Discussion

Interaction Studies by Electrical Conductance Measurement

Measurement of electrical conductivity is widely used to provide information regarding the critical micelle concentration (CMC) and degree of counter ion binding (β) of aqueous surfactant solutions [57, 58]. We investigated the properties of aqueous 14-6-14,2Br$^-$ in the presence and absence of IL, [Hmim][Br] and [Omim][Br]. One expects two linear regimes for conductance in the pre- and post-micellar region of an aqueous ionic surfactant solution where the slope becomes smaller, once the micelles have been formed as per the Onsager theory of electrolyte conductivity [57]. In the current investigation, we noticed similar linear fragments (Fig. 1a). The concentration at which the two linear fragments intersect is assigned to the CMC. The slope change at the CMC is due to an effective loss of ionic charges because a fraction of the counterions are confined to the micellar surface. The aggregation of the molecules, or micelles, start to form at the concentration corresponding to this break point. The CMC of aqueous 14-6-14,2Br$^-$ gemini surfactant is in excellent agreement with the reported value [20, 29, 31, 59] 1.58×10^{-4} mol dm^{-3}. The CMC of the aqueous 14-6-14,2Br$^-$ decreases as the IL concentration increases as shown in Figures S1–S2 and reported in Table 1.

Farah *et al.* [60] studied the effect of linear primary alcohols and amines on the CMC values of 12-4-12 gemini surfactants and observed that CMC decrease with increasing the concentration as well as the alkyl chain length of the additives. Further, alcohols are more effective than amines in decreasing the CMC due to the less specific interaction between the surfactant head groups and amines than alcohols. Increasing the concentration of organic salts as well as the hydrophobicity of the salt anion also decreases the CMC [17]. Yu *et al.* [61] investigated the effect of organic and inorganic electrolytes on the micellization behavior of two cationic gemini surfactants and the results suggest that the CMC decreases with increasing concentration of the electrolyte. Tiwari and Subit [62] investigated the aggregation behavior of cationic gemini surfactants with hydroxyl groups in the spacer with IL in water and water–organic solvent media and reported that the CMC increases with increasing cosolvent concentration. Further, with decreasing the polarity of the solvent, the surfactant tails have more affinity toward the bulk phase solvent which results in decreased hydrophobicity of the surfactant molecules and results in higher CMC.

Among the most important observations from the conductance data is the degree of counter ion binding (β). In the current investigation, as the concentration of IL increases, surfactant molecules bind more closely with the IL, which results in increased β values as shown in Table 2. This result is quite logical as strongly bound counter ions weaken head group repulsion, which would lead to micelle formation at a lower concentration. The observed increase in β is probably due to the decrease in the charge density at the micellar surface caused by the decrease in the aggregation number of the micelle. This observation is well supported by the fluorescence quenching measurement, which clearly indicates that as the IL concentration increases, the aggregation number initially decreases up to 0.4 wt% addition of the IL and then increases, which may be due to the cosurfactant like behavior at higher concentration. The lower CMC is either due to the increasing counterion binding or to formation of mixed micelles (cations of the surfactant + cation of the IL).

One important observation from the CMC measurement by electrical conductance is, at a fixed IL concentration of 0.6 wt%, the CMC decreases more due to [Omim][Br] than for [Hmim][Br]. At higher concentration no appreciable change in CMC was noticed [50, 60, 61]. Increasing the salt [22, 63] concentration reduces the electrostatic repulsion between the charged groups and favors micelle aggregation. In our case, at lower concentration the same phenomena were observed; where the IL forms charged ions, which reduces the electrostatic repulsion between the charged head groups of the gemini surfactant and lowers the CMC. It is reported that increasing the chain length of alcohols and alkyl amines as additives, the CMC of the aqueous cationic gemini surfactants decreased [64].

As observed in the supplementary material (Figs. S1–S2), conductance increased as the wt% of the IL increased, which is due to the dissociation of the IL in the solution. At a fixed concentration, [Hmim][Br] containing surfactant solutions have significantly higher conductance as compared to those containing [Omim][Br] as shown in Fig. 2. This may be due to the higher limiting ionic conductivity of [Hmim$^+$] as compared to that of [Omim$^+$] at ambient conditions.

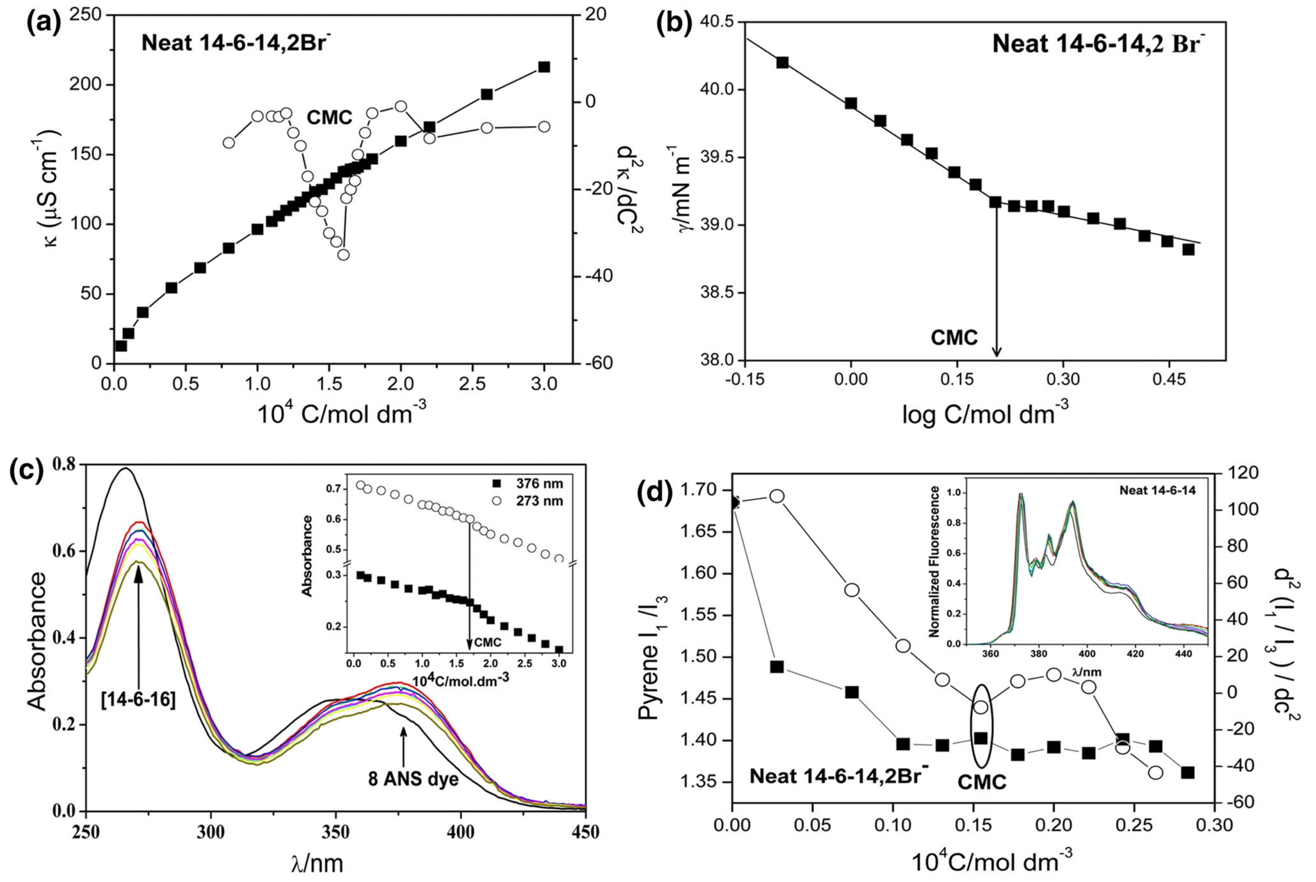


Fig. 1 Representative plots of variation of different physical quantities with concentration for determining the critical micelle concentration (CMC) of 14-6-14,2Br$^-$ in water at 298.15 K. **a** Specific-conductance *versus* 14-6-14,2Br$^-$ concentrations in water, **b** surface tension *versus* log concentration, **c** UV–Vis absorbance *versus* wavelength (*inset* shows the absorbance *versus* concentration of gemini surfactant), **d** pyrene fluorescence intensity *versus* concentration of cationic gemini surfactant in water (*inset* shows the normalized fluorescence *versus* wavelength). (*Filled square*) I_1/I_3, (*open circles*) $d^2(I_1/I_3)/dc^2$

The CMC of a surfactant is regarded as a measure of the stability of its micellar form relative to its monomeric form, the lower the CMC, the greater the stability. According to the mass action model and approximation suggested by Zana [65], ΔG_m^0 value depends on both the CMC and β and can be written as (in solution, gemini surfactants give 2 alkyl chains and two polar head groups):

$$\Delta G_m^0 = 2RT(1.5-\alpha)\ln X_{CMC} = 2RT(1.5-\alpha)\ln\frac{C_{CMC}}{55.4} \qquad (1)$$

where X_{CMC} is the CMC in mole fraction unit, C_{CMC} is that in mol dm^{-3}, α the degree of counter ion binding and 55.4 comes from that 1 dm^3 of water corresponds to 55.4 mol of water at 298.15 K. The value of ΔG_m^0 becomes more negative as the IL concentration increases, which is due to stronger hydrophobic–hydrophobic interactions.

The overall effect of the synthesized IL on the CMC of the aqueous 14-6-14,2Br$^-$ gemini surfactant is mainly a combination of the electrolyte effect and hydrophobic effect. The dominance of these two factors depends on the various physical parameters such as concentration and the alkyl chain length of the added IL.

Interaction Studies by Surface Tension Measurement

One of the significant aspects of surfactants is the ability to lower the interfacial tension between an aqueous solution and some other phase. In the current investigation, we examined the surface tension (γ) of aqueous 14-6-14,2Br$^-$ in the presence and absence of IL. The threshold surfactant concentration required to saturate the air/solution interface is the CMC which results in a break point in the γ *versus* log [14-6-14,2Br$^-$] plot as shown in Fig. 1b. Eastoe *et al.* [5] reported on possible interferences of inorganic as well as surface active impurities on the surface tension of dimeric anionic surfactants. The presence of residual inorganic and surface active

Table 1 CMC of aqueous cationic gemini surfactant (14-6-14,2Br$^-$) obtained using different methods in the presence of [Hmim][Br] and [Omim][Br]

IL in wt%	10^4 CMC (mol dm^{-3})			
	Conductivity	Surface tension	UV–Vis	Fluorescence
[Hmim][Br]				
0.0	1.60 (1.60) [29]	1.60	1.70	1.80
0.2	1.30	1.30	1.60	1.60
0.4	1.00	1.00	1.30	–
0.6	0.94	0.60	1.00	1.30
0.8	0.50	0.50	0.15	–
1.0	0.15	0.12	0.06	1.10
[Omim][Br]				
0.2	1.00	1.00	1.40	1.10
0.4	0.60	1.00	1.10	–
0.6	0.20	0.20	0.80	0.80
0.8	0.10	0.10	0.08	–
1.0	0.05	0.05	0.05	0.60

Standard uncertainties u are: $u(\mathrm{CMC}) = \pm 0.03 \times 10^{-4}$ mol dm^{-3}. All the experiments were carried out in an inert atmosphere and at atmospheric pressure

Table 2 Counter ion binding (α), interfacial parameters: surface pressure at CMC (Π_{CMC}), surface excess ($\Gamma_{\max} \times 10^6$), minimum area per molecule ($A_{\min}$) and Gibbs free of micellization ($-\Delta G^0_{\mathrm{mic}}$) for aqueous 14-6-14,2Br$^-$ in absence and presence of different additives at 298.15 K

IL in wt%	α	Π_{CMC} (mNm^{-1})	$\Gamma_{\max} \times 10^6$ (mol m^{-2})[a]	$A_{\min}$ (Å^2)[a]	$-\Delta G^0_{\mathrm{mic}}$ (kJ mol^{-1})
[Hmim][Br]					
0.0	0.35 (0.36) [29]	32.10	0.50 (0.64)	329 (259)	−79.80 (−71.71) [29]
0.2	0.14	35.57	0.52 (0.77)	322 (215)	−73.26
0.4	0.23	37.70	0.56 (0.84)	296 (197)	−80.80
0.6	0.66	38.30	0.50 (0.75)	332 (222)	−90.70
0.8	0.86	39.13	0.45 (0.68)	369 (245)	−143.68
1.0	–	41.77	0.40 (0.60)	415 (275)	–
[Omim][Br]					
0.2	0.10	35.70	0.51 (0.74)	326 (224)	−72.20
0.4	0.42	38.60	0.52 (0.76)	319 (218)	−80.70
0.6	0.51	39.10	0.48 (0.71)	346 (233)	−94.66
0.8	0.82	40.70	0.43 (0.67)	386 (248)	−143.30
1.0	–	42.93	0.38 (0.57)	437 (289)	–

Standard uncertainties u are: $u(\beta) = \pm 0.04$, $u(\Pi_{\mathrm{CMC}}) = \pm 0.70$ mN m^{-1}, $u(\Gamma_{\max}) = \pm 0.05 \times 10^{-6}$ mol m^{-2}, $u(A_{\min}) = \pm 0.60$ Å^2, $u(\Delta G^0_{\mathrm{mic}}) = \pm 5.00$ kJ mol^{-1}. All the experiments were carried out in an inert atmosphere and at atmospheric pressure

[a] Values in the parentheses for $\Gamma_{\max}$ and $A_{\min}$ are calculated by taking the pre-factor value $n = 2$

impurities can greatly affect the surface tension of aqueous anionic gemini surfactant solutions and it was well documented by recording the neutron reflection and surface tension for the synthesized anionic surfactants adsorption isotherm at the air–water interface. In the current investigation, we have taken proper care in the synthesis of the cationic gemini surfactants so that the level of the impurities will be as low as possible.

A careful examination of the γ *versus* log [14-6-14,2Br$^-$] plots after addition of the IL (Figures S3–S4) reveals that as the concentration and alkyl chain length of the IL increases surface tension of the aqueous 14-6-14,2Br$^-$ decreases. The surface tension decreases more for the [Omim][Br], which may be due to the longer alkyl chain, which increases the hydrophobicity in the system. The addition of IL causes the compression of the diffuse electric double layer, which reduces the repulsions between the surfactant head groups and reduces the CMC. Similar synergistic effects for mixtures of cationic gemini surfactants with different aromatic hydrotropes and salt anions have also been reported [17, 63].

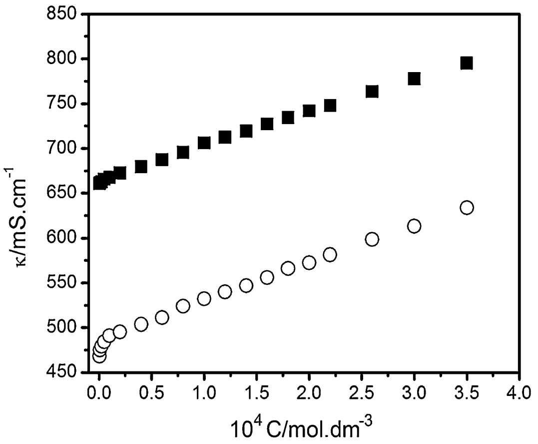


Fig. 2 Specific-conductance *versus* 14-6-14,$2Br^-$ concentration with the addition of 0.2 wt% of (*filled squares*) [Hmim][Br] and (*open circles*) [Omim][Br]

It is important to mention that the CMC of our aqueous 14-6-14,$2Br^-$ obtained by surface tension measurements is in good agreement with that reported in the literature [20, 29, 31, 59]. The CMC of the aqueous 14-6-14,$2Br^-$ decreases from 1.60×10^{-4} to 0.10×10^{-4} mol dm^{-3} with the addition of only 0.8 wt% of [Omim][Br]. For the [Hmim][Br], the same trend was observed but the CMC decreases up to 0.12×10^{-4} mol dm^{-3}. Generally, the addition of inorganic salt decreases the CMC of ionic surfactants [22, 66, 67], the depression being mainly due to the decrease in the thickness of the ionic atmosphere surrounding the ionic head groups and consequently decreased electrostatic repulsion between ionic surfactants in the micelle.

The area per molecule at the air/water interface, effectiveness and efficiency of the surfactants are also calculated from the $\gamma - \log[\text{14-6-14,2Br}^-]$ plots. As reported earlier [5], trace level impurities can also affect the area per molecule at the interface from 72 ± 3 Å^2 for untreated samples to 56 ± 3 Å^2 for the purified surfactant. Care was taken at the time of synthesis of the gemini surfactants to remove possible impurities to avoid discrepancies in the results. The maximum surface excess, $\Gamma_{\max}$, at the air/water interface was calculated by application of Gibbs adsorption isotherm to the surface tension (γ) *versus* concentration data. The Gibbs adsorption isotherm may be expressed as [66]:

$$\Gamma_{\max} = -\frac{1}{2.303nRT}\left(\frac{\delta\gamma}{\delta\log C}\right) \tag{2}$$

where $\Gamma_{\max}$ is the surface excess concentration, R the universal gas constant, C is the concentration of the surface active compound and n is taken as 3 corresponding to complete dissociation of the *m-s-m* type gemini surfactant to give one divalent surfactant ion and two monovalent counter ions. Comparison of small angle neutron scattering (SANS) and surface tension studies of cationic gemini surfactants resulted in a value for n close to 2, except for the compound with the xylyl spacer, for which n was about 3 [63]. Further, Eastoe *et al.* [5] had reported the pre-factor value as 2 for the dimeric anionic surfactants. As reported earlier, cationic surfactants form surfactant-counter ion complexes at the interface [68, 69]. Looking at all these aspects of the cationic gemini surfactants we have used both values of the pre-factor; 3 and 2 (values in the parentheses) and reported in Table 2. For the comparison, we used the value of $n = 3$ throughout the manuscript. Nevertheless, the value of n used to calculate $\Gamma_{\max}$, and so $A_{\min}$, does not affect the role of IL, which is an important point. The effective area of surfactant molecule at the air/water interface, $A_{\min}$, can be calculated by:

$$A_{\min} = 1/(N_A\Gamma_{\max}) \tag{3}$$

where N_A is Avogadro's number. $\Gamma_{\max}$ and $A_{\min}$ are listed in Table 2. As stated in Eq. 3, the higher the adsorption, the smaller is the effective area of the surfactant molecule at the surface. The calculated value of $A_{\min}$ in water for 14-6-14,$2Br^-$ (329 Å^2) is in good agreement with the recent literature (326 Å^2) [70]. The values of $A_{\min}$ increase with increasing spacer length for *m-s-m* type gemini surfactants for $m = 12$ and $s < 10$, and decreases when $s > 10$ [71]. The variation in the molecular area with the number of methylene groups in the spacer might be due to the arrangement of the spacer as a flat surface at the air/water interface when $s < 10$, which at a higher spacer unit ($s > 10$, due to higher hydrophobicity of the spacer) becomes wicket-like [71]. Similar results were found for the $m = 14$, 16 and 18 and $s = 3$, 4, 5, 6 and 8 containing gemini surfactants [70, 72]. Comparing our results with the previously published results for the $m = 14$ and $s = 2$, 4, 5 and 6, we found similar correlation, i.e. $A_{\min}$ for the 14-6-14,$2Br^-$ is higher than the 14-2-14,$2Br^-$ (90 Å^2 [51]), 14-3-14,$2Br^-$ (123 Å^2 [73]), 14-4-14,$2Br^-$ (291 Å^2 [70]) and 14-5-14,$2Br^-$ (295 Å^2 [70]).

The effect of alkyl chain length on the $A_{\min}$ for the *m-s-m* type gemini surfactant were also correlated. The reported $A_{\min}$ are: 8-3-8,$2Br^-$ (156 Å^2, [74]), 10-3-10,$2Br^-$ (124 Å^2 [74]), 12-3-12,$2Br^-$ (105 Å^2 [71], 107 Å^2 [50], 128 [73]), 14-3-14,$2Br^-$ (123 Å^2 [73]), 16-3-16,$2Br^-$ (121 Å^2 [74]) and 18-3-18,$2Br^-$ (128 Å^2, [72]), which indicates quasi parabolic dependence of the $A_{\min}$ when the length of the alkyl substituent increases in the range of $m = 8$–18 and $s = 3$. For $s = 6$, the reported $A_{\min}$ are, 143, 329, 326, 200, 205 Å^2 for $m = 12$ [71], 14 [Exp], 14 [70], 16 [75] and 18 [72], respectively.

The data in Table 2 indicate that $\Gamma_{\max}$ and $A_{\min}$ varies with the kind and the concentration of IL added [76, 77]. It reveals that the variation of the effective area of surfactant molecules at the surface decrease with the addition of IL. As we know, the addition of inorganic electrolyte to ionic surfactant solution can obviously influence the surface adsorption. The presence of counter ions near the polar heads of surfactant molecules decreases the electrostatic repulsion force between the head groups and makes it possible for the surfactant molecules to approach each other more closely. Thus the maximum adsorption increases and the area occupied per surfactant molecule decreases. However, the effective area of surfactant molecules at the surface decreases at the lower concentration of the IL and then increases with increasing the concentration of the IL from 0.4 wt%. The increase in the Γ_{max} at lower concentration of IL indicates the greater preference of the gemini surfactant solutions to be adsorbed at the air/water interface than in pure water. The presence of the IL at lower concentration decreases the repulsion among head groups and more gemini surfactant molecules can adsorb at the interface. This is confirmed by low values of A_{min} [63]. With the addition of NaBr, a continuous increase in Γ_{max} and decrease in A_{min} was observed, which is expected for inorganic electrolytes [50, 70]. It may be due to the reduction of repulsive forces between the head groups of the surfactant in the presence of inorganic electrolyte.

Rodrıguez *et al.* [67] obtained similar results in their investigation on the surface area of the gemini surfactants 12-*s*-12 ($s = 3$–5) in pure water and water–EG mixtures. The addition of IL changes the effective area of the surfactant molecule at the air/water interface parabolically [50]. At higher concentrations of the IL (>0.4 wt%), A_{min} increases, which suggests that IL can easily enter into the micellar structure by replacing the monomers of the gemini surfactants [59, 78]. Noori *et al.* [76] have studied similar phenomena for their synthesized counter ion-coupled gemini (COCOGEM) surfactants. At lower concentrations of the gemini surfactant, Γ_{max} decreases which on the formation of a monolayer increases when the gemini surfactant concentration increases from a 0.025 mol fraction of the total concentration. This phenomenon occurs due to the hydrophobicity of the gemini surfactant, due to which it also tries to adsorb at the interface and helps in the formation of the monolayer. A_{min} is considerably more for the [Omim][Br] as compared to [Hmim][Br] which is the result of the more hydrophobic nature of the [Omim][Br]. The increasing A_{min} at higher concentration of the IL suggest its co-surfactant like behavior.

The surface pressure at the CMC (Π_{CMC}) was obtained by using the following equation:

$$\Pi_{CMC} = \gamma_0 - \gamma_{CMC} \tag{4}$$

where γ_0, and γ_{CMC} are the surface tension of the solvent and the mixture at the CMC. Π_{CMC} is the measure of the interfacial area occupied by the surfactant molecule at the air/solution interface. The Π_{CMC} values depend on the structure of the surfactants and their orientation at the interface. In addition, the greater the Π_{CMC} values, the higher the effectiveness of the surfactants. As shown in Table 2, the Π_{CMC} values increase with increasing IL concentration. Π_{CMC} is larger in the case of [Omim][Br] as compared to [Hmim][Br], which confirms the better efficiency [51].

The surface parameters obtained by the surface tension measurement suggest possible interaction between the cationic gemini surfactant and IL ([C$_n$mim][Br] with $n = 6$ and 8) molecules, which can modify the interfacial and aggregation behavior of the aqueous gemini surfactant solution.

Interaction Studies by the UV–Vis Technique

The interaction between ionic surfactants and oppositely charged dye can change the aggregation behavior to a large extent. Different behavior of the dye in the pre and post-micellization will be treated as the best characteristic of the dye molecule in the spectroscopic determination of the metal ions [77, 79]. Beyaz *et al.* [41] had studied the aggregation behavior of the anionic single chain surfactant in IL by using 8-ANS dye. In the current investigation, we have used 8-ANS dye to study the interaction between the 14-6-14 and IL.

A 50-μL aliquot of ANS from a 1.6×10^{-6} mol dm^{-3} stock solution was added to a quartz cuvette containing 3 mL of the respective IL. Incremental amounts (10 or 100 μL) of gemini surfactant were added using a micro syringe and a series of spectra were recorded. The components were thoroughly mixed after each incremental addition of 14-6-14,2Br$^-$. The absorption spectra in the range of 200–500 nm were recorded after allowing the solution to reach steady state (about 4 min). Absorbance maximum were observed at 270 and 380 nm. The absorbance at both wavelengths shows an inflection with increasing surfactant concentration as shown in Fig. 1c. The inflection point of the absorbance *versus* [14-6-14,2Br$^-$] plot was taken as the CMC [80–82]. About 40 spectra were accumulated for each CMC determination. The CMC values obtained by this method are given in Table 1 and they are somewhat higher than the CMC obtained by conductivity, surface tension as well as with literature values [20, 29, 31, 59], which may be due to the interaction of the anionic dye with the cationic surfactant [77, 79].

Careful examination of the absorption data suggests that as the concentration of 14-6-14,2Br$^-$ increases, the absorption maxima is red shifted, which might be due to increased hydrophobicity of the solution. The red shift for

[Omim][Br] is greater than [Hmim][Br] (Figs. S5–S6) which supports this hypothesis. Using crystal violet dye, Javadian *et al.* [44] reported a similar shift for single chain anionic surfactants.

Interaction Studies by Pyrene Fluorescence

We have used pyrene as a fluorescence probe to obtain the CMC of 14-6-14,2Br$^-$ in the presence and absence of IL. Pyrene fluorescence has been used to measure various important micellar parameters such as the CMC, aggregation numbers (N_{agg}), dipolarity, microfluidity, etc. [57, 83–86]. The pyrene polarity scale, defined by the ratio "I_1/I_3" of the monomer fluorescence intensities at bands I (ca. 373 nm) and III (ca. 384 nm), is a function of solvent dielectric (ε) and the refractive index (n) via the dielectric cross term [$f(\varepsilon,n2)$]. Pyrene I_1/I_3 changes dramatically with change in the dipolarity of the cybotactic region of the probe. A more polar microenvironment results in a higher I_1/I_3 and vice versa. Pyrene fluorescence spectra were collected from solutions of varying [14-6-14,2Br$^-$] in the presence of different concentrations of IL, [Hmim][Br] and [Omim][Br]. Figure 1d shows the variation in I_1/I_3 *versus* [14-6-14,2Br$^-$] for the neat gemini surfactant in an aqueous medium. The plot of I_1/I_3 *versus* [14-6-14,2Br$^-$] show a rapid decrease as the surfactant concentration is increased, associated with the formation of aggregates. The minimum for the second derivative in the graph shows the CMC.

The pyrene fluorescence provides interesting and useful information on IL-added aqueous [14-6-14,2Br$^-$] solutions (Fig. S7–S8). The CMC values determined by this method are slightly larger than those determined by conductance as well as surface tension (Table 1), which may be due to the partition of pyrene between micelles and the bulk phase. Similar behavior was also reported by Zana *et al.* [87]. It is noteworthy to mention that the CMC decreases with increasing concentration of IL in 14-6-14,2Br$^-$ aqueous solutions. CMC for the addition of [Omim][Br] is greater than that obtained with [Hmim][Br]. Our CMC data for the aqueous [14-6-14,2Br$^-$] by this technique is in good agreement with that reported in the literature [20, 29, 31, 59].

Micellar Aggregation Number from Fluorescence Quenching

The aggregation number (N_{agg}) of 14-6-14,2Br$^-$ micelles in the presence and absence of [Hmim][Br] and [Omim][Br], was obtained by fluorescence quenching of pyrene by CPC according to the following equation [61, 88–91]:

$$\ln\left(\frac{I_0}{I_Q}\right) = \frac{Q_{\text{micelle}}}{[\text{micelle}]} = \frac{[\text{CPC}]_{\text{micelle}}}{[\text{micelle}]_{14-6-14,2\text{Br}^-}} = [\text{CPC}]_{\text{micelle}}\left[\frac{N_{\text{agg}}}{[14-6-14,2\text{Br}^-]-\text{CMC}_{14-6-14,2\text{Br}^-}}\right] \qquad (5)$$

where I_0 and I_Q are the fluorescence intensities of pyrene in the absence and presence of quencher CPC, respectively. $[\text{micelle}]_{14-6-14,2\text{Br}^-}$ $[\text{CPC}]_{\text{micelle}}$ and [14-6-14,2Br$^-$] are the concentrations of 14-6-14,2Br$^-$ micelles, quencher CPC within the micellar pseudo phase and 14-6-14,2Br$^-$ gemini surfactant, respectively. The graph of $\ln(I_0/I_Q)$ *versus* $[\text{CPC}]_{\text{micelle}}$ in 100 mM 14-6-14,2Br$^-$ solution in the presence of [Hmim][Br] and [Omim][Br] are shown in Fig. 3. The data fit a linear regression at each concentration of [Hmim][Br] and [Omim][Br] from zero to 1.0 wt%. The

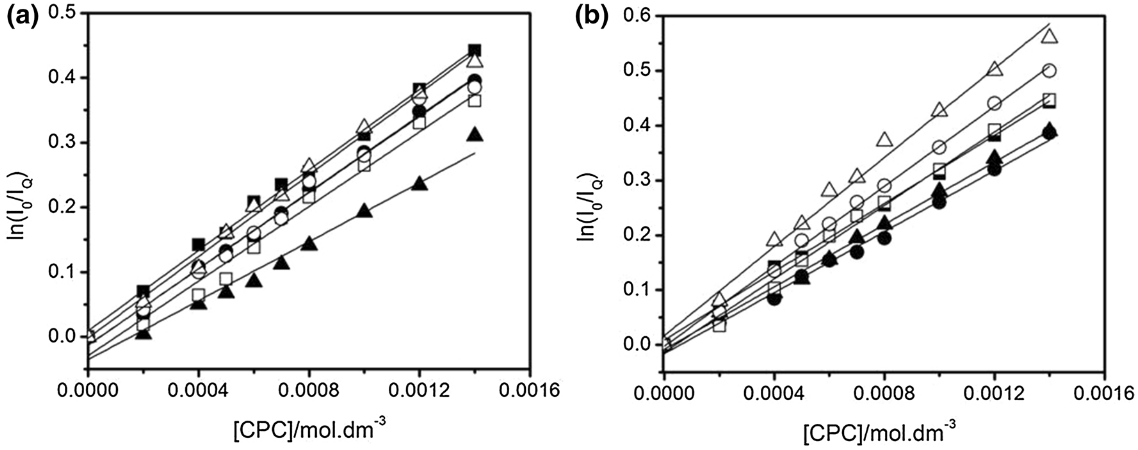


Fig. 3 Pyrene fluorescence quenching by CPC in 100 mM aqueous 14-6-14,2Br$^-$ solutions in the presence of different wt% **a** [Hmim][Br] and **b** [Omim][Br]. (*Filled squares*) Neat 14-6-14, (*filled circles*) 0.2 wt%, (*filled triangles*) 0.4 wt%, (*open squares*) 0.6 wt%, (*open circles*) 0.8 wt% and (*open triangles*) 1.0 wt%, respectively, under ambient conditions

slopes decrease upon addition of IL up to 0.4 wt% and then increase. The decrease in slope is greater for [Hmim][Br] than for [Omim][Br]. We calculate that as the concentration of IL increases, N_{agg} decreased up to 0.4 wt% and then increases; the decrease being significantly more drastic for [Hmim][Br] compared to that of [Omim][Br]. The decrease in slope is due to the decreased efficiency of quenching, which increases after 0.4 wt% addition of IL. N_{agg} of aqueous 14-6-14,2Br$^-$ is in good agreement with that reported in the literature [59].

The N_{agg} behavior can be explained on the basis of electrostatic and hydrophobic interactions between the cations of the IL and the head group of the gemini surfactant. The results suggest that electrostatic repulsion dominates over the hydrophobic interactions. This leads to the formation of a loosely packed micellar structure. As the concentration of the IL increases beyond 0.4 wt%, more IL molecules enter into the micellar structure. The decrease of N_{agg} along with the increased average size of aggregates (Table 3) may be due to water penetration into at the aggregates [37]. Water penetration is more apparent in the presence of [Hmim][Br] than [Omim] [Br]. The decrease in N_{agg} is significantly greater in the presence of [Hmim][Br] than [Omim][Br], which may be due to the lesser hydrophobicity of [Hmim][Br] as compared to [Omim][Br].

Table 3 Aggregation number (N_{agg}) and micellar size (nm) of aqueous gemini surfactant (14-6-14,2Br$^-$) in presence of [Hmim][Br] and [Omim][Br] at 298.15 K

IL in wt%	[Hmim][Br]		[Omim][Br]	
	N_{agg}	Diameter (nm)	N_{agg}	Diameter (nm)
0.0	30 (32) [59]	2.96	30	2.96
0.2	29	3.46	28	3.46
0.4	22	4.08	24	4.07
0.6	29	4.10	32	4.09
0.8	29	4.10	29	4.09
1.0	31	4.10	43	4.09

Standard uncertainties u are: $u(N_{agg}) = \pm 2$, $u(D) = \pm 0.40$ nm

Dynamic Light Scattering for Average Aggregate Size

Dynamic light scattering was used to measure the average size of micellar aggregates in 100 mM 14-6-14,2Br$^-$ solution with and without the addition of IL. Figure 4 shows the scattering intensity *versus* diameter (D) measured at 298.15 ± 0.1 K upon addition of [Hmim][Br] and [Omim][Br]. Monomodal distribution is observed at all concentration of additives. From the DLS data (Table 3) it is clear that the peak diameter of micellar aggregates is similar for both IL. The diameter increases sharply up to 0.4 wt% after which there is no change in diameter with increasing IL concentration. Several factors can influence the micellar structure of the cationic gemini surfactant upon the addition of IL. These factors include electrostatic interactions, changes in the structure of water, and the hydrocarbon–hydrocarbon repulsion. The Br$^-$ ions from the IL can diminish the repulsive force between the head groups of the gemini surfactant, which makes it possible for the surfactant molecules to pack tighter and form the larger aggregates, which is reflected in the increase in the diameter. Addition of the inorganic electrolyte (KBr) has a similar effect on cationic gemini surfactants [15]. According to Yu *et al.* [61], addition of organic electrolyte induces a morphology change from micelles to vesicles whereas the inorganic electrolytes only change the size of the aggregates. At higher IL concentrations, the peak diameter remains constant but the N_{agg} increases slightly and its value is higher for [Omim][Br] than for [Hmim][Br].

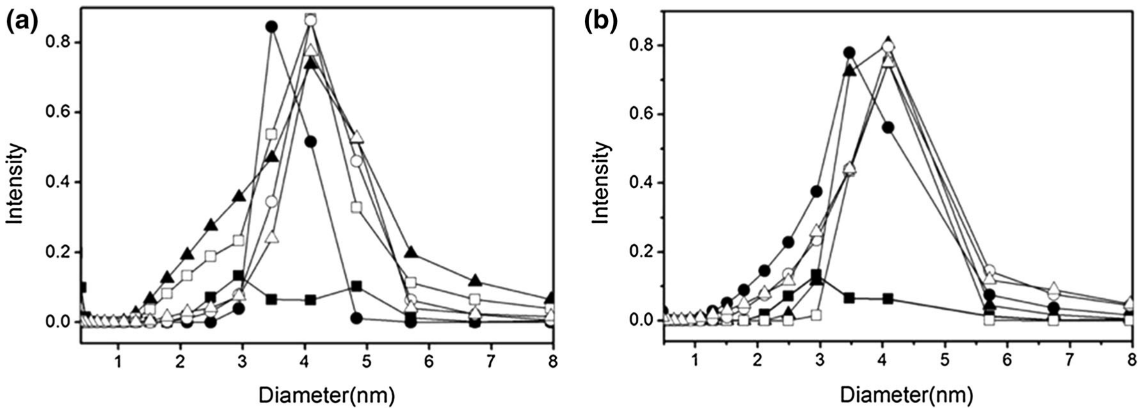


Fig. 4 Dynamic light scattering (DLS) results of 100 mM aqueous 14-6-14,2Br$^-$ in the presence of increasing concentration of **a** [Hmim][Br], **b** [Omim][Br]. (*Filled squares*) Neat 14-6-14, (*filled circles*) 0.2 wt%, (*filled triangles*) 0.4 wt%, (*open squares*) 0.6 wt%, (*open circles*) 0.8 wt% and (*open triangles*) 1.0 wt%, respectively, under ambient conditions

Conclusion

The behavioral changes of cationic gemini surfactants in the presence of cationic IL were studied using a number of different techniques. The CMC of cationic gemini surfactant, 1,6-hexanediyl-α,ω-bis(dimethyltetradecyl)ammonium bromide (14-6-14,2Br$^-$) studied herewith decreased with increasing IL concentration and the behavior was compared with common electrolytes. Increasing the alkyl chain length of the IL, decreases the CMC due to an increased hydrophobicity of the medium and the spacing between the adjacent molecules increases. The somewhat higher value of the CMC measured by dye solubilization may be due to the interaction of the anionic dye with the cationic gemini surfactant. The increased hydrophobicity of the medium was confirmed by the red shift of the $\lambda_{\max}$. Decreases in N_{agg} with increasing average size of aggregates may be due to water penetration into the aggregates [37] which is more apparent in the presence of the less hydrophobic IL. Overall, IL behave like common electrolytes at lower concentrations and more like cosurfactants at higher concentrations.

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