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ORIGINAL CONTRIBUTION

Effect of chain length and counter-ion on interaction study of mixed micellar system of isoquinoline-based surface active ionic liquid and cationic surfactants in aqueous medium

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Abstract

In the present study, we have investigated the effect of nature of surfactant, chain length and counter-ion on the mixed micellization behaviour ofvarious cationic surfactants, tetradecyltrimethylammonium bromide (TTAB), dodecyltrimethylammonium chloride (DTAC) and cationic gemini surfactant, bis(tetradecyldimethylammonium)hexane dibromide(C14-6-C14,2Br) with surface active ionic liquid (SAIL) tetradecylisoquinolinium bromide [C_{14}iQuin][Br]. The interactions and mixed micellar behaviour of cationic surfactants and SAIL in aqueous medium have been studied by employing conductometry measurements and ^{1}H NMR technique. The critical micelle concentration (cmc) and various thermodynamic parameters like standard Gibbs free energy of micellization ($\Delta G_m{}^0$), change in standard enthalpy ($\Delta H_m{}^0$) and entropy of micellization ($\Delta S_m{}^0$) have been calculated from conductometry measurements. Mixed micellar parameters such as ideal cmc (cmc*), micellar mole fraction ($X_1{}^m$), micellar interaction parameter (β_m) and activity coefficients, (f_1 and f_2) have been evaluated by applying Clint, Rubingh and Motomura theoretical models. Synergistic and non-ideal interactions have been found between SAIL and surfactants.

Keywords Tetradecyltrimethylammonium bromide (TTAB) · Dodecyltrimethylammonium chloride (DTAC) · Tetradecylisoquinolinium bromide [C_{14}iQuin][Br] · Mixed micellization · Activity coefficients

Introduction

Today, surfactant systems are generating great interest due to their extensive uses in different technological and industrial field like cosmetics, paints, enhanced oil recovery, pharmaceutical and also food industry [1–4]. All these applications are useful gehlas well as interesting because of their amphiphilic nature. This amphiphilic nature depends on the type of the surfactant, temperature and presence of additives. Because of possibility of design and synthesis of different types of surfactants, the interest of researchers is increasing day by day in this field. Along with the conventional surfactants, gemini surfactants are gaining major attention. Gemini surfactants are those compounds in which two surfactant monomers are bonded chemically at head position by some spacer molecules. The nature and length of the spacer has remarkable effect on the various physiological properties of the geminisurfactants. Generally, the micellization behaviour of all the surfactants is observed at a particular concentration called critical micelle concentration (cmc) and gemini surfactants have very low cmc value and better properties in comparison with the conventional surfactants which is well reported in literatures [5–8].

It is well known that surfactants show good but expensive surface activities that limited the individual uses of surfactants at industrial scale. So, surfactants are generally blended with other surface-active compounds like ionic liquids, drugs, electrolytes and co-surfactants to improve the surface activity [9–12]. Surfactants are mostly used in mixed form because the properties of mixed systems have been found superior than single component. A huge literature survey is available on systems like cationic-cationic, cationic-anionic, cationic-nonionic and so on [13–17].

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But nowadays, the ionic liquid has become one of the popular choice as additive because of its versatile properties like negligible vapour pressure, good thermal stability, outstanding catalytic properties and non-flammability [18–20]. Ionic liquids are actually the organic compounds composed of organic cation and organic or inorganic anion and also famous as greener solvents. Therefore, ILs have become everyone's priority because of wide spread application area. Nowadays, ILs have been extensively utilized in chemical industry, drug-delivery, electrochemistry, paint industry and so on [21–24]. From past few years, many different types of ILs have been synthesized and reported in literatures [25–28]. They all have good viscosity and thermal stability but most of them are non-surface active in nature. Some ionic liquids behave like surface-active agent also known as surface active ionic liquids (SAILs). They have drawn the attention of researchers towards them because they show similar properties just like conventional surfactants and have some different and improved properties [29–33]. Most of SAILs synthesized are based on imidazolium, pyridinium cations. SAILs have been widely used to modify the physiological properties of surfactants in mixed state [34–39].

From last few years, SAILs are extensively utilized as second component with surfactants in mixed systems. Their properties in mixed state have been studied by applying different techniques such as conductometry, tensiometer, dynamic light scattering, ^{1}H NMR and fluorescence. Formation of mixed state takes place after a complex balance of synergism from both the components. The non-ideal behaviour has been shown by ionic surfactants while non-ionic systems show ideal behaviour. Generally stronger interactions have been found between cationic-anionic mixed systems due to charge neutralization while similar charged systems show weak interactions [15, 24]. Various models, like Rubingh, Clint and Motomura, have been applied to quantify the synergistic or antagonistic interactions in terms of micellar interaction parameter (β_m).

Extensive studies have been reported in literature on mixed systems of surfactants-SAILs, and most of the SAILs synthesized and used in mixed systems are based on imidazolium, pyridinium cations. But the research work at isoquinolinilium-based SAILs is still less reported. Synthesis of isoquinolinilium-based SAILs has been first time reported by Zhang et al. [40]. They have reported the synthesis of SAILs of different carbon chain lengths (C_8–C_{12}).

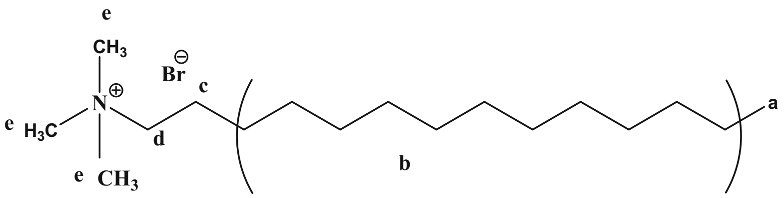
Previously, we have reported the mixed micellization behaviour of cationic surfactant Dodecyltrimethylammonium bromide (DTAB) with isoquinolinilium-based SAILs ([C_{12}iQuin][Br] and [C_{14}iQuin][Br]) in aqueous medium and conclude that higher alkyl chain length SAIL shows better synersgistics interactions with surfactant [41]. Now, in continuation of that study, we want to explore the effect of chain length, counter-ion and nature of surfactant on the formation of mixed micelles. So in the present study, we have reported the detail study on mixed systems of three different cationic surfactants TTAB/DTAC/C14-6-C14,2Br+[C_{14}iQuin][Br] SAIL. So in this study, the conductometry and spectrometry (^{1}H NMR) techniques have been applied and various theoretical models have also been employed to calculate the value of cmc, thermodynamic parameters such as standard Gibbs free energy change ($\Delta G_m{}^0$), standard enthalpy change($\Delta H_m{}^0$) and standard entropy change ($\Delta S_m{}^0$), micellar mole fraction in ideal state X_1^{ideal}, activity coefficients (f_1 and f_2), micellar interaction parameter (β_m) and degree of counter-ion dissociation (g). The NMR techniques have been applied to study the interaction behaviour deeply whether the interaction takes place at surface or inside the micellar core.

Material and methods

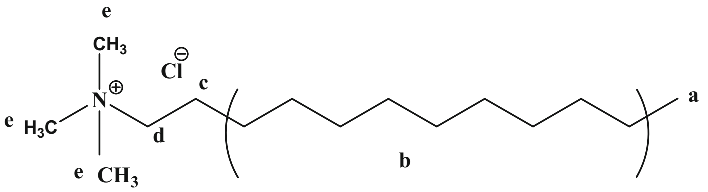
N,*N*-Dimethyltetradecylamine (> 95%), 1,6-dibromohexane (96%), 1-bromotetradecane (> 98%), isoquinoline (97%), dichloromethane (98%), dodecyltrimethylammonium chloride (98%) and tetradecyltrimethylammonium bromide (98%) were purchased from Sigma-Aldrich. Triply distilled water was used for making all the solutions. The ionic liquid,tetradecylisoquinolinium [C_{14}iQuin][Br] and cationic gemini surfactant (C14–6-C14,2Br) involved in the study have been synthesized in the laboratory according to the procedure, reported elsewhere [40, 42]. By ^{1}H NMR technique, purity of the ionic liquid as well as gemini surfactant has been checked. A detail of all the chemicals used in this study has been provided in Table 1. The molecular structures of the cationic surfactants and SAIL was shown in Scheme 1.

Table 1 Specifications of chemicals

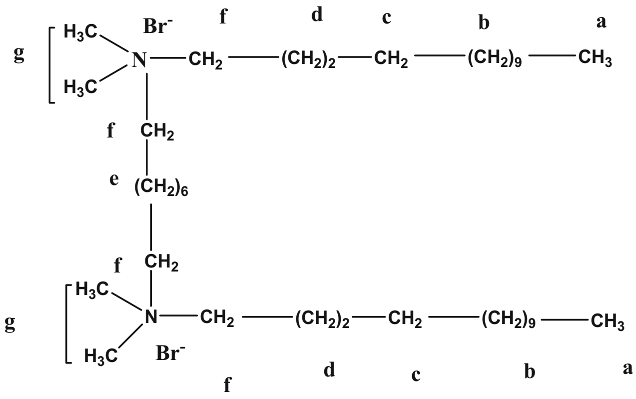
Chemical name	Provenance	Mass fraction purity (%)
DTAC	Sigma-Aldrich, USA	> 99
TTAB	Merck-Schuchardt, Germany	98
1-Bromotetradecane	Sigma-Aldrich, USA	> 98
Dichloromethane	Sigma-Aldrich, USA	99.9
Isoquinoline	Sigma-Aldrich, USA	97
N, *N*-Dimethyltetradecylamine	Sigma-Aldrich, USA	>95
1,6-Dibromohexane	Sigma-Aldrich, USA	96
Ethanol	SD Fine, India	98
Deuterium oxide	Sigma-Aldrich, USA	> 99.9



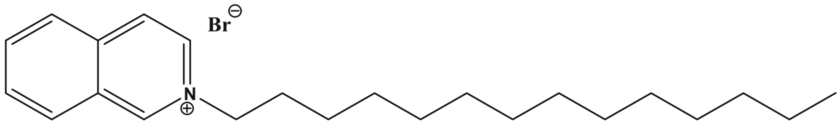
Tetradecyltrimethylammonium bromide



Dodecyltrimethylammonium chloride



bis(tetradecyldimethylammonium)hexane dibromide(C14-6-C14)



Tetradecylisoquinolinium bromide

Scheme 1 Chemical structures of surfactants tetradecyltrimethylammonium bromide [TTAB], dodecyltrimethylammonium chloride [DTAC],bis(tetradecyldimethylammonium)hexane dibromide [C14-6-C14][2Br] and surface active ionic liquid, tetradecylisoquinolinium bromide [C_{14}iQuin][Br].

Synthesis of surface-active ionic liquid

The surface-active ionic liquid tetradecylisoquinolinium [C_{14}iQuin][Br] has been synthesized according to the reported procedure [40]. Both the reactants n-alkyl bromide and isoquinoline were weighed in a particular amount and added to a round-bottom flask in the presence of acetonitrile as a solvent. After refluxing the reaction mixture for 2 h, dichloromethane was added in it. Activated carbon was used for removing the coloured impurities. After decolourization, thick red colour oil was obtained which was cooled and washed several times with n-hexane to remove any unreacted reactant impurity. Then it was dried under vacuum for 3 days to remove any kind of solvent residue. The Karl-Fischer titration method assures that moisture content was found to be less than 0.02 wt%. The structural characterization was done by ^{1}H NMR technique.

The detailed ^{1}H NMR spectra of corresponding protons for [C_{14}iQuin][Br] are given as follows: DMSO-d6 0.82(t,3H), 1.24(m,24H), 4.77(t,2H), 8.08(t,1H), 8.28(t,1H), 8.53(d,1H), 8.65(d,1H), 8.89(d,1H) and 10.31(s,1H).

Synthesis of gemini surfactant bis(tetradecyldimethylammonium)hexane dibromide (C14-6-C14,2Br)

The cationic gemini surfactants were also synthesized according to the procedure of Zana et al. [42]. For the synthesis, *N*,*N*-dimethyltetradecylamine and 1,6-dibromohexane have been mixed and refluxed in 1:2 ratio in a round-bottom flask in the presence of dry ethanol for 48 h at 80-°C temperature. The completion of the reaction has been monitored by TLC. After the completion of reaction, the final product has been recrystallised and dried. The purity of the compound has been checked by NMR technique. The ^{1}H NMR data has been given below:

0.864–0.897(6H, alkyl chain $2 \times 1CH_3$), 1.255–1.351 (44H, alkyl chain $2 \times 11CH_2$), 1.557 (4H, spacer chain $2 \times 1CH_2CH_2CH_2N^+$), 1.752(4H, alkyl chain $2 \times 1CH_2CH_2N^+$), 1.973(4H, spacer chain $2 \times 1CH_2CH_2N^+$), 2.844(12H, $2 \times 2CH_2N^+$), 3.419–3.461(4H,$2 \times 1CH_2N^+$) and 3.509–3.711(4H, spacer chain $2 \times 1CH_2N^+$).

All aqueous solutions have been prepared with triply distilled de-ionized water obtained from a Millipore, having a conductivity value ≤ 5 μS cm^{-1}. Required amount of materials was weighed using an A&D Co. Ltd. electronic balance (Japan, model GR- 202) with a precision of ± 0.1 mg.

The equimolar solutions of all the cationic surfactants and the SAIL have been prepared in aqueous medium. The different mole fraction ratios (0.25, 0.50 and 0.75) of the mixtures of cationic surfactants and SAIL [C_{14}iQuin][Br] were obtained by mixing appropriate volume of stock solutions. The mixed solutions were stirred for 30 min at room temperature for the complete mixing of solutions.

Conductometry measurements

Electrical conductivity meter CM-183 microprocessor-based EC-TDS analyser having ATC probe purchased from Elico Ltd., India, has been used to measure the conductance of the mixtures. Before the measurements, the conductivity cell, having cell constant of 1.0021 cm^{-1} , was calibrated with standard solutions of potassium chloride (KCl) solutions having concentration range 0.01–1.0 mol kg^{-1} of known specific conductance. The instrument work on power supply of 90–260 V alternating current and at frequency of 50–60 Hz. The conductivity was measured in a water-jacketed dilution cell and the temperature of the cell was maintained by water bath. At least three measurements were made for each concentration and only mean of these values has been considered. The uncertainty in the results was less than 4%. Microsoft Excel and Origin software program were used for the calculation of various parameters and graphical representations.

^{1}H NMR measurements

The ^{1}H NMR technique has been employed to understand the interaction phenomena between various cationic surfactants (TTAB, DTAC, (C14-6-C14,2Br) and isoquionolinium-based ionic liquid [C_{14}iQuin][Br]. The ^{1}H NMR spectrum has observed using the instrument Bruker Avance–III 400 MHz spectrometer. All the samples have been prepared in D_2O. The peak pick facility has been used to analyse the data.

Results and discussion

Conductometry measurements

Critical micelle concentration and degree of counter-ion dissociation determination

The critical micelle concentration (cmc) and degree of counter-ion dissociation (*g*) have been calculated at three different temperatures, 298.15–318.15 K by employing conductometric technique. The characteristic feature of this technique is that when graph is plotted between concentration versus conductance value obtained, a sharp infringement in graph has been observed and it is recognized as cmc value of the system. The representative illustrations for all the pure surfactants and SAIL have been given in Fig. 1 a–c and for their mixtures (TTAB/DTAC/C1–-6-C14,2Br) + [C_{14}iQuin][Br] are presented in Figs. 2a–d and 3a–e at different mole fractions of surface-active ionic liquid (SAIL). The cmc value of all the pure amphiphiles is in good agreement with literature values [34, 43, 44]. The cmc values obtained for mixtures of all the studied systems (TTAB/DTAC/C14-6-C14,2Br) + [C_{14}iQuin][Br]) (Tables 2, 3 and 4) are in between the cmc value of both the individual components (TTAB (4.1 mM) DTAC (23.5 mM), C14-6-C14,2Br (0.18) and [C_{14}iQuin][Br] (1.2 mM).

Further, the obtained cmc value depends on two main factors: (a) primarily on the electrostatic repulsion due to having similar charge on the head groups, and (b) secondary on the hydrophobic interactions between the hydrocarbon tails of both components. In our present study, all the used cationic surfactants and SAIL have similar (positive) charge on their head groups, so repulsion among head groups restricts the micelle formation but increasing hydrophobic interactions overcome this and enhance the micellization process.

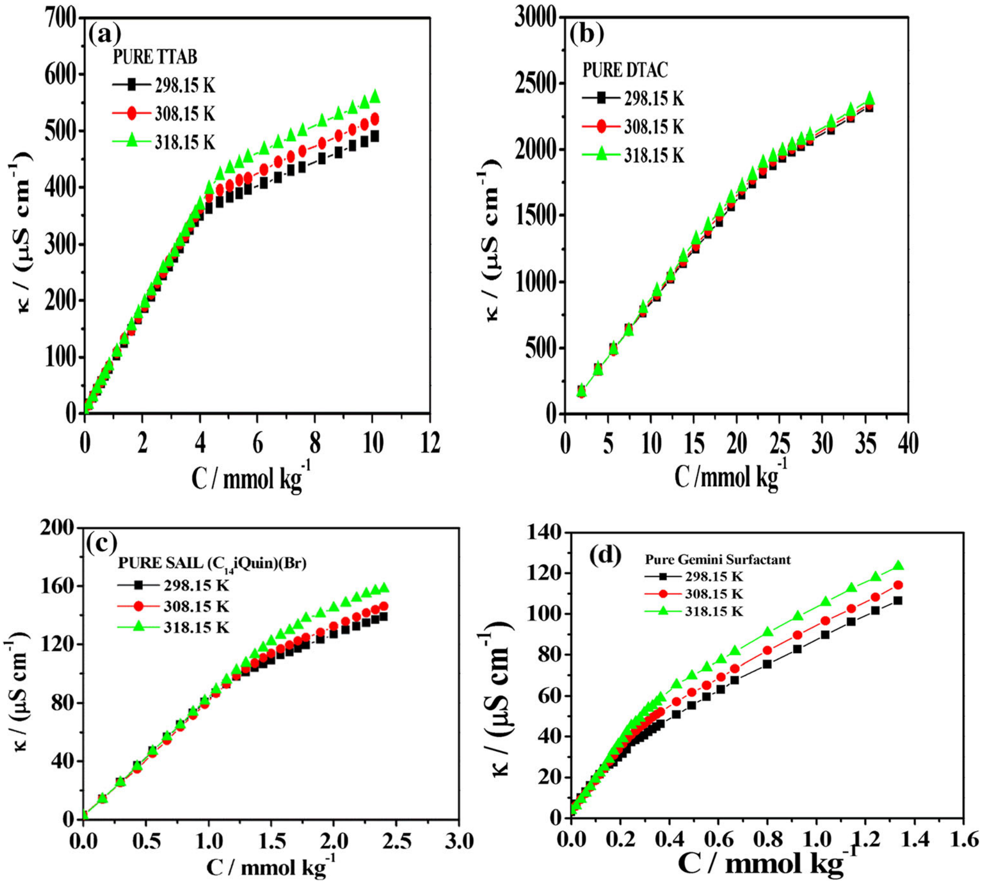


Fig. 1 **a-d** Representative plot of specific conductivity (κ) against surfactant concentration **a** pure TTAB, **b** pure DTAC, **c** pure SAIL and **d** pure C14-4-C14,2Br gemini in H_2O at three different temperatures, 298.15, 308.15 and 318.15 K

From Tables 2 and 3, it can be seen that the cmc values of both the surfactants (TTAB, DTAC) and their mixtures with SAIL lie in between the cmc of pure components, which signifies favourable mixing in the mixed state. With increasing mole fractions of SAIL (α_1), the value of cmc in both the studied systems decreases,suggesting increased hydrophobic interactions in mixed systems (Fig. 4). It demonstrates synergism in both of these systems. But in third case, (C14-6-C14,2Br) + SAIL increase in cmc values (0.21–0.38) (Table 4) is observed; this indicates less favourable micelle formation due to head group repulsion and stearic hindrance because both the components carry positive charge on their head group. On comparing the TTAB/DTAC + SAIL mixed systems, it can be seen that major decrease in cmc value is observed in DTAC + SAIL, in this case, cmc decrease up to 19-fold at higher mole fraction ratio of SAIL and only 3.5-fold in case of TTAB + SAIL. This shows more favourable micelle formation in the first case.

Further, the conductivity data demonstrate a continued rise in cmc value with increasing temperature. It is most probably due to these two observable facts: first one is due to dehydration of the charged head group that results in increase in cmc value and second one is breaking of water structure present near by the hydrophobic chains of surfactants that promotes the micellization and reduce the cmc. In present system, the first factor predominates and hence rise in cmc value is observed.

From the ratio of slope of post-micellar to pre-micellar region, obtained from the plot of specific conductance versus concentration of surfactants+SAIL, degree of dissociation (*g*) of counter-ions has been calculated [45]. A quantitative measurement of the counter-ion dissociation (*g*) is required to understand the various aspects of the micellization behaviour of the surfactants. The corresponding values of *g* for all the surfactants in pure and in mixed state with SAIL have been reported in Tables 2, 3 and 4. By looking at Table 2 and 3, we can see that increase in degree of counter-ion dissociation (*g*) has been observed with increasing content of SAIL in mixed system of TTAB /C14-6-C14,2Br + SAIL. From this, we conclude that less compact mixed micelle formation takes place. It is due to less surface charge density that is responsible for lower binding of counter-ions at micellar surface. While in case of DTAC+SAIL, opposite trend has been observed that is illustrated in Table 3. On comparing all the three cases, we observed more compact micelle formation takes place in case of DTAC+SAIL

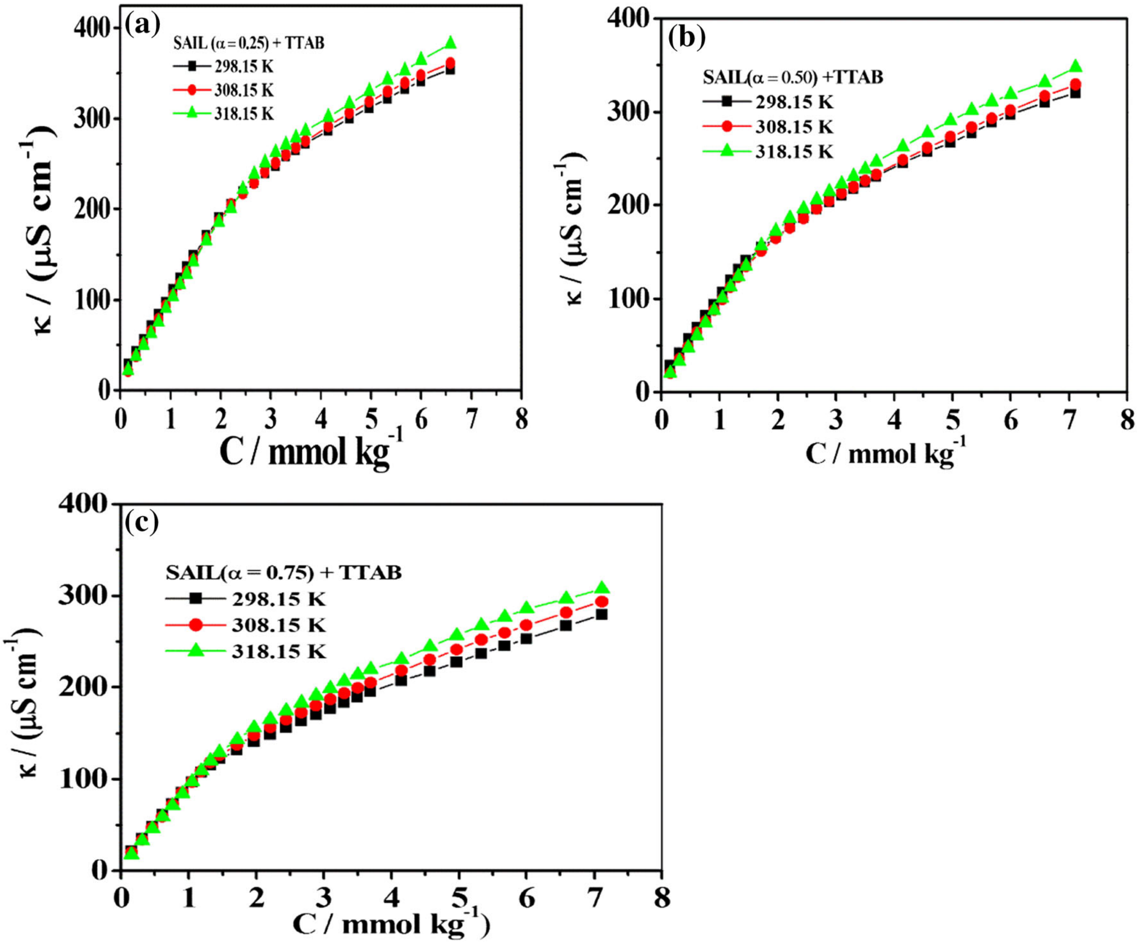


Fig. 2 **a–c** Plot of specific conductivity (κ) as a function of total surfactant concentration for mixed system of TTAB + SAIL at different concentrations

mixed system due to more counter-ion binding. It was concluded that better sysnergism has been onserved in case of DTAC + SAIL mixed system.

Thermodynamics of mixed micellization in the absence and presence of SAIL

From conductivity measurements, various thermodynamic parameters of micellization, standard Gibbs free energy of micellization ($\Delta G_m{}^0$), change in standard enthalpy of micellization ($\Delta H_m{}^0$) and change in standard entropy of micellization ($\Delta S_m{}^0$) were obtained for all the mixed systems by using the following equations [1–3, 46] for conventional surfactants and equations [4–6] for gemini surfactant [47, 48]:

$$\Delta G_m^0 = (2-g)RT\ln X_{\text{cmc}} \tag{1}$$

$$\Delta H_m^0 = -RT^2\left[(2-g)\frac{d\ln X_{\text{cmc}}}{dT} + \ln X_{\text{cmc}}\frac{d(1-g)}{dT}\right] \tag{2}$$

$$\Delta S_m^0 = \frac{\Delta H_m^0 - \Delta G_m^0}{T} \tag{3}$$

$$\Delta G_m^0 = (3-2g)RT1nX_{\text{cmc}} \tag{4}$$

$$\Delta H_m^0 = -RT^2\left[(3-2g)\frac{d\ln X_{\text{cmc}}}{dT} + \ln X_{\text{cmc}}\frac{d(1-g)}{dT}\right] \tag{5}$$

$$\Delta S_m^0 = \frac{\Delta H_m^0 - \Delta G_m^0}{T} \tag{6}$$

where g represents degree of counter-ion dissociation, R is gas constant, T is absolute temperature and X_{cmc} is the cmc expressed in terms of mole fraction. The values obtained for corresponding parameters are included in Tables 2, 3 and 4. A close look of Tables 2, 3 and 4 shows overall negative values of the standard Gibbs free energy of micellization ($\Delta G_m{}^0$) for all the concentrations. The negative values of $\Delta G_m{}^0$ indicate the spontaneous micellization. The more negative values of $\Delta G_m{}^0$ with increasing content of SAIL shows that the presence of SAIL enhances the spontaneous aggregate formation. Furthermore, change in standard enthalpy of micellization

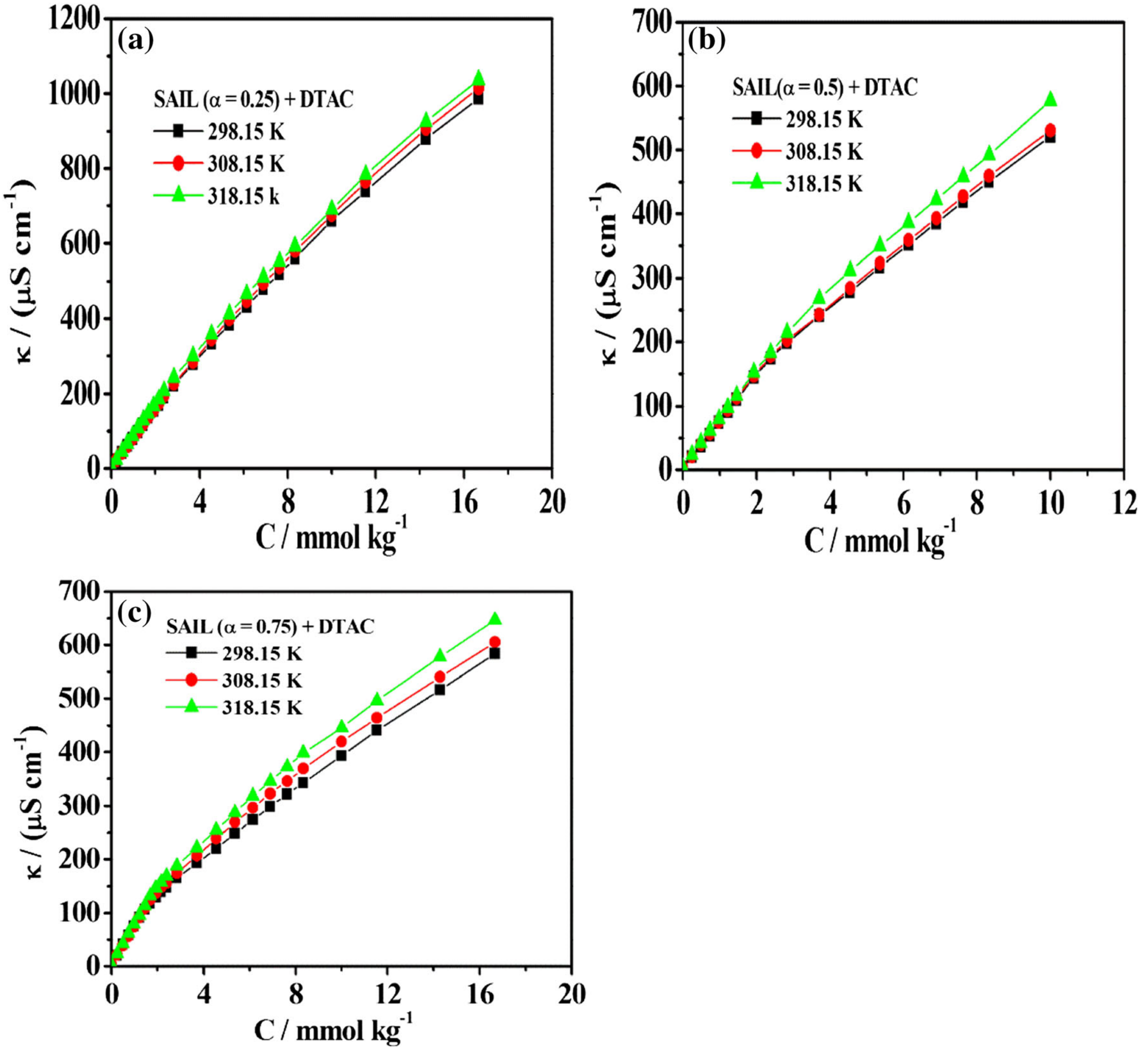


Fig. 3 **a–c** Plot of specific conductivity (κ) as a function of total surfactant concentration for mixed system of DTAC + SAIL at different concentrations

($\Delta H_m{}^0$) value also comes out negative which implies that micellization phenomena is exothermic in nature.The standard entropy value ($\Delta S_m{}^0$) comes out positive and found to decrease with increasing SAIL content. This is due to most probable increasing hydrophobic interaction in the mixed systems. These interactions take place because of formation of more ordered arrangement of water molecules around the hydrophobic moieties; this type of clustering is always enthalpy favourable and entropy unfavourable hence results in decrease in entropy. On comparing the cmc values of cationic surfactant TTAB and SAIL, it has been observed that both the amphiphiles have similar chain of carbon but cmc of SAIL (1.2 mM) was lesser than the TTAB (4.1 mM) at the temperature 298.15 K. It shows that aggregation in pure SAIL takes place at lower concentration. After the observation of thermodynamic parameters, it has been concluded that the aggregation in case of TTAB is entropy favourable.

On comparing all the three systems, it is observed that major change in thermodynamic parameter ($\Delta G_m{}^0$, $\Delta H_m{}^0$ and $\Delta S_m{}^0$) values has been noticed in case of second system, i. e. DTAC + SAIL. It shows that stronger interaction takes place here.

The molar heat capacity is a very important thermodynamic parameter through which we may notice the structural rearrangement, binding of drugs-surfactant, solvent effects and types of interactions that take place during binding [49, 50]. It was associated with the motion restriction event. The molar heat capacity changes ΔC_p° for the mixed micelle formation were obtained from the slope of the plot of standard enthalpy values ($\Delta H_m{}^0$) versus temperature (T) by using the following equation: [51].

$$\Delta C_p^\circ = \left(\Delta H_m^\circ/\Delta T\right)_p \qquad (7)$$

Table 2 The critical micelle concentration (cmc) and various thermodynamic parameters of micellization for TTAB+ SAIL mixed systems at various temperatures

TTAB + SAIL	Mole fraction of SAIL	cmc (mmol kg^{-1})	*g*	$\Delta G_m{}^0$ (kJ mol^{-1})	$\Delta H_m{}^0$ (kJ mol^{-1})	$\Delta S_m{}^0$ (J K^{-1} mol^{-1})	ΔC_p° (J K^{-1} mol^{-1})
298.15	0.0	4.1	0.246	− 41.31	− 16.67	82.64	
308.15		4.3	0.262	− 42.12	− 17.23	80.78	− 0.05
318.15		4.7	0.270	− 42.93	− 17.68	79.37	
298.15	0.25	2.5	0.338	− 41.30	− 20.26	70.56	
308.15		2.5	0.361	− 41.98	− 20.31	70.34	− 0.07
318.15		2.7	0.373	− 42.68	− 21.71	65.93	
298.15	0.50	1.7	0.377	− 41.92	− 21.65	67.89	
308.15		1.7	0.398	− 42.58	− 21.79	67.46	− 0.06
318.15		1.9	0.407	− 43.26	− 22.90	63.98	
298.15	0.75	1.3	0.384	− 42.63	− 26.20	55.09	
308.15		1.5	0.402	− 43.17	− 27.47	50.96	− 0.14
318.15		1.7	0.422	− 43.67	− 29.09	45.83	
298.15	1.00	1.2	0.482	− 40.52	− 28.83	39.21	
308.15		1.3	0.498	− 40.92	− 28.89	39.04	− 0.01
318.15		1.5	0.516	− 41.31	− 28.97	38.78	

Standard uncertainties *s* are $s(\Delta G_m{}^0) = \pm 0.02$ (kJ mol^{-1}), $s(\Delta H_m{}^0) = \pm 0.01$ (kJ mol^{-1}), $s(\Delta S_m{}^0) = \pm 0.02$ (J K^{-1} mol^{-1}), $s(T) = \pm 1 \times 10^{-2}$ K and $s(p) = \pm 2$ kPa respectively

The corresponding value of ΔC_p° for the pure and mixed micelles has been tabulated in Tables 2, 3 and 4. The ΔC_p° are negatives for the TTAB/C14-6-C14 + SAIL mixed systems while positive values have been noticed in case of DTAC + SAIL. The negative values of heat capacity may be related with the hydrophobic interactions presumably resulting from dehydration of water molecules surrounding the hydrophobic tails. Similar behaviour is also reported in case of biomolecules [52]. The slightly negative or little positive value of heat capacity indicates less structural change/specific binding

Table 3 The critical micelle concentration (cmc) and various thermodynamic parameters for DTAC+ SAIL mixed systems at various temperatures

DTAC + SAIL	Mole fraction of SAIL	cmc (mmol kg^{-1})	*g*	$\Delta G_m{}^0$ (kJ mol^{-1})	$\Delta H_m{}^0$ (kJ mol^{-1})	$\Delta S_m{}^0$ (J K^{-1} mol^{-1})	ΔC_p° (J K^{-1} mol^{-1})
298.15	0.0	23.1	0.470	− 29.54	4.50	114.3	
308.15		22.9	0.462	− 30.69	− 1.78	93.82	− 0.2
318.15		23.3	0.463	− 31.63	− 0.32	98.41	
298.15	0.25	3.0	0.788	− 29.51	− 12.03	58.62	
308.15		3.2	0.797	− 30.09	− 10.69	62.97	0.15
318.15		3.4	0.803	− 30.72	− 8.95	68.43	
298.15	0.50	2.7	0.582	− 34.99	− 29.24	19.28	
308.15		2.8	0.612	− 35.16	− 24.29	35.28	0.36
318.15		3.1	0.632	− 35.51	− 22.01	42.42	
298.15	0.75	1.8	0.478	− 39.10	− 35.76	11.19	
308.15		1.9	0.515	− 39.18	− 30.41	28.47	0.29
318.15		2.1	0.534	− 39.47	− 30.01	29.73	
298.15	1.0	1.2	0.482	− 40.52	− 28.83	39.21	
308.15		1.3	0.498	− 40.92	− 28.89	39.04	− 0.01
318.15		1.5	0.516	− 41.31	− 28.97	38.78	

Standard uncertainties *s* are $s(\Delta G_m{}^0) = \pm 0.02$ (kJ mol^{-1}), $s(\Delta H_m{}^0) = \pm 0.01$ (kJ mol^{-1}), $s(\Delta S_m{}^0) = \pm 0.02$ (J K^{-1} mol^{-1}), $s(T) = \pm 1 \times 10^{-2}$ K and $s(p) = \pm 2$ kPa respectively

Table 4 The critical micelle concentration (cmc) and various thermodynamic parameters for C14-6-C14+ SAILmixed systems at various temperatures

C14-6-C14+ SAIL	Mole fraction of SAIL	cmc (mmol kg^{-1})	g	$\Delta G_m{}^0$ (kJ mol^{-1})	$\Delta H_m{}^0$ (kJ mol^{-1})	$\Delta S_m{}^0$ (J K^{-1} mol^{-1})	ΔC°_p (J K^{-1} mol^{-1})
298.15	0.0	0.18	0.471	− 64.59	− 20.35	148.39	
308.15		0.20	0.476	− 65.91	− 21.64	143.66	− 0.1
318.15		0.23	0.507	− 65.11	− 22.37	134.34	
298.15	0.25	0.21	0.481	− 63.12	− 20.94	141.45	
308.15		0.23	0.507	− 62.99	− 21.79	133.70	− 0.11
318.15		0.28	0.511	− 63.91	− 23.15	128.11	
298.15	0.50	0.27	0.514	− 59.87	− 21.17	148.39	
308.15		0.30	0.516	− 61.12	− 22.55	143.66	− 0.14
318.15		0.36	0.518	− 62.10	− 24.00	134.34	
298.15	0.75	0.38	0.544	− 56.4	− 22.54	113.57	
308.15		0.43	0.554	− 57.09	− 23.83	107.91	− 0.12
318.15		0.52	0.569	− 57.06	− 25.01	100.71	
298.15	1.0	1.2	0.482	− 40.52	− 28.83	39.21	
308.15		1.3	0.498	− 40.92	− 28.89	39.04	− 0.01
318.15		1.5	0.516	− 41.31	− 28.97	38.78	

Standard uncertainties s are $s(\Delta G_m{}^0) = \pm 0.02$ (kJ mol^{-1}), $s(\Delta H_m{}^0) = \pm 0.01$ (kJ mol^{-1}), $s(\Delta S_m{}^0) = \pm 0.02$ (J K^{-1} mol^{-1}), $s(T) = \pm 1 \times 10^{-2}$ K and $s(p) = \pm 2$ kPa respectively

during the formation of mixed micelles. This variation might be due to some structural rearrangement during the formation of mixed micelles.

Micellar parameters

Ideal cmc calculation

By applying the pseudo-phase model, we have investigated the ideal and non-ideal behaviour of mixed micelles of all the cationic surfactants and SAIL. According to this model, in an ideal state (cmc*), the cmc of mixed systems can be evaluated from cmc of pure components SAIL ($c_1{}^m$) + (TTAB/DTAC/C14-6-C14, 2Br ($c_2{}^m$), respectively reported in Tables 5, 6 and 7. Under equilibrium conditions, ideal cmc (cmc*) can be calculated by using Clint equation [53]:

$$\frac{1}{\mathrm{cmc}*} = \frac{\alpha_1}{f_1 c_1^m} + \frac{(1-\alpha_1)}{f_2 c_2^m} \tag{8}$$

where $c_1{}^m$ and $c_2{}^m$ are the cmc of pure components SAIL and surfactants in bulk, and cmc* is cmc in ideal state; α_1 is the mole fraction of component 1 (SAIL); (1-α_1) is the mole fraction of component 2 (surfactants); f_1 and f_2 stands for the activity coefficient of components 1 and 2 in mixed micelle.

A sharp decrease in the cmc values has been observed with increase in SAIL content in case of TTAB/DTAC + SAIL system, but increase in the cmc values has been observed in case of gemini surfactant (C14-6-C14,2Br) that indicates non-favourable interaction which takes place in this mixed system. It is clear from Fig. 5 a and c and Tables 5, 6 and 7 that experimental values of cmc at different mole fractions of mixtures are lower than that of each individuals in the mixture (cmc < cmc*) and show negative deviations from ideal cmc (cmc*) specifying synergisticinteraction between cationic surfactants and SAIL, [C$_{14}$iQuin][Br]. Further, the ideal cmc values (cmc*) calculated by applying Clint model indicate the non-ideal mixing behaviour which shows that micellization formation takes place at lower concentration rather than expected one. It also demonstrates that micellization phenomena is favourable for these systems. In comparing all the three systems, it is clear that the DTAC surfactant shows the larger non-ideal behaviour than others, which is again due to higher contribution of SAIL in mixed micelle formation.

Micellar mole fraction of the mixture and interaction parameter determination

Holland and Rubingh have proposed a model in order to study the mixing behaviour of amphiphilic compounds [54]. This model considers the systems as non-interacting and first component does not meddle the micellization behaviour of second component. By applying the regular solution theory (RST theory), approximation quantitative evaluation of the results has been

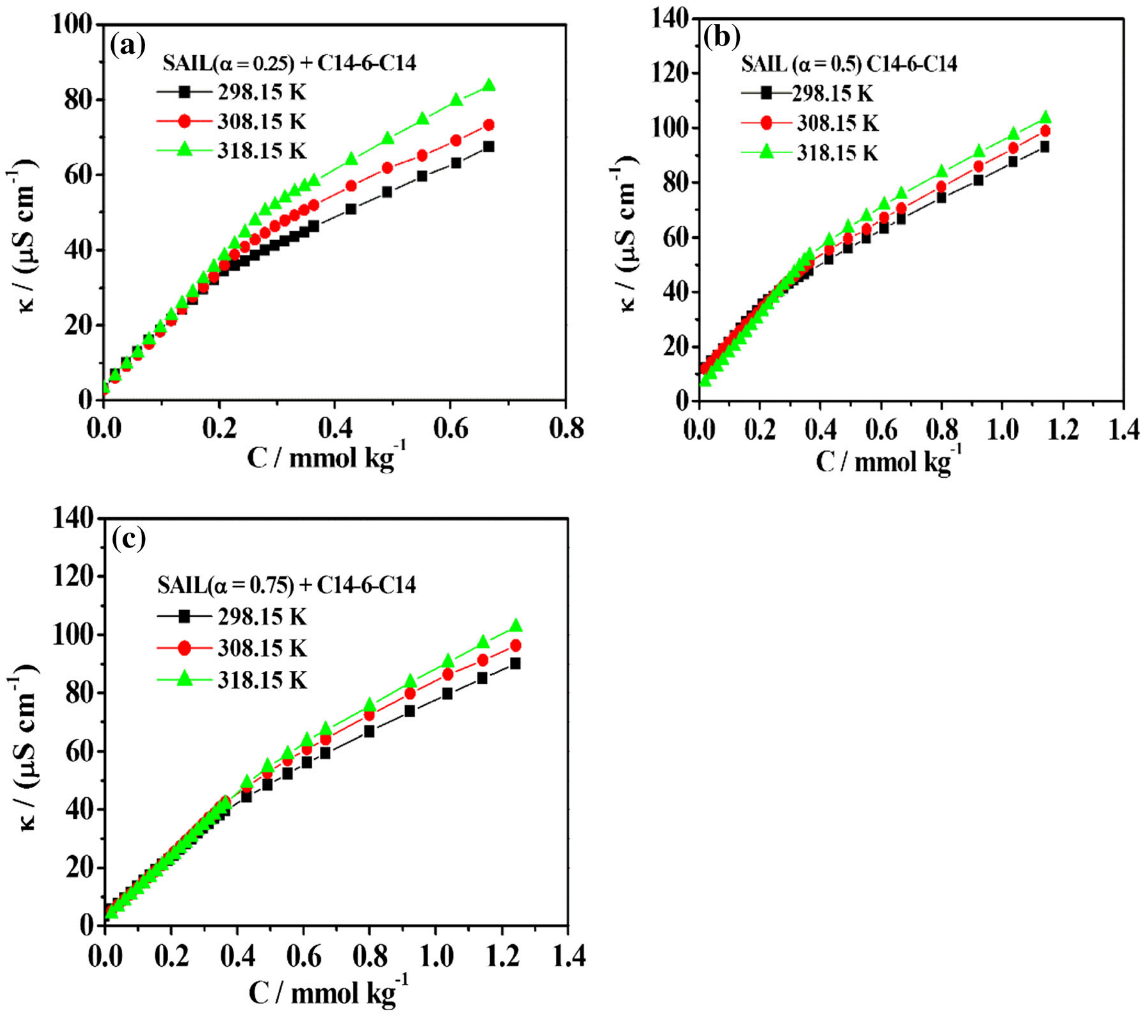


Fig. 4 **a–c** Plot of specific conductivity (κ) as a function of total surfactant concentration for mixed system of C14-6-C14,2Br + SAIL at different concentrations

made.Hence, the following equation can be employed to calculate the value of micellar mole fraction of the SAIL component $X_1{}^m$.

$$\frac{\left[\left(X_1^m\right)^2 \ln\left(\frac{\alpha_1 \mathrm{cmc}}{X_1^m c_1^m}\right)\right]}{\left[\left(1-X_1^m\right)^2 \ln\left[\left(1-\alpha_1\right)\mathrm{cmc}/\left(1-X_1^m\right)c_2^m\right]\right]} = 1 \tag{9}$$

Further, the ideal micellar mole fraction in mixed state, $X_1{}^{\mathrm{ideal}}$ has been computed by applying Motomura theory [55]. The following equation has been used here:

$$X_1^{\mathrm{ideal}} = \frac{\alpha_1 c_2^m}{\alpha_1 c_2^m + (1-\alpha_1) c_1^m} \tag{10}$$

From Tables 5, 6 and 7, we can see that the values of both $X_1{}^{\mathrm{ideal}}$ and $X_1{}^{\mathrm{m}}$ increase with increase in mole fraction of SAIL for all the studied systems which seems to be due to favourable mixed micelle formation as compared with micelles of the pure components. The deviation of $X_1{}^m$ from $X_1{}^{\mathrm{ideal}}$ indicates non-ideal behaviour of mixed systems.The population of SAIL ($X_1{}^m$) in the micellar phase is higher at all the mole fraction ratio (α_1) as shown in Tables 5 and 6, because the cmc of SAIL is lower than TTAB/DTAC surfactants: therefore, it shows relatively higher affinity of the SAIL towards self-aggregation.

The values of $X_1{}^{\mathrm{ideal}} > X_1{}^m$ suggest that more surfactant molecules are present in mixed micellar phase. Similar behaviour has been found in both TTAB/DTAC + SAIL mixed systems. But very interesting results have been observed in case of gemini surfactant where $X_1{}^{\mathrm{ideal}} < X_1{}^m$ even at low mole fraction of SAIL (α_1). This is due to the reason that increase in concentration of SAIL molecules contributes more towards formation of mixed micelles than in its ideal state. Less number of surfactant (gemini) molecules shift from solution to micellar phase and thus delay when micellization takes place [8].

Table 5 The various physiochemical parameters for TTAB + SAIL mixed systems at different mole fraction of SAIL and at various temperatures

TTAB + SAIL	cmc (mmol kg^{-1})	cmc* (mmol kg^{-1})	X_1^m	X_1^{ideal}	β_m	f_1	f_2	ΔG_{ex} (kJ mol^{-1})
T = 298.15 K								
0.0	4.1	–	–	–	–	–	–	–
0.25	2.4	2.5	0.539	0.541	− 0.115	0.976	0.967	− 0.07
0.50	1.7	1.8	0.736	0.780	− 0.511	0.965	0.758	− 0.25
0.75	1.3	1.4	0.865	0.914	− 0.701	0.987	0.592	− 0.20
1.0	1.2	–	–	–	–	–	–	–
T = 308.15 K								
0.0	4.3	–	–	–	–	–	–	–
00.25	2.5	2.8	0.516	0.519	− 0.398	0.911	0.899	− 0.25
0.50	1.7	2.0	0.699	0.764	− 0.841	0.926	0.663	− 0.44
0.75	1.5	1.6	0.840	0.907	− 0.960	0.976	0.508	− 0.32
1.0	1.3	–	–	–	–	–	–	–
T = 318.15 K								
0.0	4.7	–	–	–	–	–	–	–
0.25	2.7	3.1	0.509	0.511	− 0.453	0.896	0.889	− 0.28
0.50	1.9	2.3	0.694	0.758	− 0.836	0.924	0.668	− 0.44
0.75	1.7	1.8	0.824	0.904	− 1.07	0.967	0.480	− 0.39
1.00	1.5	–	–	–	–	–	–	–

Uncertainties s are $s(\alpha) = \pm 0.01$, $s(\text{cmc}) = \pm 0.1$ mM and $s(T) = \pm 1 \times 10^{-2}$ K

Interaction parameter (β_m)

The type of interaction (synergistic and antagonistic) or its strength is determined by measuring the value of micellar interaction parameter (β_m). The value of micellar mole fraction, X_1^m, calculated above and experimentally determined cmc value are utilized to calculate the value of micellar interaction parameter (β_m). Negative value of (β_m) signifies

Table 6 The various physiochemical parameters for DTAC + SAIL mixed systems at different mole fractions of SAIL and at various temperatures

DTAC + SAIL	cmc (mmol kg^{-1})	cmc* (mmol kg^{-1})	X_1^m	X_1^{ideal}	β_m	f_1	f_2	ΔG_{ex} (kJ mol^{-1})
T = 298.15 K								
0.0	23.1	–	–	–	–	–	–	–
0.25	3.0	4.1	0.735	0.868	− 1.83	0.878	0.370	− 0.89
0.50	1.8	2.2	0.824	0.952	− 2.21	0.934	0.222	− 0.79
0.75	1.5	1.5	0.964	0.983	− 0.92	0.998	0.424	− 0.08
1.0	1.2	–	–	–	–	–	–	–
T = 308.15 K								
0.0	23.0	–	–	–	–	–	–	–
0.25	3.2	4.6	0.710	0.851	− 2.02	0.843	0.360	− 1.03
0.50	2.0	2.5	0.811	0.945	− 2.24	0.922	0.228	− 0.85
0.75	1.7	1.8	0.956	0.980	− 0.96	0.998	0.418	− 0.10
1.0	1.3	–	–	–	–	–	–	–
T = 318.15 K								
0.0	23.3	–	–	–	–	–	–	–
0.25	3.4	5.0	0.694	0.783	− 2.13	0.819	0.358	− 1.12
0.50	2.2	2.8	0.803	0.939	− 2.25	0.916	0.232	− 0.89
0.75	1.9	2.0	0.954	0.979	− 0.96	0.998	0.417	− 0.10
1.00	1.5	–	–	–	–	–	–	–

Uncertainties s are $s(\alpha) = \pm 0.01$, $s(\text{cmc}) = \pm 0.1$ mM and $s(T) = \pm 1 \times 10^{-2}$ K

Table 7 The various physiochemical parameters for [C14-6-C14][2Br] + SAIL mixed systems at different mole fractions of SAIL and at various temperatures

[C14-6-C14] [2Br] + SAIL	cmc	cmc* (mmol kg^{-1})	X_1^m	X_1^{ideal}	β_m	f_1	f_2	ΔG_{ex} (kJ mol^{-1})
T = 298.15 K								
0.0	1.2	–						
0.25	0.21	0.22	0.100	0.048	− 0.99	0.445	0.989	− 0.22
0.50	0.27	0.31	0.209	0.046	− 0.97	0.546	0.959	− 0.24
0.75	0.38	0.49	0.375	0.049	− 1.14	0.641	0.852	− 0.46
1.00	0.18							
T = 308.15 K								
0.0	1.3	–						
0.25	0.23	0.25	0.096	0.131	− 0.96	0.454	0.991	− 0.21
0.50	0.30	0.34	0.202	0.127	− 0.92	0.555	0.963	− 0.38
0.75	0.42	0.54	0.369	0.133	− 1.09	0.647	0.862	− 0.65
1.00	0.20							
T = 318.15 K								
0.0	1.5	–						
0.25	0.28	0.29	0.093	0.311	− 0.85	0.494	0.992	− 0.19
0.50	0.36	0.40	0.199	0.305	− 0.92	0.599	0.968	− 0.34
0.75	0.52	0.63	0.368	0.316	− 0.88	0.703	0.887	− 0.57
1.00	0.23							

Uncertainties *s* are *s*(α) = ± 0.01, *s*(cmc) = ± 0.1 mM and *s*(*T*) = ± 1 × 10^{-2} K

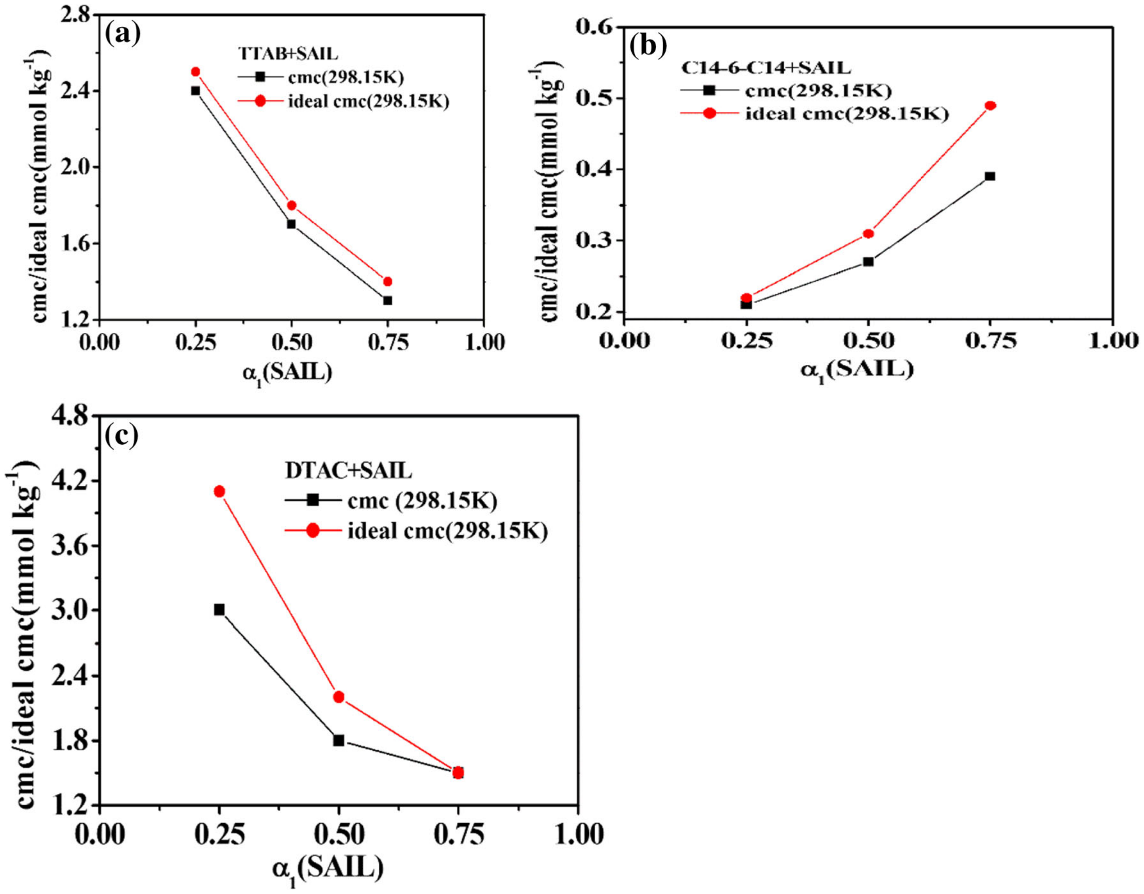


Fig. 5 **a**–**c** Variations of cmc and ideal cmc with increasingα_1 of SAIL at 298.15 K

Table 8 Chemical shifts values determined by ^{1}H NMR titrations of TTAB with increasing mole fractions of SAIL

δ values of TTAB protons (ppm) in the presence of SAIL [C_{14}iQuin][Br]					
Mole fraction(α_1) of SAIL	*a*	*b*	*c*	*d*	*e*
0.0	0.8064	1.223–1.304	1.7076	3.3279	3.0922
0.25	0.6875	1.079–1.327	1.7560	3.3706	3.1169
0.50	0.6025	0.978–1.325	1.7795	3.3723	3.1329
0.75	0.5388	0.902–1.317	1.7954	3.4096	3.1415

attractive or synergistic interactions and more the value of (β_m) stronger the interactions. The following equation is employed to calculate the value of interaction parameter:

$$\beta_m = \frac{\ln\left(\frac{\mathrm{cmc}\alpha_1}{c_1^m X_1^m}\right)}{\left(1-X_1^m\right)^2} \tag{11}$$

The value of micellar interaction parameter (β_m) has been found to be negative for all the systems, which again confirms the synergistic interactions among present systems. The corresponding values obtained from above used equations have been tabulated in Tables 5, 6 and 7. The micellar interaction parameter (β_m) values become more negative with rise in temperature as well as with increasing mole fraction of SAIL in case of TTAB/DTAC + SAIL system while opposite results have been observed in case of C14-6-C14,2Br + SAIL mixed system. It suggests stronger synergistic interactions present in conventional surfactants in comparison with gemini surfactants. This enhanced sysnergism at elevated temperature and with increasing content of SAIL can be related to reduction in head group repulsions and predominance of hydrophobic interactions in the mixed system. The intercalation of SAIL molecules in the pure surfactant micelle enhances the hydrophobic interactions and thus the micellization takes place at lower concentration that has been noticed as reduction of cmc values.

Activity coefficients (f_1, f_2)

The values of activity coefficients provide information about role of both the components in formation of mixed micelle. So the value of activity coefficients (f_1 and f_2) of SAIL and surfactants were evaluated by utilizing the value of micellar mole fraction $X_1{}^m$ and interaction parameter ($\beta_{m.}$) from following equations:

$$f_1 = \exp\left[\beta_m\left(1-X_1^m\right)^2\right] \tag{12}$$

$$f_2 = \exp\left[\beta_m\left(X_1^m\right)^2\right] \tag{13}$$

The magnitude of the value of activity coefficients (f_1 and f_2) is found to be less than unity for all the mole fractions reported in Tables 5, 6 and 7. It implies non-ideal behaviour in the whole range of mole fraction, signifying attractive interactions between TTAB/DTAC/C14-6-C14,2Br and [C_{14}iQuin][Br] in the mixtures. Similar behaviour had been reported in literatures [12, 33]. The values of activity coefficients (f_1 and f_2) have been found to be an increasing order (towards unity) with increase in SAIL concentration which suggests decrease in non-ideal behaviour of the mixed system. The similar trend has been observed earlier by Hoque et al. during the study of mixed micellization behaviour of cationic surfactants (TTAB+DATC) in the presence and absence of NaCl salt [45]. They suggested that increasing value of f_1 and f_2 with increasing mole fraction of TTAB in the presence of salt NaCl shows the ideality of the solution decreases. These are also decreased with rise in temperature in TTAB/DTAC + SAIL mixed system.

Excess Gibbs free energy (ΔG_{ex})

The value of excess Gibbs free (ΔG_{ex}) explain the non-ideal behaviour of studied mixed systems. Its value is determined

Table 9 Chemical shifts values determined by ^{1}H NMR titrations of DTAC with increasing mole fractions of SAIL

δ values of DTAC protons (ppm) in the presence of SAIL [C_{14}iQuin][Br]					
Mole fraction (α_1) of SAIL	*a*	*b*	*c*	*d*	*e*
0.0	0.8014	1.2243–1.3029	1.6899	3.237	3.0459
0.25	0.6767	0.9572–1.3010	1.7295	3.3028	3.0975
0.50	0.5994	0.8587–1.3109	1.7652	3.3471	3.1067
0.75	0.5667	0.8355–1.3020	1.7809	3.3766	3.3594

Table 10 Chemical shifts values determined by ^{1}H NMR titrations of gemini surfactant (C14-6-C14) with increasing mole fractions of SAIL

δ values of protons Gemini (14-6-14) (ppm) in the presence of SAIL [C_{14}iQuin][Br]						
Mole fraction (α_1) of SAIL	*a*	*b–c*	*d*	*e*	*f*	*g*
0.0	0.8186	1.2327–1.4143	1.7022	–	3.3448	3.1035
0.25	0.7502	1.1025–1.3837	1.6880	1.8076	3.2824	3.0708
0.50	0.6569	1.1027–1.3921	1.7024	1.8026	3.2953	3.0866
0.75	0.5745	0.9323–1.3922	1.7136	1.8041	3.3127	3.0998

by using the estimated values of activity coefficients (f_1 and f_2) and X_1^m by utilizing the following equation:

$$\Delta G_{ex} = RT[X_1 \ln f_1 + (1 - X_1) \ln f_2] \qquad (14)$$

The estimated values are reported in Tables 5, 6 and 7. The value of ΔG_{ex} comes out to be zero if the system is ideal, in our case its value was found to be negative and increased as we increase the mole fraction of the SAIL. This behaviour shows the stable micelle formation in mixed state rather than pure individual one and also their stability rises with rise in α_1 of the IL. On comparing all the three systems, the value of ΔG_{ex} was found negative for the mixed system of DTAC + SAIL, which again support the formation of stable mixed micelle. This fact is also supported by the value of interaction parameter ($\beta_{m.}$).

^{1}H NMR measurements

^{1}H NMR measurements have been employed to monitor the morphology of aggregating moieties in mixed systems. ^{1}H NMR spectra of all the studied systems in pure and mixed states have been reported in supplementary information. Also the change in chemical shift values of pure components after addition of SAIL has been tabulated in Tables 8, 9 and 10 (TTAB/DTAC/C14-6-C14,2Br+SAIL). It can be seen from both the Tables 9 and 10 that hydrophobic moieties of both TTAB/DTAC surfactant, i.e. tail protons (a, b), show strong shielding effect and the corresponding chemical shift values (δ) of them decrease with increasing concentration of SAIL (Fig. 6(a, b).

It is well known that upfield and downfield in the chemical shift values depend on protons present in surrounding environment [40]. The higher the electron density in nearby environment, the more will be the shielding effect. It reflects the presence of stronger hydrophobic interactions among tail protons of the present system that leads to shielding of tail protons. As we move towards the head of the surfactant, the protons near the head group (c, d and e) show deshielding effect and increase in chemical shift (δ) value has been observed.The increasing counterion dissociation of SAIL leads to electrostatic attraction among Br- and surfactant cation (N^+) rather than repulsion that is responsible for decrease in electron density of surfactant cation (N^+) and it results in downfield shift in head group protons.

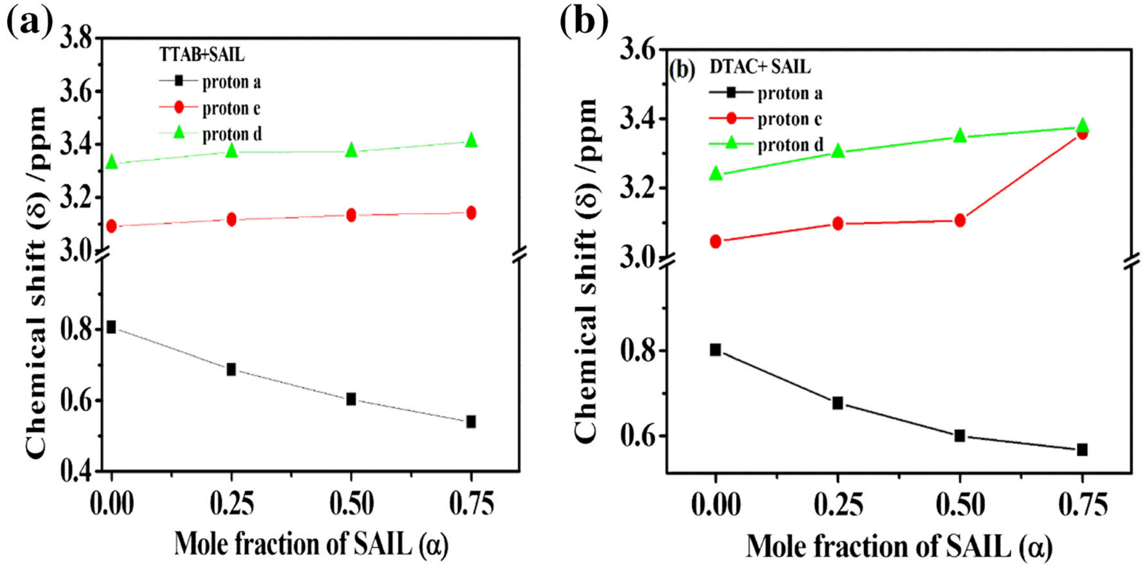


Fig. 6 **a, b** Variation in chemical shift value (δ) of surfactants with increasing mole fractions of SAIL.

Conclusion

Mixed micelle formation between tetradecyltrimethylammonium bromide (TTAB), dodecyltrimethylammoniumchloride (DTAC),cationic gemini surfactant (C14-6-C14,2Br) and isoquinolinium-based surface active ionic liquid, [C_{14}iQuin][Br], has been studied by conductometry and spectrometry. The critical micelle concentration (cmc), degree of dissociation (*g*) and various thermodynamic parameters like (standard Gibb free energy of micellization ($\Delta G_m{}^0$), change in standard enthalpy ($\Delta H_m{}^0$) and entropy of micellization ($\Delta S_m{}^0$) has been evaluated from conductometry. The cmc values are found to decrease in case of TTAB/DTAC + SAIL mixed system while reverse behaviour is noticed in case of (C14-6-C14,2Br) + SAIL binary system. The negative values of Gibbs free energy of micellization indicate mixed micelle formation in all three systems is spontaneous in nature. Largest decrease in cmc has been observed in DTAC + SAIL system showing strongest synergistic interaction. The cmc values obtained by applying Clint's model show non-ideal behaviour (cmc < cmc*) for all the surfactant + SAIL systems. The value of $X_1{}^{\text{ideal}} > X_1{}^m$ indicates more involvement of surfactant molecules in formation of mixed micelles. The values of activity coefficient (f_1 and f_2) were observed less than unity, implying synergistic interactions. The magnitude of interaction parameter (β_m) comes out negative for all the studied systems; such value of β_m also indicates the synergistic interaction between surfactant and SAIL molecules. The negative value of excess free energy (ΔG_{ex}) reveals that the mixed micelles formed are more stable than individual one. The ^{1}H NMR measurements have also been performed to study the interaction phenomena in mixed systems. The tail protons of all the surfactant show upfield in chemical shift values (shielding effect) while head protons show downfield chemical shift values with increasing mole fraction value of SAILs in mixed systems. It indicates the stronger interaction between hydrophobic chains present in micellar core. On compairing all the thermodynamic and interaction parameters, it has been concluded that among all the cationic surfactants (TTAB, DTAC and C14-6-C14,2Br), the major deviation is noticed in the case of DTAC. That is well supported by the value of calculated cmc, degree of dissociation (*g*), standard Gibbs free energy of micellization ($\Delta G_m{}^0$) and interaction parameter (β_m).

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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