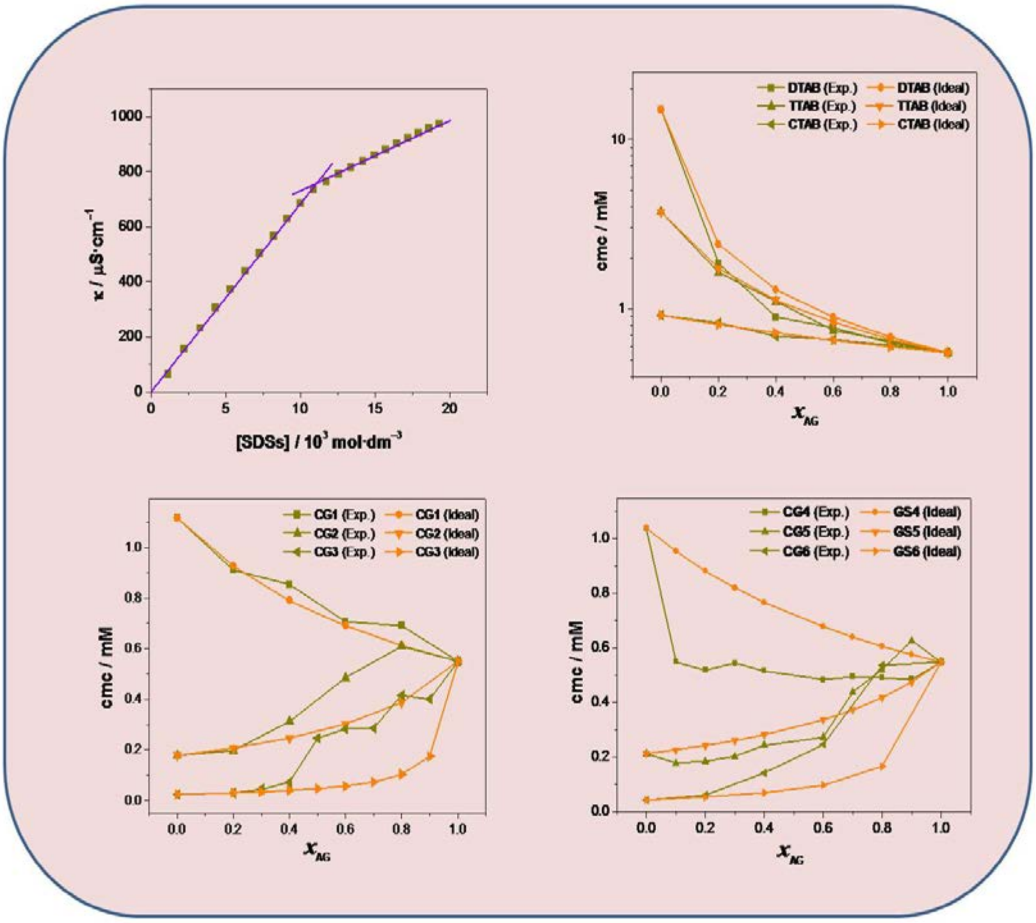
Chapter 3

Micellization/Mixed Micellization Study of Various Classes of Ionic Surfactants



3.1. Introduction

Surfactant based systems are widely used for various applications ranging from extraction of DNA to remediation of soil [1-3]. Surfactant monomers aggregate in solution due to their amphiphilic nature via hydrophobic interactions [4]. Solution properties have been found to be dependent on the nature of surfactant monomer (ionic or nonionic) [5-8].

From application point of view, selection of surfactant or surfactant mixture is required to optimize the desired treatment or formulation [9, 10]. Surfactant mixtures usually show synergistic behaviour and thus bring about more intriguing properties than their constituting components. Synergism refers to the increased interfacial activity and decreased cmc of the mixtures. In view of this numerous binary combinations of ionic and nonionic surfactants mixtures have been studied in respect of mixed micellization and adsorption in/at the air-water interface [11-13].

Although, synergism in the cmc by mixing two different surfactants is known for decades, mixing an ionic surfactant with a organic salt containing different counterion (mixed counterion systems) has been comparatively less highlighted [14-16]. Literature on the effect of organic counterions on the micellization of cationic surfactants exceed the investigations with anionic surfactant [17, 18].

Studies on mixtures of two single-chain surfactants have found that the synergism decreases in the order of anionic/cationic > ionic/zwitterionic > ionic/nonionic. Normally, cationic/anionic mixed surfactants can more closely pack at the air-water interface and in micelles, and thus exhibit stronger synergism because of electrostatic attraction between their oppositely charged headgroups besides hydrophobic interaction of their alkyl chains [19, 20]. Electrostatic interaction between oppositely charged headgroups, hydrophobic interaction between hydrocarbon chains, and/ or hydrogen binding between some groups are the main driving forces to the formation of aggregates in oppositely charged surfactant mixtures.

With the progress of surfactant research, gemini surfactants have been used to the mixtures of surfactants in the present decade [21-23]. The presence of two charged sites in a gemini produces stronger interaction with the neutral and oppositely charged ionic surfactants than that of the conventional surfactant combinations [24–29]

Investigation of structural changes of known molecular structure and composition, which takes place in surfactants upon mixing of surfactant solutions, provides information that may be useful in predicting the nature of highly complex co-aggregates. It has been shown that gemini surfactants control the morphology and micellar growth in water in mixed Gemini–CTAB micelles. It was also found that an increase in the spacer length generally suppress the tendencies of mixed micelles towards micellar growth [30].

Anionic bio-surfactants, bile salts, are synthesized from cholesterol in the liver. They work as solubilizers and emulsifiers for various bio-molecules (cholesterol, bilirubin, lecithin and hydrophobic vitamins) in gastrointestinal tract [31]. Due to typical chemical structure [32] of bile salts, their solution properties are different from conventional anionic surfactant. The solution properties of bile salt are also exploited in drug permeation, cosmetics and models in pharmaceutical research [33, 34]. Bile salts mixed with steroids, phospholipids or surfactants associate into giant morphologies [35, 36]. This prompted for continuous attention on the mixed micellar systems containing bile salt and conventional surfactant/polymer/drug [37-44].

Limited number of studies have been attempted regarding mixed micellization of oppositely charged amphiphilic molecules. The purpose of the study embodied in the present chapter is to investigate mixed micellization in three different surfactants systems. First system is related to anionic surfactant + quaternary counterions. Another system contains two oppositely charged gemini surfactants. Last system contains gemini surfactant in combination of oppositely charged bile salt.

3.2. Results and Discussion

3.2.1. Micellization of Anionic Surfactant with or without Quaternary Salts

Figure 1 shows the variation of κ with SDSo concentration at 30°C. cmc of SDSo has been determined from the intersection point of nearly two straight lines. α value is calculated by the ratio of the slopes of the post-micellar to the pre-micellar portions of the plot given in Figure 1. The obtained cmc and α values are given in Table 1. cmcs of SDS and SDBS together with their α values are also complied in the Table 1 [14,45,46].

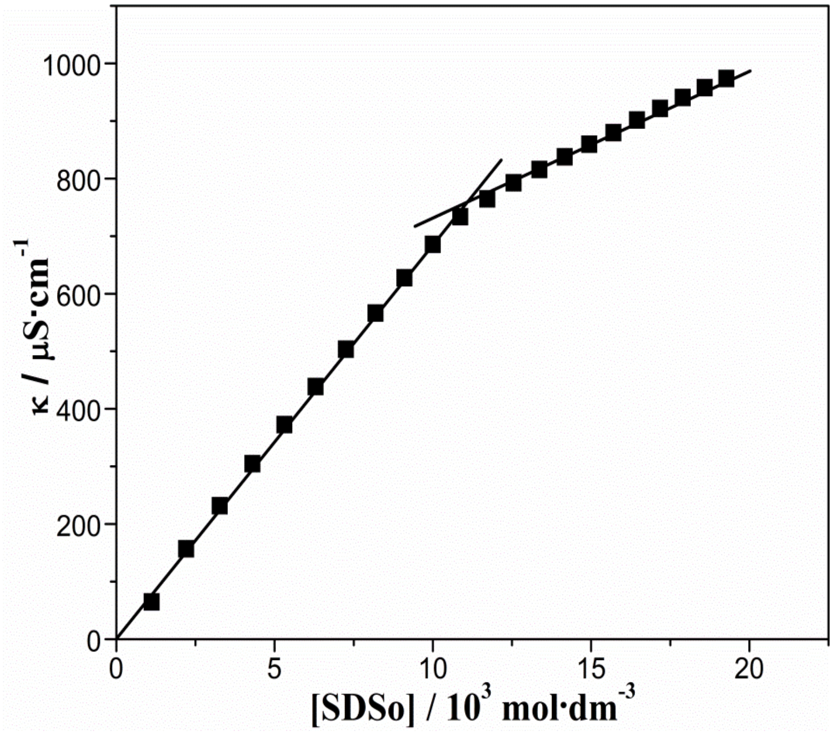


Figure 1. Variation of specific conductance (κ) with [SDSo] at 30°C.

All the three anionic surfactants (SDS, SDBS and SDSo) have different cmc values, though they have same dodecyl chain in the molecule. The difference is due to the nature of the head group present in each surfactant. It is known that the nature of the head group affects the phenomenon of micelle formation [45].

Table 1. Critical micellar concentration (cmc) and apparent degree of counterion dissociation (α) for different surfactant systems at 30°C.

Surfactant system	cmc (mM)	α
SDS	7.90	0.50
SDBS	2.30	0.80
SDSo	10.65	0.39
SDS + 4.4 mM TBAB	0.30	-
SDBS + 1 mM TBAB	1.4	-
SDSo + 1mM TBAB	3.91	0.78
SDSo + 1mM TBPB	2.78	0.78
SDSo + 1mM BTAC	2.59	0.80
SDSo + 1mM TPhPB	2.22	0.86
SDSo + 0.5mM TPeAB	1.82	0.89

In Figure 2, cmc plots of SDSo + quaternary salts systems are shown. cmc decreases with the addition of salt and follows the order TPeAB < TPhPB < BTAC < TBPB < TBAB. Thus, a mixture of sodium and quaternary counterions induces synergism in the cmc. The extent of synergism increase with the alkyl chain length of the quaternary counterion (case of TBA^+ and $TPeA^+$) or with nature of counterion (TBA^+ and BTA^+ cases). This behaviour is similar to what is observed with other anionic surfactant + quaternary counterion combinations (Table 1) [14, 45, 46].

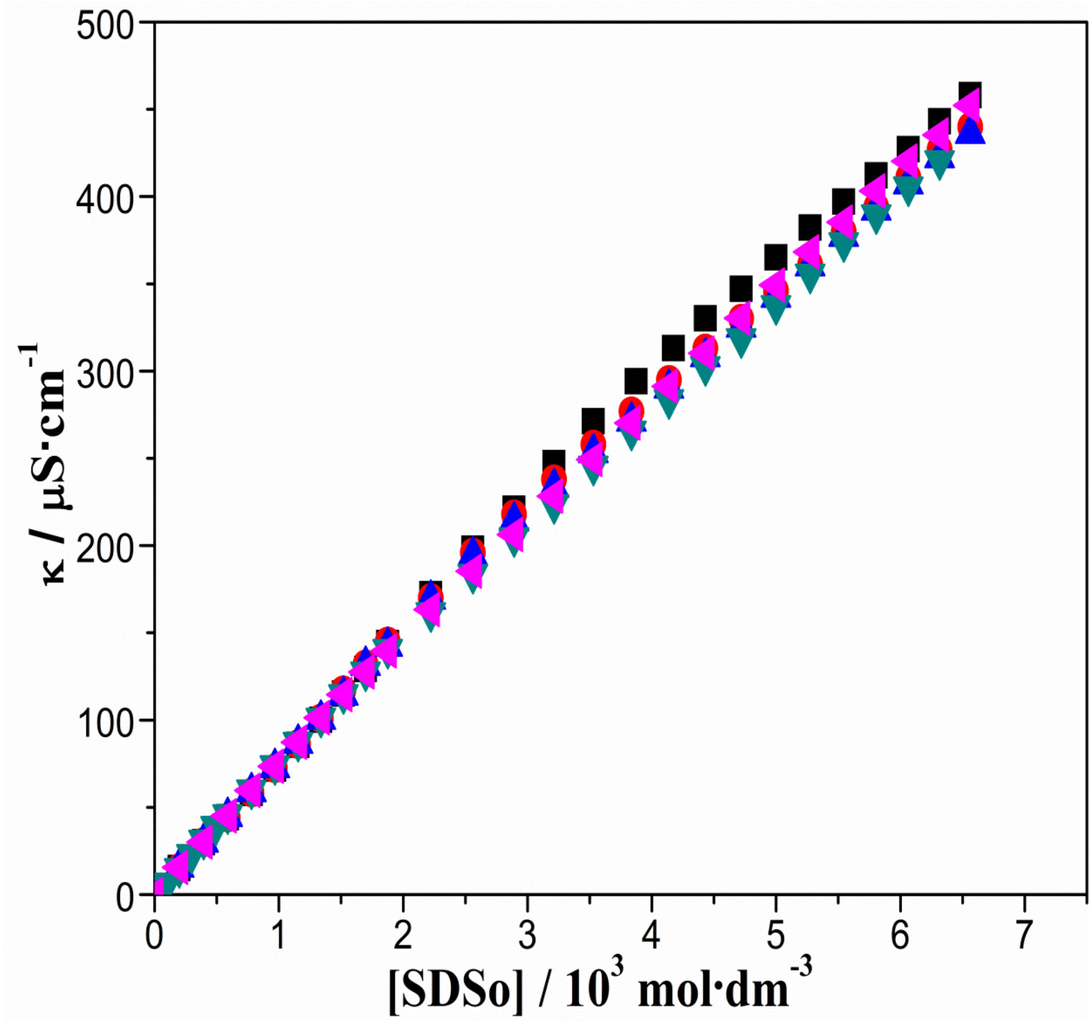


Figure 2. Variation of specific conductance (κ) with [SDSo] at fixed concentration of quaternary salts 30°C: ■, 1mM TBAB; ●, 1mM TBPB; ▲, 1mM BTAC; ▼, 1mM TPhPB and ◄, 0.5mM TPeAB.

The micellization phenomenon is facilitated by the presence of the quaternary counterion, which can interact with the micellar surface electrostatically and hydrophobically. However, the effect was more pronounced with SDSo in the presence of TPeAB (even at 0.5mM), which may be due to the presence of longer alkyl chains present in the salt.

Changing temperature can influence various interactions involved in micellization phenomenon. Therefore, micellization of SDSo, in the presence of 1mM quaternary salts, has been studied at different temperatures (30-50°C). Figure 3 shows the cmc variation with temperature. cmc decreases and then increase with continuous increase in temperature (U-shped behaviour).

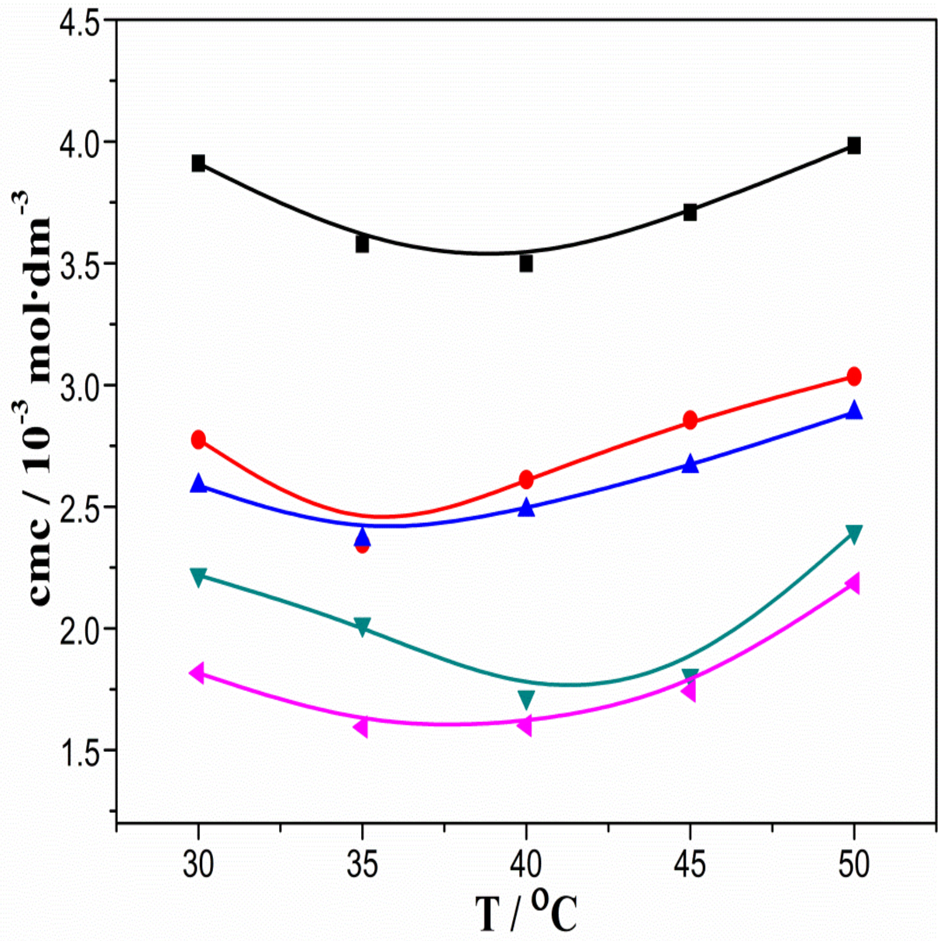


Figure 3. Plots of cmc *vs* Temperature for SDSo in different quaternary salts: colored symbols are similar as used in the caption of Figure 2.

The initial temperature increase decreases the hydration of the polar head group, which favours a decrease in cmc. Further, temperature increase may also break the water structure around the dodecyl part of SDSo, which opposes micelles formation. These two competing factors are responsible for the U-shaped behaviour shown in Figure 3. Similar observation was reported for SDS in presence of some trivalent metal ion and thionin and explained in the light of the facts mentioned above [47]. However, the nature of the counterion has only a weak influence on the temperature of minimum cmc (cmc_m). cmc and thermodynamic data for SDSo +

quaternary salt system are compiled in Table 2. The negative values of ΔG and ΔH indicate the formation of micelles, in presence of quaternary salts, is an spontaneous process.

Table 2. cmc and thermodynamics parameters of SDSo in presence of different quaternary salts at various temperatures.

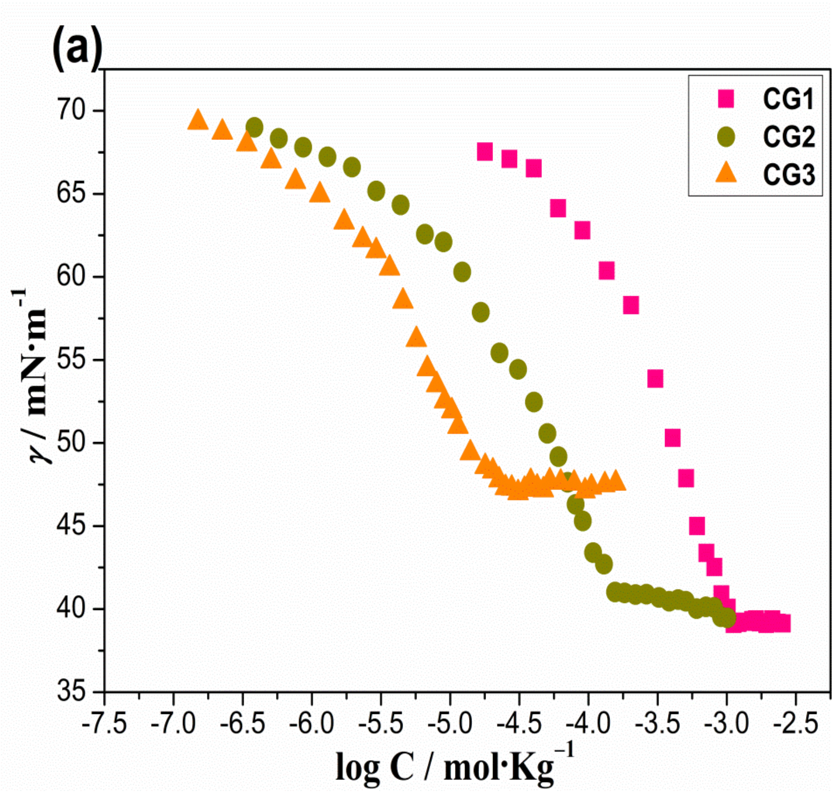
Quaternary salts	T / K	$10^{3\cdot}$CMC / mol·dm^{-3}	ΔG^{o}_{mic} / kJ·mol^{-1}	ΔH^{o}_{mic} / kJ·mol^{-1}	ΔS^{o}_{mic} / J·mol^{-1}K^{-1}
0.5 mM	303	1.816	-28.76	-26.11	8.75
TPeAB	308	1.595	-30.35	-28.16	7.10
	313	1.599	-29.58	-28.40	3.78
	318	1.742	-30.03	-30.04	-0.05
	323	2.185	-28.52	-30.14	-5.02
1 mM	303	2.587	-30.16	-27.32	9.39
BTAC	308	2.366	-30.65	-27.15	11.35
	313	2.487	-30.51	-26.78	11.91
	318	2.667	-30.93	-26.93	12.60
	323	2.887	-31.25	-26.96	13.26
1 mM	303	3.910	-29.34	-12.11	56.87
TBAB	308	3.578	-29.51	-11.93	57.08
	313	3.498	-30.39	-12.10	58.42
	318	3.709	-30.90	-12.21	58.75
	323	3.983	-30.60	-12.01	57.56
1 mM	303	2.776	-30.38	-62.91	-107.36
TBPB	308	2.347	-31.29	-62.84	-102.43
	313	2.612	-31.49	-62.95	-100.51
	318	2.856	-31.07	-61.65	-96.17
	323	3.035	-32.09	-62.95	-95.53
1 mM	303	2.219	-29.08	54.88	277.09
TPhPB	308	2.016	-29.99	55.21	276.61
	313	1.716	-31.15	55.52	276.89
	318	1.805	-31.37	55.17	272.14
	323	2.396	-30.70	54.43	263.57

3.2.2. Mixed Micellization of Oppositely Charged Surfactant Systems

Limited number of studies are attempted regarding mixed micellization of oppositely charged cationic and anionic conventional and gemini surfactants. This study has been designed to show micellization behaviour of (i) conventional, gemini and bile salt (singly), (ii) binary mixtures of cationic (conventional and gemini) surfactant with oppositely charged anionic gemini and (iii) binary mixtures of cationic gemini with oppositely charged bile salt (SC or SDC).

3.2.2.1. Micellization of Individual Surfactants used in Mixed Micellization

Micellization of cationic conventional / gemini surfactants, anionic gemini surfactant (AG) and bile salts have been studied individually and corresponding cmc, α and C_{20} data are complied in Table 3. Typical γ vs log C plots for cationic gemini surfactants are shown in Figure 4.



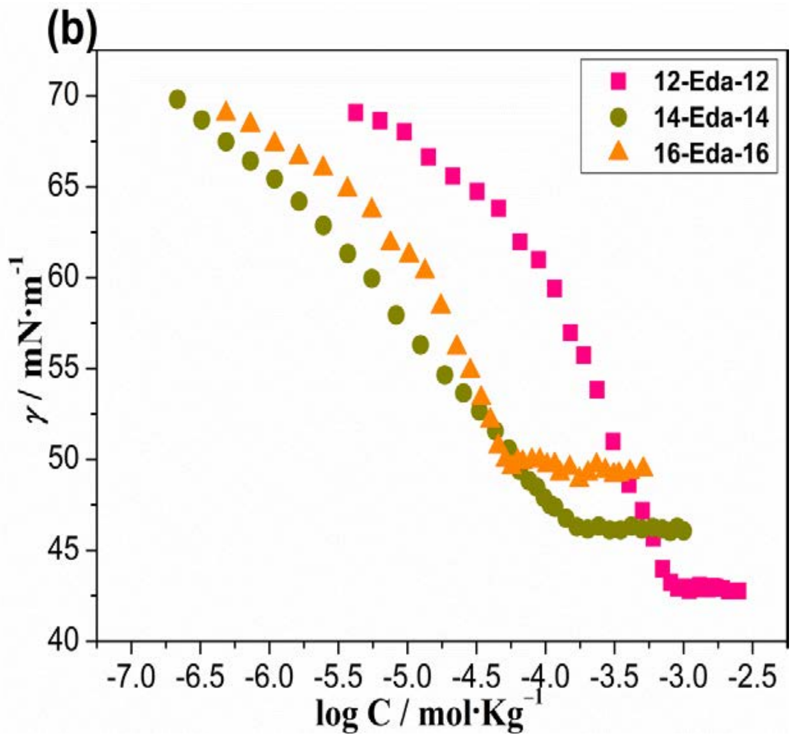


Figure 4. Variation of surface tension (γ) with concentration of various CGs: (a) with polymethylene spacer; (b) with amide spacer:

The cmc values determined by two techniques (conductometry and tensiometry) are found nearly same for all the surfactant used in the study and indicate the validity of the measurements. The cmc values of the individual surfactants agree well with the literature [48-50]. SC and SDC have higher values of cmc than the gemini surfactants. This is due to the difference in hydrophobic and hydrophilic moieties of two classes of surfactants (Chapter 2, Schemes 2 and 3). AG has even lower cmc than the corresponding CG (CG1 and CG4), indicating that head group and nature of charge play role in the micellization. It has also been observed that α value of geminis are higher than the conventional surfactants (Table 3). Gemini has larger area per head group compare to conventional one and, hence, responsible for the larger value of α. The values of α within geminis are found higher for chloride containing gemini than bromide containing one. This indicates less binding of chloride counterions to the head group compared with Br^-.

Table 3. Critical micelle concentration (cmc), degree of counterion dissociation (α) and surfactant concentration required to reduce the surface tension by 20 mN/m (pC_{20}) of all conventional and gemini surfactants (at 303 K) used in the solubilization study.

Surfactant	Conductometry		Tensiometry	
	cmc/m.mol.dm^{-3}	α	cmc/m.mol.dm^{-3}	pC_{20}
DTAB	14.96	0.28	14.30	2.17
TTAB	3.74	0.26	3.75	2.98
CTAB	0.92	0.28	0.94	3.33
SC	10.2	0.85	-	-
SDC	4.5	0.78	-	-
AG	0.55	0.73	0.50	3.57
CG1	1.12	0.28	1.10	3.38
CG2	0.18	0.47	0.15	4.27
CG3	0.02	0.69	0.02	4.90
CG4	1.04	0.40	0.91	3.47
CG5	0.21	0.61	0.16	4.22
CG6	0.04	0.59	0.05	4.43

pC_{20} values are also complied in Table 3. The larger value of pC_{20} denotes the higher adsorption efficiency of surfactant molecules and greater potential in reducing γ. pC_{20} value increases with the increase in size of hydrophobic tail (***m***) indicating that the surfactant with higher ***m*** has better surface activity.

3.2.2.2. Mixed Micellization of Cationic Conventional/Gemini Surfactant with Anionic Gemini Surfactant

cmc measurements have also been performed in mixed surfactant system (AG with CG or conventional cationic surfactant) at various mole fractions (0.2,0.4,0.6 or 0.8). Figures 5 and 6 show variation of cmc with mole fraction of AG to conventional and gemini surfactants (CG), respectively. cmc values of CG-AG mixtures are also determined by tensiometry (Figure 7) to compare the cmc data from the two techniques. The cmc and α data together with surface parameters are complied in Table 4.

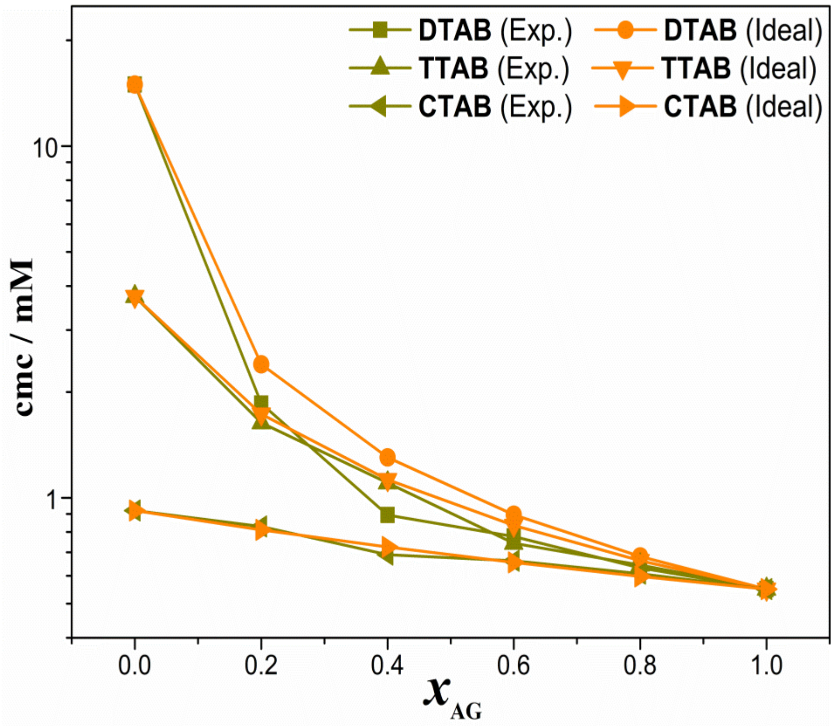


Figure 5. Critical micelle concentration (cmc) variation of mixed surfactant systems (cationic-anionic) with mole fraction of anionic gemini surfactant (x_{AG}) in aqueous solution at 303 K. The plot represents experimental and ideal values (calculated from Clint model).

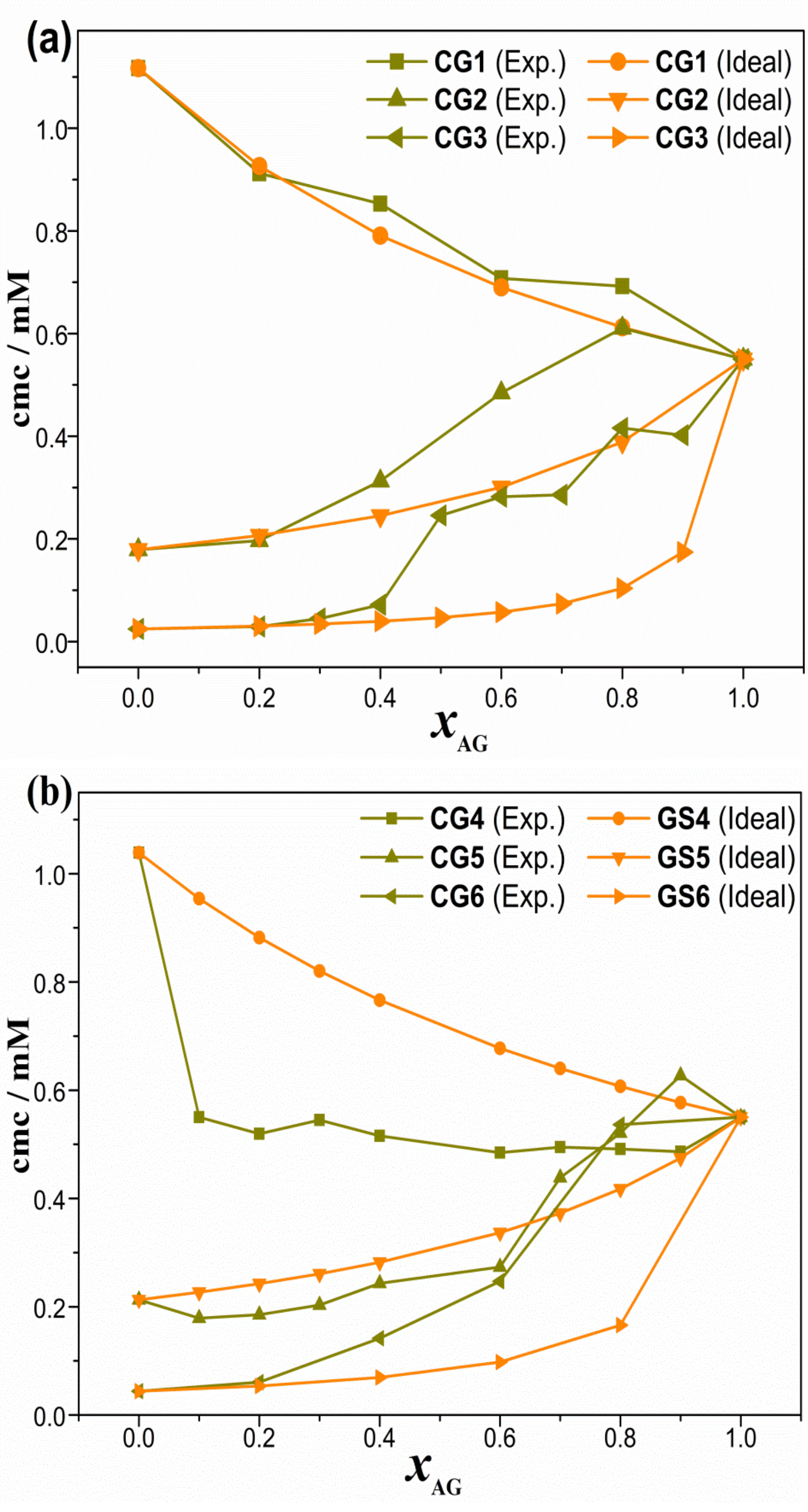


Figure 6. Critical micelle concentration (cmc) variation of mixed surfactant systems (cationic-anionic) with mole fraction of anionic Gemini surfactant (x_{AG}) in aqueous solution at 303 K. The plot represents experimental and ideal values (calculated from Clint model).

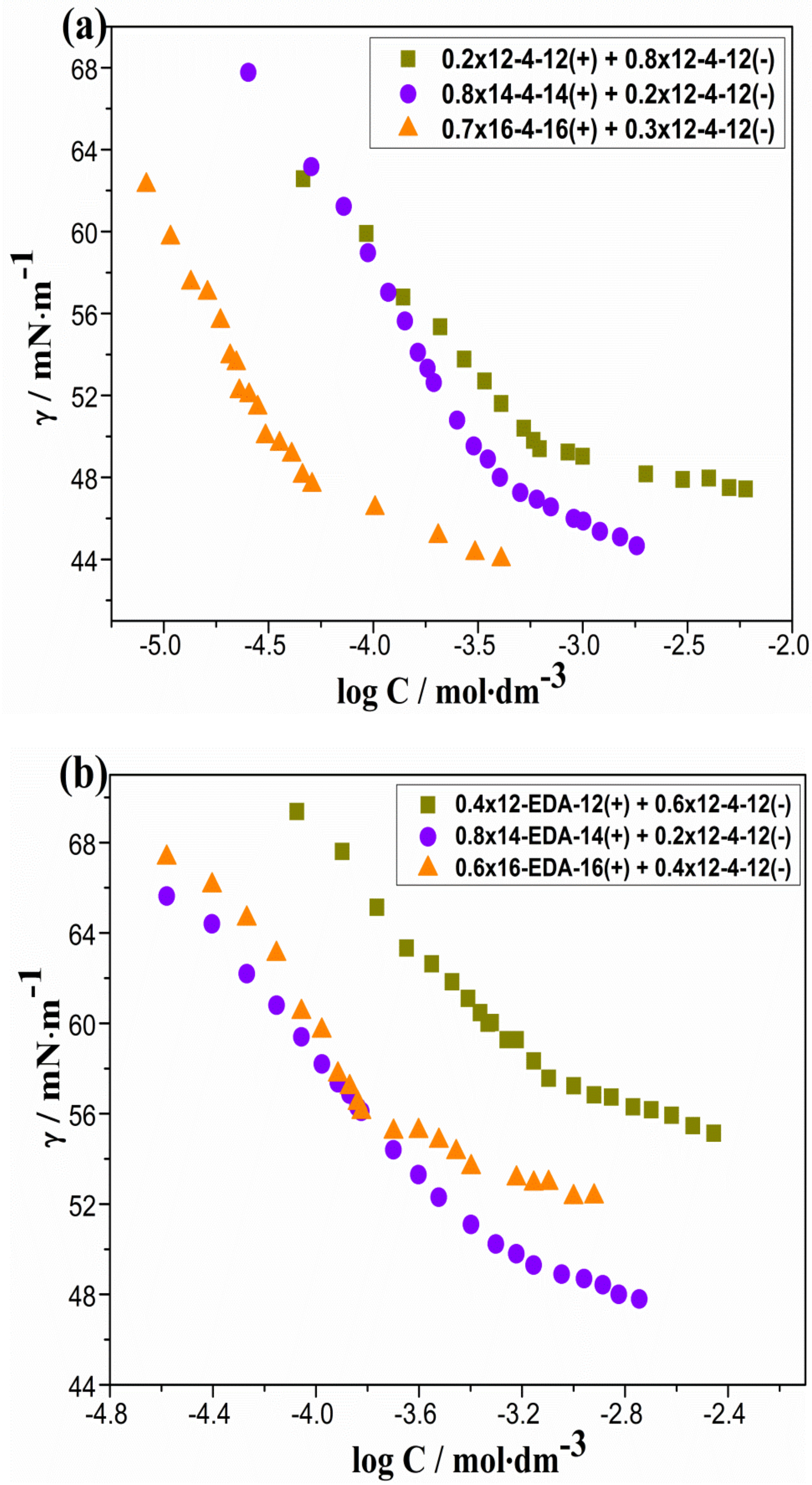


Figure 7. Variation of surface tension with the log of polymethylene and biocompatible spacers based gemini surfactant concentration (C) in aqueous solution at 303 K.

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Table 4 Critical micelle concentration (cmc) and surface properties of gemini surfactants (m-4-m/m-Eda-m + 12-4-12-A) as determined from the surface tension and conductivity measurements in aqueous solution at 303 K.

Gemini surfactant	cmc^a (mM)	cmc^b (mM)	α	γ $nM{\cdot}m^{-1}$	Γ_{max} 10^6 $mol.m^{-2}$	A_{min} nm^2	pC_{20} $mol.dm^{-3}$	$Л_{cmc}$ $nM{\cdot}m^{-1}$
$0.2(12\text{-}4\text{-}12^+)$	0.692	0.636	0.759	49.17	1.066 (0.711)	1.558 (2.335)	3.473	23.69
$0.8(14\text{-}4\text{-}14^+)$	0.168	0.377	0.662	47.44	1.600 (1.067)	1.038 (1.556)	3.556	23.56
$0.7(16\text{-}4\text{-}16^+)$	0.045	0.042	0.789	48.44	1.202 (0.802)	1.381 (2.071)	4.591	24.06
$0.4(12\text{-Eda-}12^+)$	0.485	0.675	0.919	58.02	-	-	-	15.25
$0.8(14\text{-Eda-}14^+)$	0.185	0.321	0.837	51.02	1.162 (0.775)	1.429 (2.143)	3.604	22.05
$0.6(16\text{-Eda-}16^+)$	0.142	0.163	1.116	55.78	-	-	-	13.85

α, degree of micellar ionization; γ_{cmc} surface tension at the cmc; Γ_{max}, maximum surface excess concentration; $A_{min,}$ area per molecule at the interface; $\pi_{cmc,}$ surface pressure at the CMC; $C_{20,}$ surfactant concentration required to reduce the surface tension of the water by 20 mN/m. The values are in parentheses are for n=3.

a CMC from conductivity.

b CMC from surface tension.

The cmc values of mixed surfactant systems (cmc_e) were found lower than that of individual components (cmc_1 or cmc_2, subscript 1 and 2 denotes AG and cationic conventional/gemini, respectively) as well as of ideal cmc (cmc_i, calculated using Clint expression (eq. 1) [51]) of the mixture (Tables 3 and 4).

$$\frac{1}{cmc_{\,i}} = \frac{p_1}{\mathrm{cmc}_{\,1}} + \frac{p_2}{\mathrm{cmc}_{\,2}} \qquad (1)$$

showing non ideal mixing (p_1 and p_2 are mole fractions of AG and other surfactant, respectively). Eq. 1 distingueses between ideal and non ideal mixing of surfactant components for which cmc_i and cmc_e are different The negative and positive variation from cmc_i indicate synergistic and antagonistic interactions in various mixtures. Therefore, mixing of oppositely charged surfactants is not always show a synergistic effect as proposed in earlier literature [52, 53]. However, cmc_e values for antagonistic combinations are lower than the individual member (of the mixed surfactant system) which has higher cmc among them. Probably, the packing of the individual surfactant monomers in the mixed micelle has a role to play to decide the cmc of the mixed system. An antagonistic effect of mixing monomeric and dimeric cationic gemini surfactant has been reported in a recent study [54].

Amphiphilic molecules show surface properties governed by the characteristics of the material adsorbed at the air-solution interface. Based on regular solution theory [55], Rubingh's proposed following equation

$$\frac{[(X_1^m)^2 \ln (cmc_{\,e} p_1/\mathrm{cmc}_{\,1}\, X_1^m)]}{(1-X_1^m)^2 [\mathrm{cmc}_{\,\mathrm{e}}\ (1-p_1)\ /\mathrm{cmc}_{\,2}\ (\,1-X_1^m)]} = 1 \qquad (2)$$

Where, X_1^m represents the micellar mole fraction of AG present in the mixed micelle. X_1^m could not be determined with a few systems (AG + CG1, AG + CG3 and AG + CG6) which may be due to non-convolution of the data in computer program

(Mathematica). Ideal micelle mole fraction of AG (X_1^i) can be computed using Motomura's approximation [56]

$$X_1^i = \frac{p_1 \text{cmc}_2}{p_1 \text{cmc}_2 + (1-\text{p}_1)\text{cmc}_1} \tag{3}$$

where cmc_1 and cmc_2 represent the cmc values of the AG and cationic conventional / gemini surfactant, respectively. Interaction parameter (β^m) cab be obtained using eq. (4)

$$\beta^m = [\ln(cmc_e p_1/\text{cmc}_1 X_1^m)]/(1 - X_1^m)^2 \tag{4}$$

The positive β^m value indicates an antagonistic interaction between two components of the mixed system. In the present binary systems, the cmc_e values are found lower/higher than the cmc_i. A negative β^m is the result of reduction in the free energy of micellization, (thermodynamically more stable) which denotes synergism of the mixing. Figures 5 and 6 show above two effects of mixing. The β^m value has been lowest in the case of AG + DTAB and AG + CG5 (Table 5). This result indicates that β^m is weakly dependent on the nature of the cationic surfactant (conventional or gemini). Probably, packing of hydrocarbon chains (into the micelle) of the two components of the mixture has a role to decide synergistic or antagonistic effect on $cmc_{e.}$ gemini with hexadecyl chains shows antagonistic mixing with AG (AG + CG3 or CG6). This suggests that the alkyl chains of the oppositely charged gemini surfactants should be of nearly similar chain length in order to observed a synergistic effect.

Table 5. Critical micelle concentration (cmc_{exp} and cmc_{ideal}), micellar composition (X_1^m), interaction parameter (β^m) and activity coefficients (f_i^m) of binary surfactant mixtures using Rubingh's Model at 303 K.

System	cmc_{exp} (mM)	cmc_{ideal} (mM)	X_1^m	X_{ideal}	β^m	f_1^m	f_2^m	ΔG_{ex} (KJ mol^{-1})
AG (0.6) + DTAB (0.4)	0.777	0.895	0.877	0.976	-2.229	0.967	0.180	-0.592
AG (0.6) + TTAB (0.4)	0.743	0.835	0.834	0.911	-1.057	0.971	0.479	-0.360
AG (0.4) + CTAB (0.6)	0.689	0.725	0.525	0.527	-0.204	0.955	0.945	-0.126
AG (0.8) + CG1 (0.2)	0.692	0.612	-	-	-	-	-	-
AG (0.2) + CG2 (0.8)	0.197	0.207	0.113	0.075	-0.584	0.632	0.993	-0.143
AG (0.3) + CG3 (0.7)	0.046	0.034	-	-	-	-	-	-
AG (0.6) + CG4 (0.4)	0.485	0.678	0.644	0.739	-1.558	0.821	0.524	-0.878
AG (0.2) + CG5 (0.8)	0.179	0.227	0.238	0.088	-2.231	0.234	0.882	-1.085
AG (0.4) + CG6 (0.6)	0.142	0.060	-	-	-	-	-	-

Activity coefficient (f_i^{m}) of single surfactant within the mixed micelles is related to β^m via eq. (5) and (6) [55]

$$f_1^{\mathrm{m}} = \exp[\beta^{\mathrm{m}}(1 - X_1^{\mathrm{m}})^2] \tag{5}$$

$$f_2^{\mathrm{m}} = \exp[\beta^{\mathrm{m}}(X_1^{\mathrm{m}})^2] \tag{6}$$

Since f_1^{m} and f_2^{m} are lower than the unity (Table 5), indicating the presence of mixed micelles in the solution. In most of the cases f_1^{m} has been found more than the f_2^{m} which indicates greater incorporation of AG in mixed micelle.

The excess free energy of mixing, ΔG_{ex}, can be computed from f_1^{m} and f_2^{m} using eq. (7) as

$$\Delta G_{ex} = RT[X_1^{\mathrm{m}} \ln f_1^{\mathrm{m}} + (1 - X_1^{\mathrm{m}}) \ln f_2^{\mathrm{m}}] \tag{7}$$

The higher values of $-\Delta G_{ex}$ indicate a more stable mixed micellar system. The ΔG_{ex} value was found more negative for AG + CG5 combination (Table 5) indicating higher stability of the mixed micelle than the other combination [57].

3.2.2.3. Mixed Micellization of Cationic Gemini (CG) with Anionic Bile Salt

cmc values of mixed CG + SC/SDC are also determined conductometrically (Table 6). cmc of binary mixtures decreases on mixing various CGs (with SC or SDC) indicating the formation of mixed micelles of binary mixtures (Figures 8 and 9). This may be due to the hydrophobic interactions between two individual components together with decrease in electrostatic repulsion between oppositely charged head groups (cationic quaternary amonium and anionic cholate or deoxycholate groups).

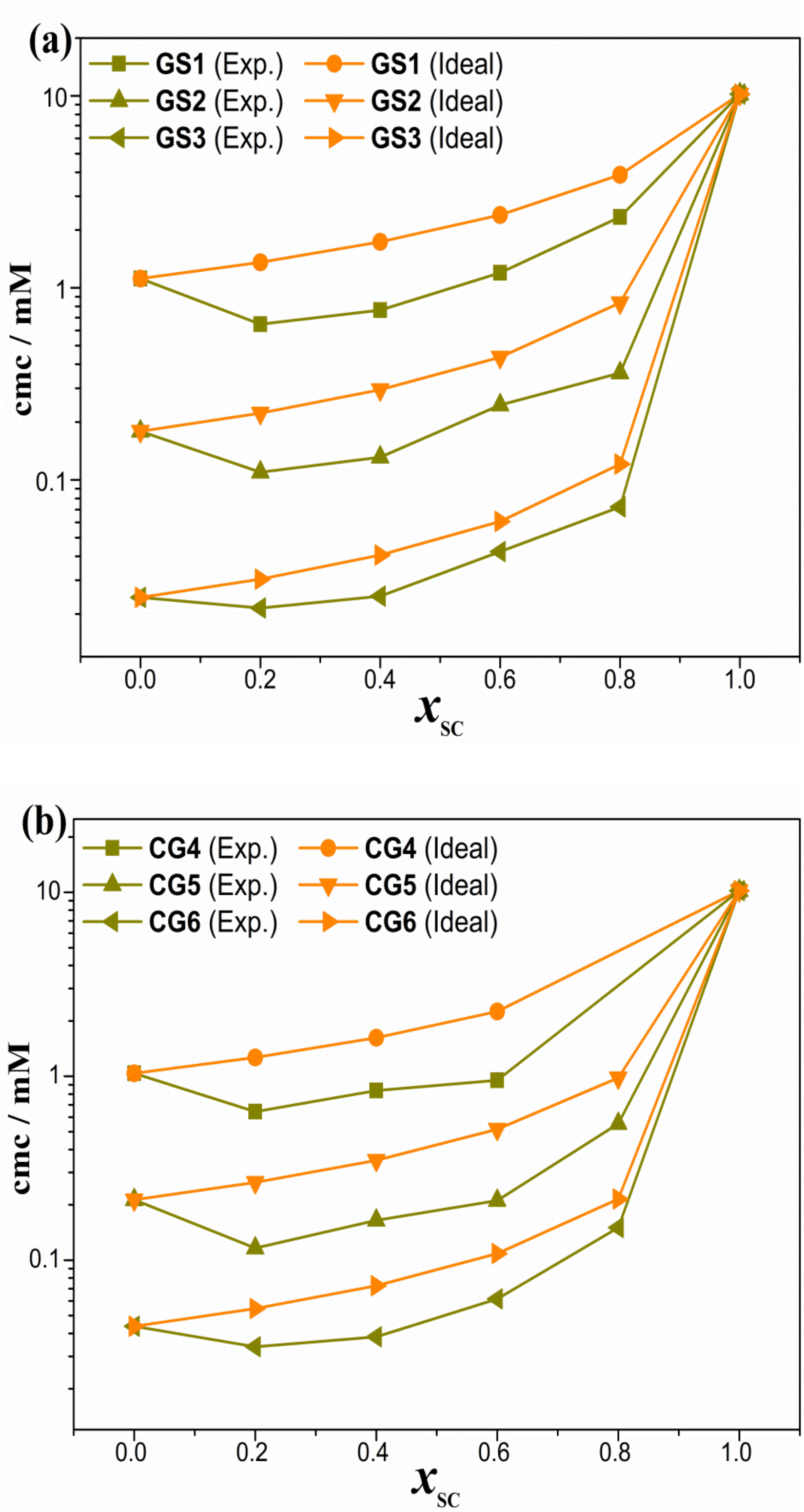

Figure 8. Variation of cmc, of mixed CG-SC system with mole fraction of SC (X_{SC}).

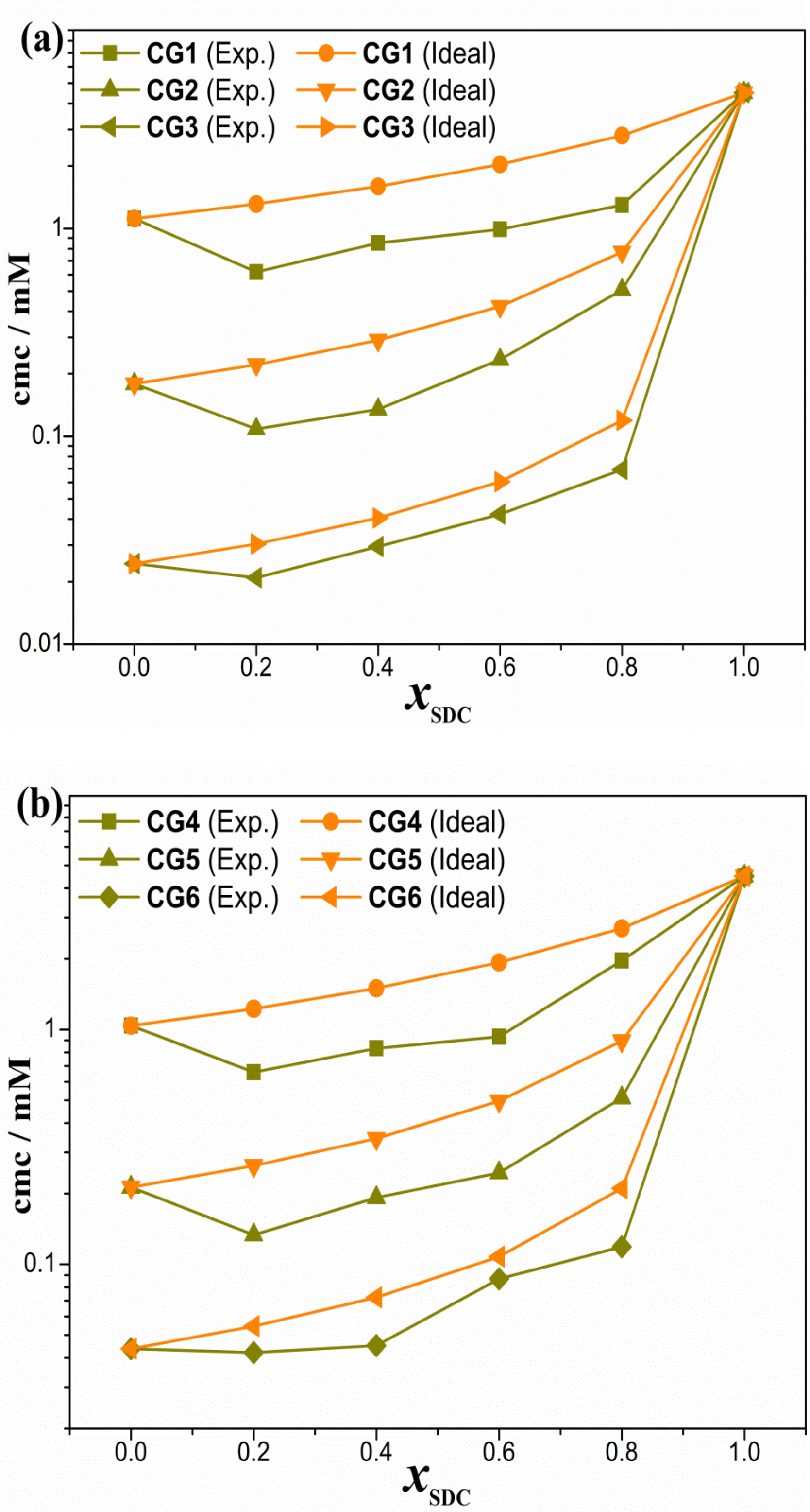

Figure 9. Variation of cmc, of mixed CG-SDC system with mole fraction of SDC (X_{SDC}).

Table 6. Micellization parameters (critical micelle concentration, **cmc**; degree of micellar ionization, α) and interaction parameters (by using Rubingh's method) of mixed gemini (mole fraction 0.6)-bile salt (mole fraction 0.4) systems in aqueous solution at 298 K.

Surfactant	System	cmc_{exp} / mM	cmc_{ideal} / mM	α	X_1^m	X_{ideal}	β^m	f_1^m	f_2^m	ΔG°_{ex} / kJ·mol^{-1}
CG1 + **SC**	Mixed	0.76	1.73	0.84	0.32	0.068	-5.06	0.095	0.60	-2.69
CG2 + **SC**	Mixed	0.13	0.29	0.95	0.27	0.011	-7.30	0.019	0.59	-3.51
CG3 + **SC**	Mixed	0.03	0.04	0.92	0.19	0.002	-8.01	0.005	0.75	-3.03
CG4 + **SC**	Mixed	0.84	1.62	0.87	0.29	0.064	-4.40	0.112	0.68	-2.24
CG5 + **SC**	Mixed	0.16	0.35	0.95	0.26	0.014	-6.79	0.025	0.63	-3.22
CG6 + **SC**	Mixed	0.04	0.07	0.89	0.22	0.003	-8.19	0.007	0.67	-3.44
CG1 + **SDC**	Mixed	0.85	1.59	0.79	0.33	0.142	-3.35	0.226	0.69	-1.84
CG2 + **SDC**	Mixed	0.13	0.29	0.83	0.28	0.026	-6.04	0.043	0.63	-2.98
CG3 + **SDC**	Mixed	0.03	0.04	0.89	0.16	0.004	-5.81	0.016	0.86	-1.93
CG4 + SDC	Mixed	0.83	1.50	0.85	0.32	0.133	-3.24	0.228	0.71	-1.75
CG5 + SDC	Mixed	0.19	0.34	0.91	0.26	0.031	-4.87	0.067	0.73	-2.28
CG6 + SDC	Mixed	0.05	0.07	0.94	0.20	0.006	-6.17	0.019	0.78	-2.47

Experimentally determined cmc data of CG-SC/SDC mixed systems (cmc_e) have been treated in similar fashion as discussed in **section 3.2.2.2.**

The negative variation from cmc_i indicates synergistic interactions in various CG-bile salt mixtures. Probably, the packing of the bile salt anion from β-side into micellar interior is responsible for the above effect. Amphiphilic molecules show surface properties controlled by the characteristics of the material adsorbed at the air-solution interface.

The negative β^m value indicates a synergistic interaction between two components of the mixed system (Table 6). Here also, a negative β^m is the result of reduction in the free energy of micellization thermodynamically more stable, which denotes synergism of the mixing (Figures 8 and 9). Data of Table 6 indicate that β^m is strongly dependent on the chain length and nature of the spacer in a particular CG as observed in previous section. Probably, packing of hydrophobic portions (into the mixed micelle) of the CG and bile salt has a role in synergism. CG3 and CG6 show more synergistic mixing with SC or SDC. The higher negative β^m value with CG6 + SC combination over CG3 + SC indicates additional interaction of amide spacer with -OH groups of the bile salt. This may be due to possible intermolecular H- bonding between above said groups and contributes toward overall interactions.

The higher values of $-\Delta G_{ex}$ indicate a more stable mixed micellar system. The ΔG_{ex} value was found more negative for CG2/CG3 + SC combination (Table 6) indicating higher stability of the mixed micelle than the other combinations [57]. Within the bile salts, SC shows better interaction with all the CGs used in the study. In earlier reports, it has been found that SC generates stronger synergism with CG due to the consequence of the hydrogen bond created by α- axial hydroxyl groups as well as packing constraints [42]. The present results confirm the role of hydroxyl groups in the interaction of SC with CG.

3.3. Conlusion

cmc measurements indicate that mixing of amphiphilic molecules (surfactant with quaternary salt or oppositely charged surfactant/bile salt) show both synergistic and antagonistic effect. Micellization has been found dependent upon alkyl chain length and nature of the quaternary salt. Mixing of oppositely charged surfactants has been described using theoretical models of Clint, Rubingh and Motomura. The study reveals that cmc decreases with the increase in CG fraction in a typical binary mixture. A synergistic interaction has been observed between CG and a bile salt in forming mixed micelles in the solutions. Interaction parameter (βm) decreases (more negative) with increase in CG content, which indicates synergistic interactions between two components of the mixture [58].

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