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Mixed Micelles in the Presence of Macrocyclic Additives: A Host–Guest Conductometric Study

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Abstract. The conductances of sodium dodecylsulphate (SDS) + sodium decylsulfate (SDeS) and decyltrimethylammonium bromide (DeTAB) + tetradecyltrimethylammonium bromide (TTAB) over the entire mole fraction range of SDS (α_{SDS}) or DeTAB (α_{DeTAB}) were measured in water, 18-crown-6 ether + water (CR + W) and β-cyclodextrin + water (CYC + W) mixtures at fixed 4 mM and 8 mM of CR or CYC in their respective binary mixtures at 30 °C. The conductivity plots for SDS + SDeS mixtures show a single break whereas two breaks are observed at most of the α_{DeTAB} for DeTAB + TTAB mixtures. From the break in the conductivity data, the mixed critical micellar concentration (cmc) and degree of counter-ion association (χ) were computed. The first break corresponds to the classical cmc of TTAB is termed as the first cmc (C_1) and the second break which is observed at concentrations about 4 times the first one, corresponding to the classical cmc of DeTAB and is considered to be the second cmc (C_2). The non-ideality in SDS + SDeS mixtures has been evaluated by using the regular solution theory and it has been observed that the mixture is close to ideal in the absence and presence of additives. The variation in C_1, C_2 and χ_1, χ_2 for DeTAB + TTAB has been discussed in terms of the mixed micelle formation which are predominantly rich in the TTAB and DeTAB monomers respectively.

Key words: Ionic surfactants, mixed micelle, macrocyclic compounds, host-guest interactions, conductivity.

1. Introduction

18-Crown-6 ether (CR) [1, 2] and β-cyclodextrin (CYC) [3–5] belong to two different categories of macrocyclic compounds which undergo predominantly hydrophilic and hydrophobic interactions, respectively. CR is a cyclic polyether which interacts mainly with a wide variety of cations [1, 2], whereas CYC is an oligosaccharide which consists of 7 glucose units [6]. The most significant property of CR and CYC is to form inclusion complexes with different kinds of guest molecules ranging from ionic and neutral to organic or inorganic chemical species [1–5]. Therefore, these additives are considered to impart significant influence on the micellar properties of ionic surfactants.

In spite of the numerous studies on cyclodextrin-surfactant and crown ether-surfactant complexation, to the best of our knowledge, there is no report on how the micellar properties of binary surfactant mixtures in the presence of such additives are influenced. The mixed micelle formation between two unlike ionic surfactants

in the presence of such additives is also considered to be interesting in view of their more favourable properties than individual surfactants in various commercial products. Mixtures of ionic-nonionic and anionic-cationic surfactants show significant non-ideal behaviour whereas mixtures of unlike surfactant monomers with identical polar head groups and different alkyl chains generally exhibit ideal mixing [7].

It has also been observed [8] that many cationic-cationic mixtures such as tetradecyltrimethylammonium chloride ($C_{14}Cl$) + benzyldimethyltetradecyl-trimethylammonium chloride, $C_{14}Cl$ + didodecyldimethylammonium bromide and hexadecylpyridinium chloride+ benzyldimethylhexadecylammonium chloride show two breaks in the conductivity versus total concentration plots which corresponds to the two critical micellar concentrations of the mixtures. Other studies like viscosity [9], NMR [10], heat capacity [11], ultrasonic velocity [12] and small angle x-ray scattering [13] are not sufficiently sensitive to detect the second break in the low concentration range; for example, in the case of hexadecyltrimethylammonium bromide, different values for the second break are reported by the above mentioned techniques.

These results have been explained [8] on the basis of structural micellar changes corresponding to the second break. Such changes may be due to the sphere to rod transitions which could be accompanied by a change in the degree of counter ion binding. This can be achieved by adding an additive which at higher surfactant concentration could lead to the change in the geometry of the micelle. Thus keeping in consideration all the above facts, the additive effect of strongly hydrophilic [1, 2] and hydrophobic [3–5] additives like CR and CYC was investigated on the mixed micelle formation by the anionic-anionic (SDS + SDeS) and cationic-cationic (DeTAB + TTAB) surfactant mixtures, respectively. Both binary mixtures are structurally similar and are expected to behave ideally in the mixed state. Therefore, it is expected that the presence of CR or CYC may also influence the proposed ideal mixing behaviour of these mixtures which can easily be noticed by comparing the mixed micelle formation in pure water. Due to this reason, the measurements have been restricted to the mixed critical micellar concentration range of both the mixtures. The measurements have been performed by the conductivity technique which seemed to be the most useful tool in order to detect the micellar transitions accurately due to its high sensitivity and reproducibility.

2. Experimental

β-Cyclodextrin (CYC) was the same product as used earlier [14]. 18-Crown-6 ether (CR), from Sigma, was dried in vacuo at 35 °C for at least 4 days before use.

Sodium dodecylsulphate (SDS) and sodium decylsulphate (SDeS), from Flüka were crystallized from ethanol. Decyltrimethylammonium bromide (DeTAB), and tetradecyltrimethylammonium bromide (TTAB), from Sigma, were crystallized

from ethanol+ethyl acetate mixture. All surfactants were dried in vacuo at 60 °C for two days.

Conductivity water having a specific conductance of 4–8 × 10^{-7} S cm^{-1} was used in the preparation of all solutions.

The precise conductances of SDeS + SDS and DeTAB + TTAB mixtures over the entire mole fraction range in W, CR + W and CYC + W containing 4 and 8 millimoles (mM) of each additive were measured at 30 ± 0.01 °C as explained earlier [15]. The error in the conductance measurements is ±0.5%.

3. Results and Discussion

In the mixed state, the conductivity (κ) plots for SDS + SDeS show only a single break (Figure 1) which represents mixed micelle formation by the unlike monomers. However, two breaks are observed in most of the DeTAB + TTAB mixtures (Figures 2 and 3) which have been assigned to the first (C$_1$) and the second critical micellar concentration (C$_2$). Garcia-Mateos et al. [16] have observed only one break in DeTAB + TTAB mixtures most likely they may have not extended their conductivity measurements upto a higher concentration range. The mixed critical micellar concentration (cmc) and the degree of counter ion association (χ), for the present surfactant mixtures were calculated from the break in the κ plots as explained elsewhere [15, 17, 18]. Obviously, for DeTAB + TTAB mixtures with two cmc values, two χ values i.e. χ_1 and χ_2 corresponding to C$_1$ and C$_2$ were computed from the three slopes (Figure 3). The computed values of cmc and χ for SDS + SDeS and DeTAB + TTAB mixtures in pure water are listed in Tables I and II respectively.

3.1. CRITICAL MICELLAR CONCENTRATION IN WATER AND WATER + ADDITIVE SYSTEMS

The mixed cmc values for SDS + SDeS and DeTAB + TTAB mixtures in pure water are plotted in Figure 4. It is to be noted that the C$_1$ values of DeTAB + TTAB mixtures could be computed upto $\alpha_{DeTAB} \approx 0.9$ whereas C$_2$ values were mainly possible in the DeTAB rich-region of the mixtures. For comparison, such values for the same binary mixtures already reported in the literature [16, 19, 20] have also been plotted in Figure 4. A good agreement can be observed between the present and the literature values. Figures 5 and 6 show the variation in the mixed cmc in the presence of additives. For DeTAB + TTAB, the curve in pure water as well as in CR + W are lying quite close to each other whereas they are significantly shifted towards the higher values in the presence of CYC. The situation is also similar in SDS + SDeS except the cmc curves in CR + W are lying lower to that in pure water. Similar behaviour [21–26] of anionic and cationic surfactants in the presence of macrocyclic compounds like CR and CYC has been observed earlier and discussed in much detail. Therefore, it can be said that this general behaviour

Table I. Values of cmc/mmol dm^{-3}, β, and χ of SDS + SDeS in pure water at 30 °C

α_{SDS}	cmc	β	χ
0.0000	33.0		0.54
			(0.52)*
0.1000	24.4	−0.23	0.55
0.2000	20.1	−0.16	0.56
0.4000	14.0	−0.46	0.58
0.6000	10.5	−1.01	0.59
0.8000	9.50	−0.70	0.61
0.9000	8.40	−1.8	0.62
1.0000	8.20		0.63
			(0.62)**
			(0.65)***

*Ref. 33.
**Ref. 34.
***Ref. 35.

Table II. Values of C$_1$/mmol dm^{-3}, C$_2$/mmol dm^{-3}, β, χ_1, and χ_2 of DeTAB + TTAB in pure water at 30 °C

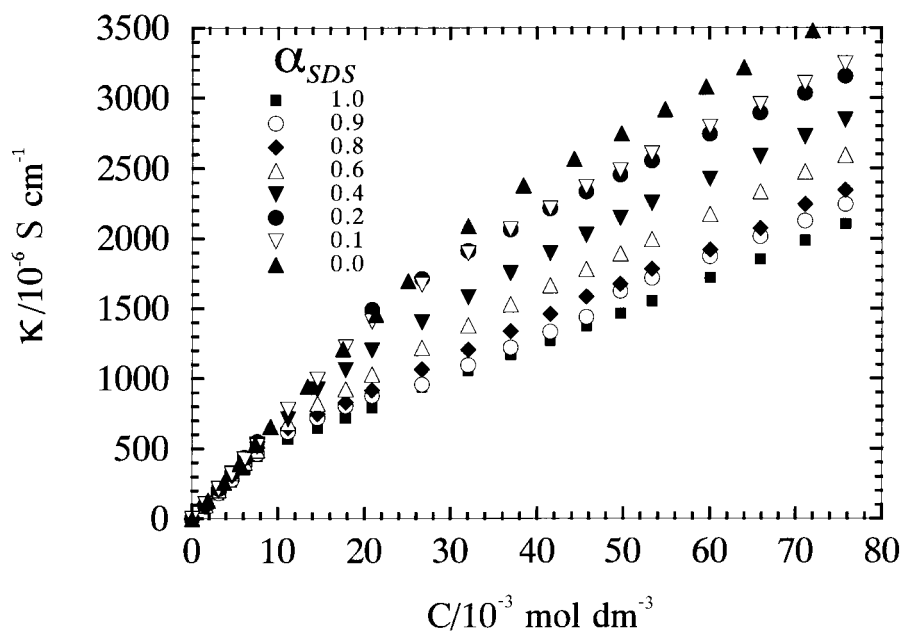| α_{DeTAB}	C_1	C_2	β	χ_1	χ_2
0.0000	3.70			0.73	
	(3.8)*				
	(3.5)**			(0.73)**	
0.1250	4.10		−1.5	0.74	
0.3120	4.45		−2.6	0.59	
0.4679	5.70		−1.9	0.54	
0.5000	6.20	40.7	−1.6	0.52	0.34
0.6454	6.70		−2.5	0.41	
0.6875	8.30	43.0	−1.9	0.44	0.29
0.7547	8.50		−2.4	0.33	
0.8602	11.3		−2.6	0.29	
0.8750	13.2	52.3	−2.3	0.32	0.30
0.9249	24.3		−0.91	0.23	
0.9610		58.6			0.36
0.9840		68.0			0.59
1.0000		70.3			0.70

*Ref. 16.
**Ref. 36.

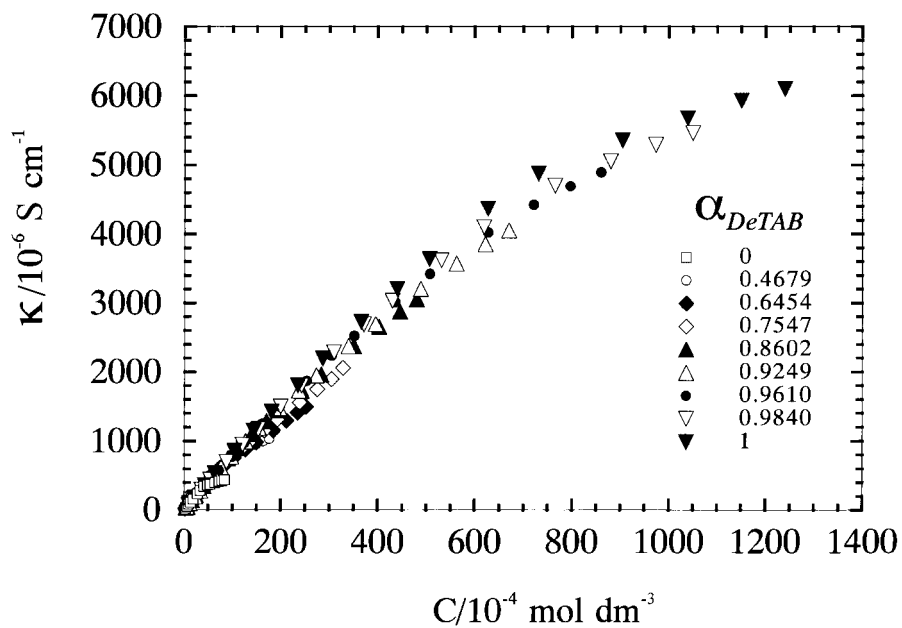*Figure 1.* Plot of κ versus C for SDS + SDeS in pure water.

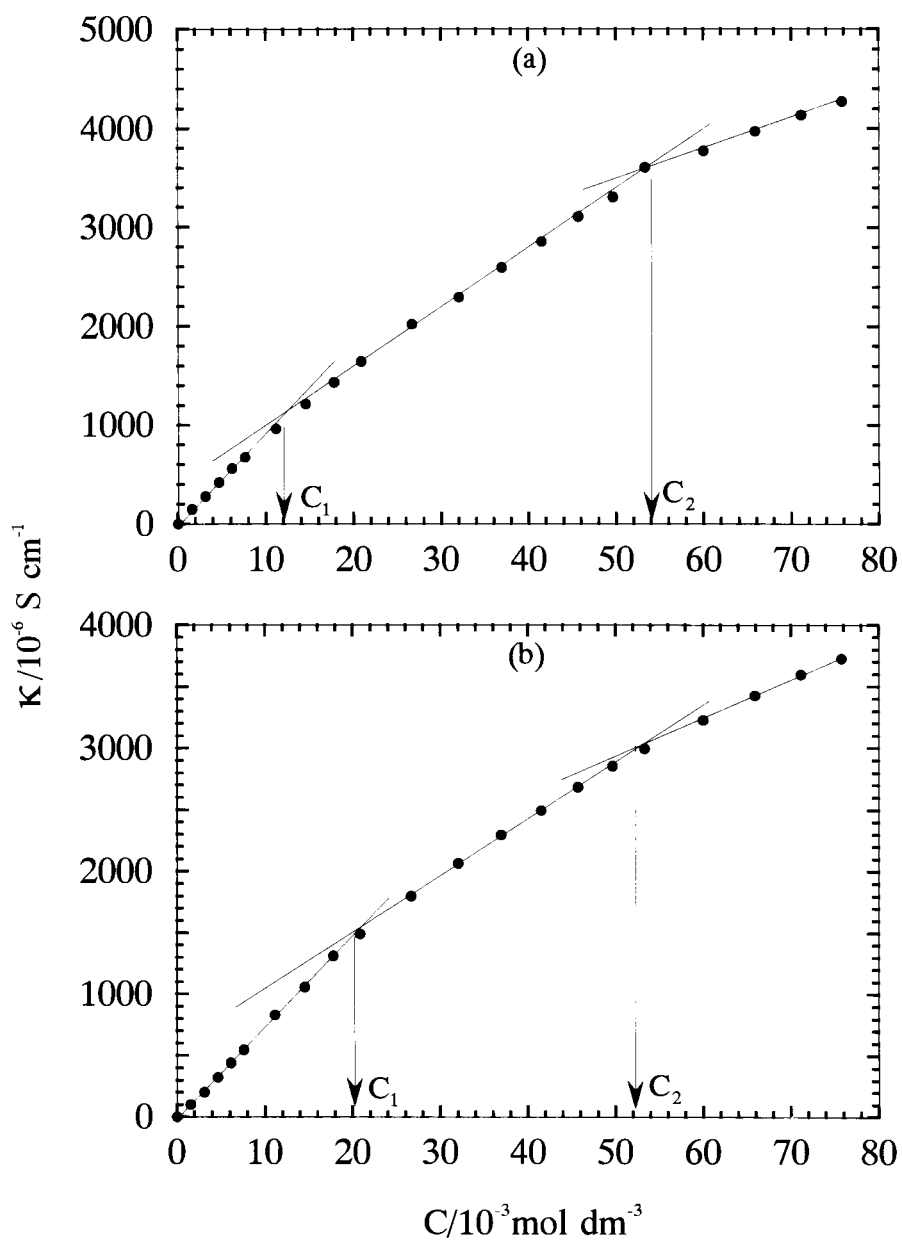*Figure 2.* Plot of κ versus C for DeTAB + TTAB in pure water.

Figure 3. Plot of κ versus C for DTAB + TTAB in (a) CR + W ([CR] = 4 mM) (α_{DeTAB} = 0.9) and in (b) CYC + W ([CYC] = 4 mM) (α_{DeTAB} = 0.8).
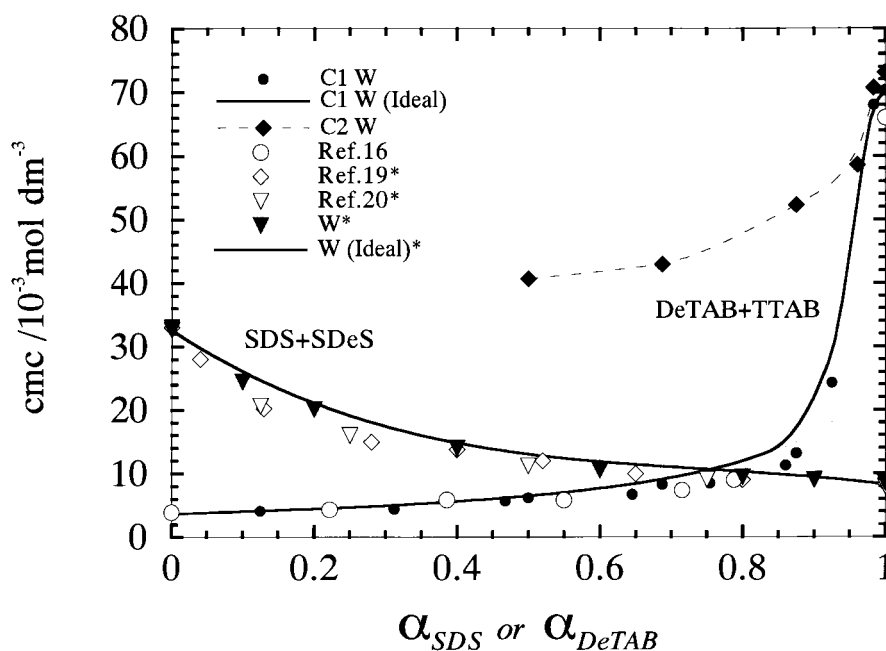
Figure 4. Plot of cmc versus α_{SDS} or α_{DeTAB} for SDS + SDeS and DeTAB + TTAB in pure water (W). Captions marked with '*' belong to SDS + SDeS mixtures.

for the single ionic surfactants in CR and CYC can also be extended to the binary ionic mixed surfactants.

From the mixed cmc values it is possible to obtain quantitative information of the micelle aggregates formed by using the pseudophase thermodynamic model [27, 28]. The model relates the mixed cmc with the cmc of the pure components by the following equation,

$$\frac{1}{\text{cmc}^*} = \frac{\alpha_1}{\text{cmc}_1} + \frac{(1-\alpha_1)}{\text{cmc}_2} \tag{1}$$

where α_1 is the mole fraction of surfactant 1 in the total mixed solute, and cmc_1 and cmc_2 are the critical micellar concentrations of component 1 and 2, respectively. For the present structurally similar binary mixtures, ideal behaviour is expected since the interactions between the monomers in the mixed micelles are considered to be similar to those in the case of homomicelles [27] and hence the activity coefficients should be taken as unity. The cmc* values thus calculated using Equation (1) have also been plotted in Figures 4–6. The variation in these values does not predict the ideal behaviour in most of the cases, probably because it does not account for the variation in the solution ionic strength with changing composition. The values of cmc_1 and cmc_2 are independent of the composition only if the ionic strength is constant. Hence, any change in the ionic strength of the mixture with the change in the composition will influence the ideality of the mixture since cmc* does not
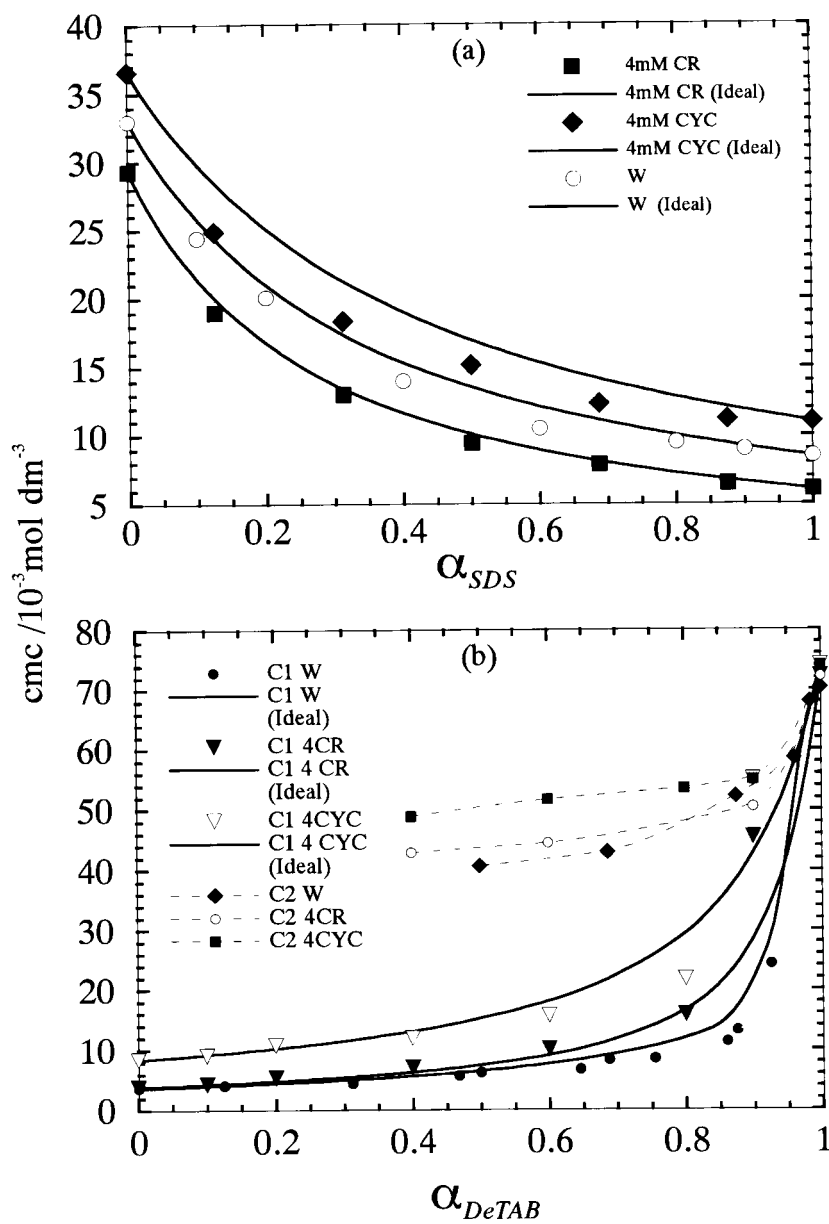
Figure 5. Plot of cmc versus α_{SDS} or α_{DeTAB} for SDS + SDeS (a) and DeTAB + TTAB (b) in CR + W and CYC + W of 4 mM CR or CYC.
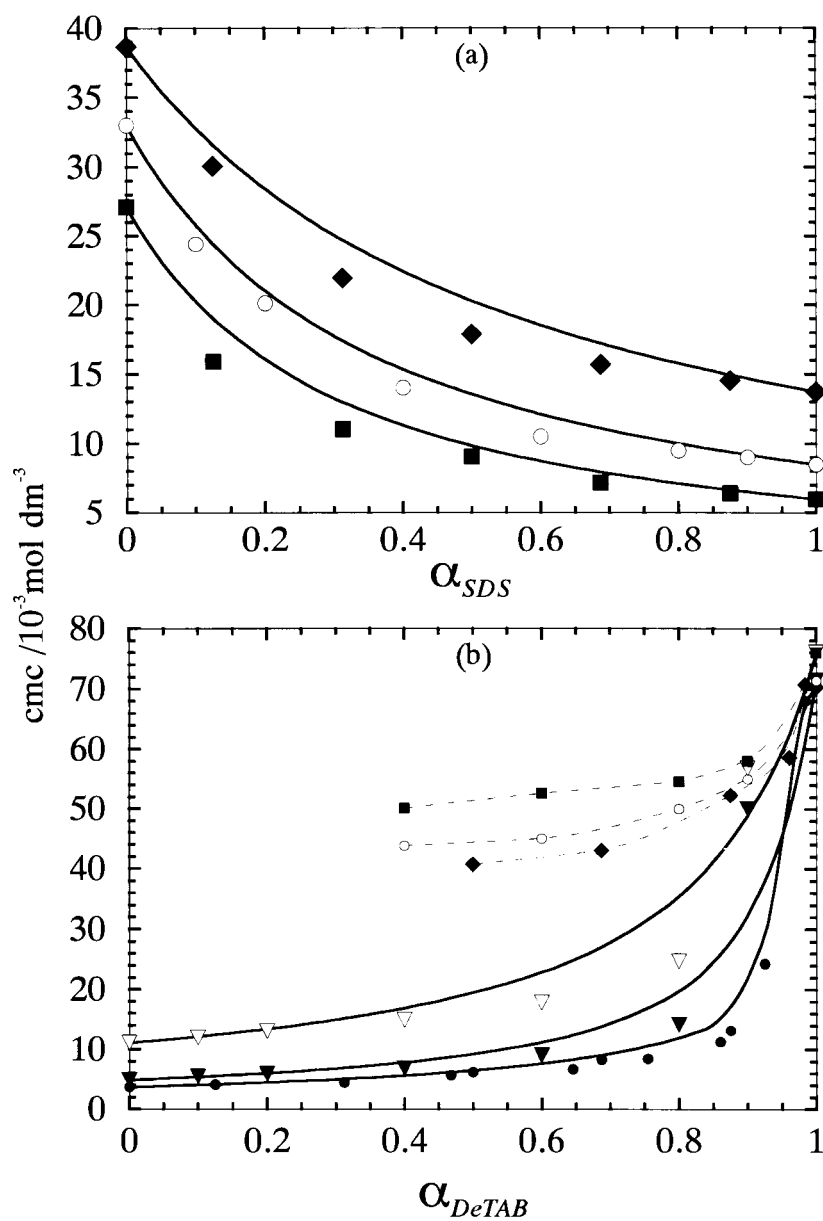
Figure 6. Plot of cmc versus α_{SDS} or α_{DeTAB} for SDS + SDeS (a) and DeTAB + TTAB (b) in CR + W and CYC + W of 8 mM CR or CYC. Symbols as for Figure 5.

account for the variation in the ionic strength. These results can be further evaluated by taking in consideration the regular solution formulation [28] based on the phase separation model of micellization with

$$\frac{x_1^2 \ln(cmc\alpha_1/cmc_1 x_1)}{(1 - x_1)^2 \ln(cmc(1 - \alpha_1)/cmc_2(1 - x_1))} = 1 \qquad (2)$$

where x_1 is the mole fraction of surfactant 1 in the mixed micelle. Equation (2) can be solved iteratively to obtain the value of x_1, from which the interaction parameter, β, can be computed using the following Equation (3)

$$\beta = \frac{\ln\left(\frac{cmc\alpha_1}{cmc_1 x_1}\right)}{(1 - x_1)^2} \qquad (3)$$

The β value demonstrates the extent of interactions between the two surfactants which lead to the deviations from the ideal behaviour and it should be constant with respect to the change in composition for a given binary surfactant mixture.

The average β-values computed for SDS + SDeS mixtures in pure water and in the presence of 8 mM of CR and CYC are -0.73 ± 0.61, -1.0 ± 0.54 and -0.86 ± 0.38 respectively. They are negative and are somewhat close to each other within the experimental uncertainties suggesting that the micelle formation takes place due to the synergistic interactions and is quite identical in the absence and presence of additives. These values are also not so significant and may be attributed to the slight deviations from the ideal behaviour. Such deviations have been explained on the basis of the interfacial interactions of micelle-solution interface [29]. The interactions are arising from the two competing contributions i.e the Gibbs energy of the formation of the micelle-solution interface and due to the steric and electrostatic interactions among the head groups at the micelle-solution interface. The dependence of the interfacial interactions on the composition of the mixed micelles governs the ideality of the mixture [30]. However, the present results show a more or less similar magnitude of β values as well as an insignificant difference between the micellar mole fraction of SDS (x_{SDS}, not shown) in the absence as well as in the pesence of additives which demonstrates that the interfacial interactions remain almost the same even in the presence of additives. In fact, the lowering in the cmc of SDS and SDeS in the presence of CR has been explained on the basis of two reasons; (i) the induction of the Na^+–CR complex into the palisade layer of the micelle [30], and (ii) the adsorption of the free Na^+ counterions on the surface of the micelles [30]. Both the factors will result in the reduction in polar head group repulsions [23, 24, 26, 30] and hence reduce the cmc. The presence of the Na^+–CR complex in the palisade layer, of course helps in the stabilization of the micelles but the overall micelle-solution interfacial interactions remains almost the same due to the similar nature of the micelle-solution interface in the absence and presence of CR. The similar behaviour of the micelles of SDS and SDeS is also

possible in the presence of CYC. Since CYC encapsulates the hydrophobic tail, therefore, it directly affects the concentration at which the micelles were to form in the absence of CYC [21, 22, 31]. However, the surfactant-CYC complex is not considered to take part in the micelle formation since the respective hydrophibicity is being neutralized due to the complex formation. Hence, unless all of the CYC is complexed, the micelle formation may not start. Therefore, in the presence of CYC, the nature of the micelle-solution interface is almost the same as in the absence of CYC. Similar arguments can also be applicable to the mixed micelle-solution interface of SDS + SDeS mixtures in the present study in view of their similar behaviour to that of SDS and SDeS which may lead to approximately the same β values in the absence as well as in the presence of CR and CYC.

On the other hand, the average β value for DeTAB + TTAB mixtures in pure water is -2.0 which is in agreement with that calculated from the data of reference 16 ($\beta = -2.6$). Such a large negative value for this mixture is quite surprising in view of their structurally similar nature and thus can be attributed to the fact that the regular solution theory is not fully applicable to this mixture. Apart from this, in the presence of additives, β values for most of the α_{DeTAB} range could not be calculated. This can be attributed to the higher experimental cmcs than those predicted by the ideal law. This may also be responsible for the non-convergence of Equation (2) which suggests that within the framework of regular solution theory, the conditions of this theory are not met by these systems. This is obvious from the complex nature of this system which may complicate the simplified analysis of this formulation based on Equations (2) and (3). This problem has already been discussed by some authors in the case of some binary ionic combinations [8, 32].

3.2. DEGREE OF COUNTER ION BINDING

In the present work, the choice of SDS + SDeS and DeTAB + TTAB mixtures was due to their respective common counter ion in the mixed state and hence the mixture can be treated as a single surfactant solution. In SDS + SDeS, only one value of χ was obtained whereas in DeTAB + TTAB mixtures, χ_1 and χ_2 corresponding to C_1 and C_2 were computed (Tables I and II). It is to be mentioned here that although χ values have been calculated in the present study by a simplified method of taking the ratios between the slopes of the linear portions above and below the break point in the conductivity curve, χ values thus obtained are in good agreement with those reported in the literature for single surfactants computed by the same and other methods (Tables I and II). The χ values of SDS + SDeS have been compared with those of DeTAB + TTAB in different media in Figure 7. It is interesting to observe that the χ values for SDS + SDeS are increasing whereas the χ_1 and χ_2 values for DeTAB + TTAB are showing an opposite variation with the increase in α_{SDS} or α_{DeTAB}. The opposite variation in χ_1 and χ_2 is quite surprising and can be discussed on the basis of the stability of the mixed micelle formation.

The stability of the micelles can be better expressed by computing the standard Gibbs energy of mixed micelle formation by using the following equation

$$\Delta G_M^0 = (1 + \chi) RT \ln \text{cmc} \tag{4}$$

This equation has been frequently used for the single as well as for the mixed surfactants [32]. The variation in the ΔG_M^0 values (Figure 8) essentially demonstrates the χ behaviour (Figure 7) which is quite significant corresponding to χ_1 rather than χ_2. This may indicate that the micelles corresponding to C_1 become less stable with an increase in α_{DeTAB} whereas the reverse is observed for C_2. Unfortunately no quantitative analysis (such as regular solution theory) could be performed in this case in order to compute the micellar mole fractions. However, we envisage that considering the stronger hydrophobicity of TTAB, the mixed micelle formed at C_1 are predominantly made up of TTAB monomers, whose stability decreases with the increase in α_{DeTAB} since the ΔG_M^0 value becomes less negative (Figure 8). On the other hand, simultaneously at higher α_{DeTAB}, another kind of micelle corresponding to C_2, starts appearing and may be predominantly made up of DeTAB whose stability increases with the increase in α_{DeTAB} which leads to more negative ΔG_M^0 values (Figure 8).

3.3. COMPARATIVE ADDITIVE EFFECT OF CR AND CYC

If the comparative additive effect of CR and CYC is considered on the mixed micelle formation of SDS + SDeS mixtures, the variation in ΔG_M^0 values (Figure 8) essentially represents the mixed cmc behaviour (Figures 5 and 6) and can be attributed to the same reasons as discussed in the previous sections. However, it is interesting to observe the comparative addtive effect on the variation of C_1 and C_2 in DeTAB + TTAB mixtures by plotting a quantity $[(C_2 - C_1)/C_2]$ verus α_{DeTAB} (Figure 9). This quantity represents the micellar changes between C_1 and C_2 in a surfactant mixture. It can be seen that the curves in pure water as well as in CR + W are lying quite close to each other whereas they are lying significantly lower in CYC + W suggesting that particularly in water and CR + W, DeTAB + TTAB undergoes similar kinds of micellar changes [8] whereas these changes may be different and less significant in CYC + W. This can be due to the fact that CYC undergoes strong hydrophobic interactions with the unlike monomers and thus reduces their chances to form the mixed micelle which subsequently leads to the weak micellar transitions. On the contrary, such kinds of interactions with CR may not be so prominent and hence, a practically insignificant additive effect of CR is observed.

4. Conclusion

It has been concluded that the mixed micelle formation process by the respective anionic and cationic surfactant binary mixtures in the presence of macrocyclic
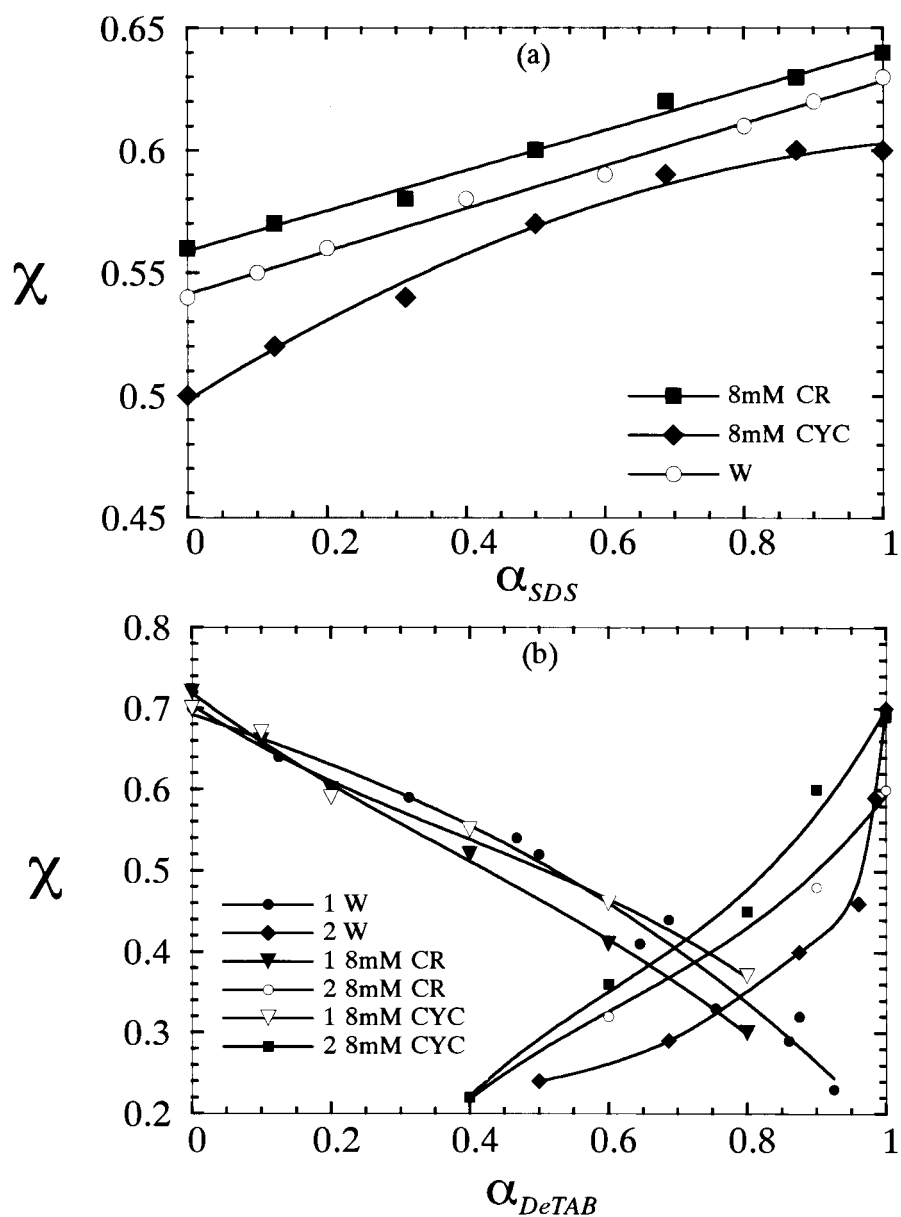
Figure 7. Plot of χ versus α_{SDS} or α_{DeTAB} for SDS + SDeS (a) and DeTAB + TTAB (b) in CR + W and CYC + W of 8 mM CR or CYC. Digits 1 and 2 in the caption of Figure (b) represent, χ_1 and χ_2 respectively.
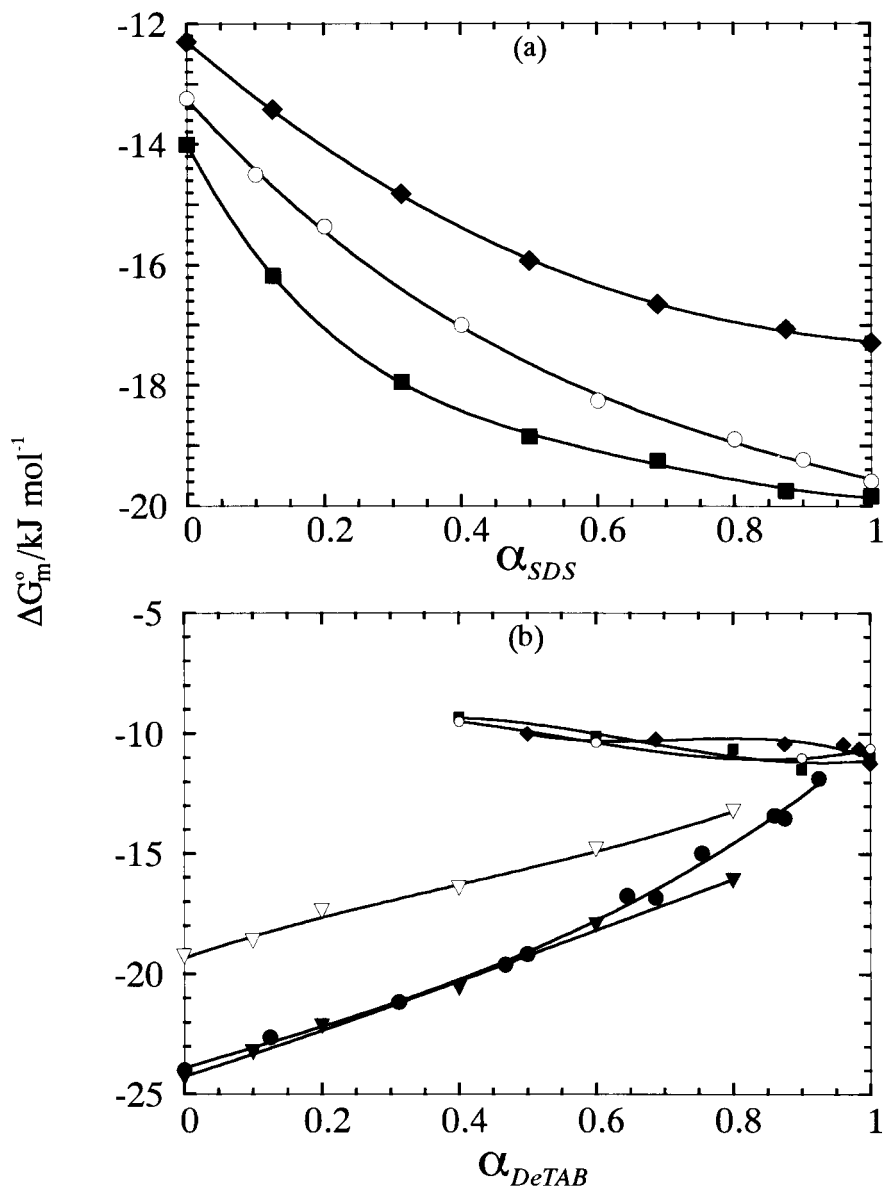
Figure 8. Plot of ΔG_M^0 versus α_{SDS} or α_{DeTAB} for SDS + SDeS (a) and DeTAB + TTAB (b) in CR + W and CYC + W of 8 mM CR or CYC. Symbols as for Figure 7.
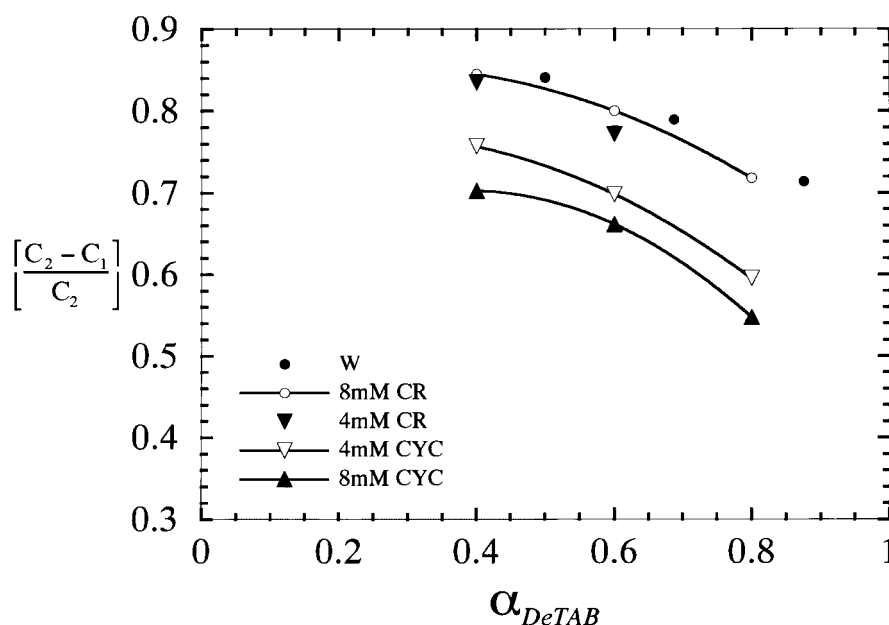
Figure 9. Plot of $[(C_2 - C_1)/C_2]$ versus α_{DeTAB} for DeTAB + TTAB in different media.

compounds like CR and CYC is quite similar to that of single surfactants of the same nature. The non-ideality evaluated from the regular solution theory for SDS + SDeS mixtures, in the absence and presence of CR and CYC, demonstrates that the nature of mixed micelles is the same in either case. The two cmc's i.e. C_1 and C_2, observed in the case of DeTAB + TTAB mixtures, have been attributed to mixed micelle formation between the unlike monomers which are predominantly consisting of TTAB and DeTAB monomers respectively. The overall variation in the micellar properties corresponding to C_1 and C_2 is almost the same in the absence and presence of additives.

Acknowledgment

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