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Micelle Formation by Anionic and Cationic Surfactants in 18-Crown-6 Ether+β-Cyclodextrin+Water Systems

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The conductances of sodium decyl sulfate (SDeS), sodium dodecyl sulfate (SDS), dodecyltrimethylammonium bromide (DTAB), and trimethyltetradecylammonium bromide (TTAB) have been determined in 18-crown-6 ether + water (CR + W), β-cyclodextrin + W (CYC + W), and in CR + CYC + W mixtures with fixed 0.0151 mol dm^{-3} of CR and varying the amount of CYC with the overall change in the mole–fraction range of CYC from 0.0 to 0.5 in a CR + CYC + W mixture at 30 °C. From the conductivity data, the critical micellar concentration (cmc), degree of counter ion dissociation (β), free energy of transfer of the surfactant hydrocarbon chain from medium to the micelle ($\Delta G^{\circ}_{\mathrm{HP}}$), and free energy of transfer of surface contributions ($\Delta G^{\circ}_{\mathrm{s}}$) of SDS, SDeS, DTAB, and TTAB have been computed. It has been found that the micelles of anionic surfactants are stabilized in a CR + W mixture in comparison to that in pure water, whereas micelles of cationic surfactants remain more or less unaffected. Micelles of all of the above surfactants are denatured as the amount of CYC is increased in the CR + CYC + W mixture. The effect of denaturisation is stronger on the micelles of SDS and TTAB in comparison to that of SDeS and DTAB, respectively.

18-Crown-6 ether[1—3] (CR) and β-cyclodextrin[4—6] (CYC) 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—3] whereas CYC is an oligosaccharide consisting of 7 glucose units.[4] They have a unique configuration which makes the outer surface hydrophilic and the inner cavity hydrophobic in nature.[7] 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—4] The factors, like the geometric capability and the polarity of the guest molecule and the medium, greatly influence the stability of the inclusion complex formation.[8—11] These macrocyclic compounds have also been found[8,9,11] to interact with amphiphilic molecules, like ionic surfactants. This is due to the fact that the micelle formation by ionic surfactants involves contributions from both repulsive and attractive interactions. The repulsive forces originate primarily from electrostatic repulsions between the polar head groups,[12,13] whereas attractive interactions have generally been attributed to hydrophobic interactions[13] between the nonpolar tails of the surfactant monomers. Considerable emphasis has also been placed on the London-dispersion interactions.[14,15]

It has been also observed that the micellar properties are significantly affected by the addition of small amounts of various additives, such as electrolytes[16,17] and nonpolar[18] and polar organic liquids.[8,19,20] The encapsulation of small cations[21—23] as well as long hydrophobic chains[24—28] by CR and CYC cavities alters many physical properties of aqueous amphiphilic molecules (i.e. solubility, transport properties etc.). Ionic surfactants consisting of anionic surfactants viz. sodium dedecyl sulfate (SDS) and sodium decyl sulfate (SDeS) as well as cationic surfactants viz. dodecyltrimethylammonium bromide (DTAB) and trimethyltetradecylammonium bromide (TTAB) are of particular interest because they can interact with CR and the CYC cavity simultaneously in a medium containing both CR and CYC molecules. Hence, keeping in view such dual interactions of ionic surfactants, the micellar properties have been evaluated for the abovementioned surfactants in CR + CYC + W mixtures in order to discriminate the additive effect of CR and CYC simultaneously on the micellisation properties of these surfactants.

Experimental

β-Cyclodextrin (CYC), Sigma, was the same product as that used before.[10] 18-Crown-6 ether (CR), Sigma, was dried in a vacuum at 35 °C for at least 4 d before use.

Sodium decyl sulfate (SDeS) and sodium dodecyl sulfate (SDS) from Flüka were recrystallized from ethanol. Dodecyltrimethylammonium bromide (DTAB) and trimethyltetradecylammonium bromide (TTAB) from Sigma were recrystallized from an ethanol + ethyl acetate mixture. All of the surfactants were dried in a vacuum 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, DTAB, and TTAB in CR + W and CYC + W containing 0.0151 mol dm^{-3} of each additive and in CR + CYC + W ternary mixtures consisting of fixed (CYC : CR) 0.00356 : 0.0151, 0.00712 : 0.0151, 0.0107 : 0.0151, and 0.0151 : 0.0151 mole ratios between the concentration range of (1—70) × 10^{-3} mol dm^{-3} were measured at 30 °C with an overall temperature variation of ±0.01°C by using a digital conductivity meter (model NDC-732) manufactured by Naina electronics Chandigarh (India) at a fixed frequency of 1000 Hz. A dip-type conductivity cell with a cell constant of 1.12 cm^{-1} was used in all of the measurements. The error in conductance measurements was ±0.5%.

Results

The critical micellar concentration (cmc) and the degree of counter ion dissociation (β) of each surfactant were calculated from the break in the conductivity ($\varkappa$) vesus the concentration plot, as explained earlier.[20] Figure 1 shows such a variation of the $\varkappa$ of SDS graphically in CR+W and CYC+W binary mixtures consisting of 0.0151 mol dm^{-3} of each additive. In order to avoid overcrowding of the plots, the $\varkappa$ values in CR+CYC+W ternary mixtures are not shown in Fig. 1.

The total Gibb's energy per surfactant molecule ($\Delta G^{\circ}_{M}=RT \ln X_{cmc}$) associated with forming micelles can be calculated from the hydrophobic contributions of the free energy of transfer of the surfactant hydrocarbon chain from the medium to the micelle (ΔG°_{HP}) and the energy associated with the surface contributions due to electrostatic interactions between the head groups and counter ions and all other contributions due to specific interactions (ΔG°_{s}) as described elsewhere.[20]

The cmc, β, ΔG°_{HP}, and ΔG°_{s} values for SDeS, SDS, DTAB, and TTAB are reported in Table 1.

Table 1. Critical Micellar Concentration (cmc), Degree of Counter ion Dissociation (β), Free Energy Change for Hydrophobic Contributions (ΔG°_{HP}) and Free Energy Change for Surface Contributions (ΔG°_{s}) for Various Surfactants in CR+CYC+W Mixtures at Corresponding Mole Fraction of CYC (x_{CYC})

x_{CYC}	cmc mol dm^{-3}	β	ΔG°_{HP} kJ mol^{-1}	ΔG°_{s} kJ mol^{-1}
		SDeS		
0.0000	0.0111	0.60	−27.6	8.59
0.1905	0.0250	0.59	−27.4	7.96
0.3200	0.0285	0.57	−27.3	8.21
0.4138	0.0320	0.57	−26.9	8.08
0.5000	0.0382	0.56	−26.4	8.07
1.0000	0.0491	0.54	−25.9	8.15
		SDS		
0.0000	0.0047	0.55	−34.3	10.6
0.1905	0.0101	0.50	−32.5	10.8
0.3200	0.0121	0.47	−32.5	11.3
0.4138	0.0139	0.46	−32.2	11.3
0.5000	0.0180	0.45	−31.4	11.1
1.0000	0.0231	0.44	−30.6	11.0
		DTAB		
0.0000	0.0160	0.28	−35.3	14.8
0.1905	0.0180	0.29	−34.6	14.4
0.3200	0.0210	0.30	−33.8	13.9
0.4138	0.0230	0.31	−33.2	13.5
0.5000	0.0250	0.31	−32.7	13.3
1.0000	0.0310	0.33	−31.5	12.6
		TTAB		
0.0000	0.0027	0.22	−44.5	19.5
0.1905	0.0073	0.24	−39.6	17.1
0.3200	0.0084	0.25	−38.9	16.6
0.4138	0.0110	0.26	−37.4	15.9
0.5000	0.0151	0.26	−35.9	15.2
1.0000	0.0203	0.29	−34.1	14.2

According to Junquera et al.,[24] the critical micellar concentration in the presence of additives, like CYC, is termed as the apparent critical micellar concentration. This concentration is the sum of the free monomeric concentration at which the micellization process occurs (essentially critical micellar concentration in water, cmc°) and the concentration of the surfactant associated with the CYC. This is given by the following equation:

$$\mathrm{cmc} = \mathrm{cmc}^{\circ} + C_{CYC}/R. \tag{1}$$

In the present study the cmc and cmc° values for SDeS, SDS, DTAB, and TTAB in 0.0151 mol dm^{-3} CYC (C_{CYC}) and in water are 0.0491, 0.0231, 0.0310, and 0.0203 mol dm^{-3} and 0.033, 0.0085, 0.0165, and 0.0031 mol dm^{-3} respectively. Using the cmc and cmc° values for the present surfactants, the R (stoichiometric cyclodextrin/surfactant ratio for the inclusion complex) values were calculated to be 0.99, 1.03, 1.04, and 0.88 for SDeS, SDS, DTAB, and TTAB respectively, which show that predominantly a 1 : 1 complex[24,25] is formed between various surfactants and CYC.

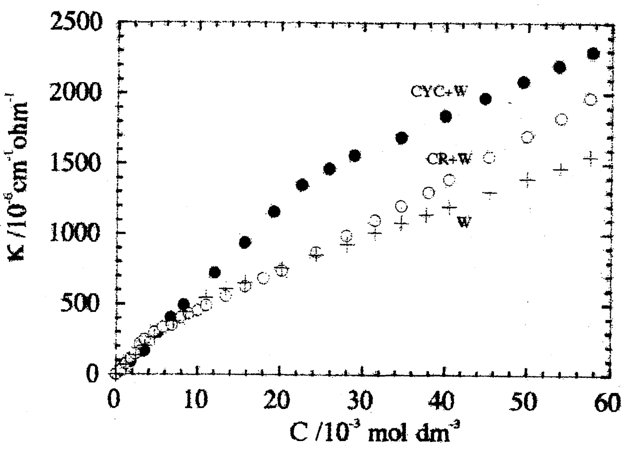

Fig. 1. Plot of conductivity ($\varkappa$) versus concentration (C) of SDS in W, CR+W and CYC+W mixtures.

Discussion

Micellization in CR+CYC+W Systems. SDS and SDeS belong to a category of anionic surfactants, whereas DTAB and TTAB belong to cationic surfactants.[29] The cmc of all surfactants is increased as the mole fraction of CYC is increased up to x_{CYC} = 0.5 in a CR+CYC+W mixture (Table 1). A similar trend in the micellization behavior of various ionic surfactants in CYC+W has also been observed.[29,30] The additive effect of CYC on the micellization of anionic as well as cationic surfactants can be compared by plotting the reduced cmc (cmc/cmc$^{\mathrm{CR+W}}$) versus the mole fraction of CYC in Fig. 2. It is interesting to note that the additive effect of CYC is stronger on the micellization of SDS rather than that of SDeS among anionic surfactants, and it is stronger for TTAB than DTAB in cationic surfactants. It had been observed earlier[29,30] that head-group modifications make less difference in the strength of the binding than does the nonpolar tail with the CYC cavity. This is due to the fact that the alkyl chain of the surfactant and not the polar head is being complexed in the CYC cavity. The binding constant is increased along with increase in the hydrophobicity[30] of the nonpolar tail, which can be achieved by increasing the length of the tail. The above facts may also be responsible for a maximum additive effect of CYC on TTAB due to its longest nonpolar tail in comparison to all other surfactants.

Such results are further supported by the variation in the $\Delta G^{\circ}_{\mathrm{HP}}$ value (Table 1). $\Delta G^{\circ}_{\mathrm{HP}}$ becomes less negative along with an increase in x_{CYC} in each case. This suggests that the free-energy contribution for micelle formation due to hydrophobic interactions between the surfactant monomers decreases as the concentration of CYC increases. It seems that the presence of CYC hinders micelle formation by interacting with the surfactant monomers due to the strong hydrophobic interactions between the hydrophobic tail and apolar CYC cavity. Therefore, the micelle formation becomes less spontaneous with an increase in the amount of CYC in the CR+CYC+W mixture. On the other hand, almost an insignificant variation in the $\Delta G^{\circ}_{\mathrm{s}}$ values of SDeS and SDS (Table 1) indicates that the surface contribution towards the micelle formation due to the electrostatic interactions between the Na^+ counter ions and oppositely charged polar head groups are negligible. This can be attributted to the strong complexation between the Na^+ counter ions and the CR cavity; also, the further addition of CYC has proven to be ineffective. In the case of DTAB and TTAB, a decrease in $\Delta G^{\circ}_{\mathrm{s}}$ value with respect to the increase in the amount of CYC (Table 1) may be attributed to the decrease in the surface charge density due to the possible distribution of the surfactant–CYC complex between the aqueous and micellar phases. Therefore, such a difference in the surface contributions of anionic and cationic micelles may be due to the difference in the distribution constant of a surfactant–CYC complex, which depends on the nature of the surfactant head group.[9,31,32]

In order to compare the energetic effects among all of the surfactants, a respective hydrophobic and surface contribution, $\Delta G^{\circ(\mathrm{II})} = \Delta G^{\circ}(\mathrm{CR+CYC+W}) - \Delta G^{\circ}\,(\mathrm{CR+W})$, for each surfactant is plotted against x_{CYC} in Figs. 3 and 4. It can be seen that there is a maximum increase and decrease in the $\Delta G^{\circ(\mathrm{II})}_{\mathrm{HP}}$ and $\Delta G^{\circ(\mathrm{II})}_{\mathrm{s}}$ values, respectively, for TTAB with the addition of CYC because of the facts discussed above.

Comparative Additive Effect of CR and CYC on Micellization. The cmc is the resultant of hydrophobic interactions between the nonpolar tails of the surfactant monomers to form the micelle core and the repulsive interactions between the micellar head groups which are pushing each other apart on the surface of the micelle. These micelles are simultaneously stabilized due to the presence of counter ions on the surfaces of micelles. However, if the counter ions are being complexed by an additive like CR, this whole complex can act as a hydrophobic moiety[9] due to neutralization of

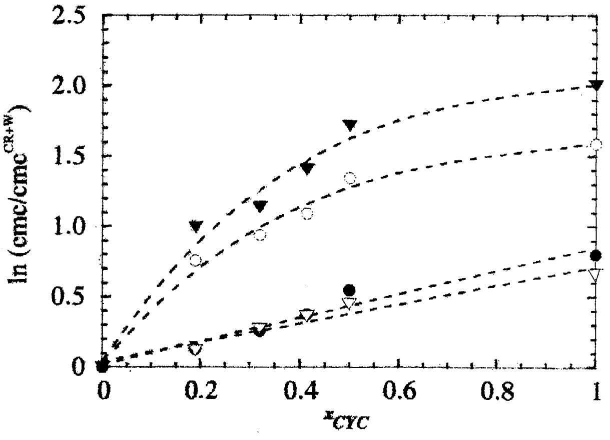

Fig. 2. Plot of $\ln(\mathrm{cmc/cmc}^{\mathrm{CR+W}})$ versus x_{CYC} for various surfactants. SDeS (●), SDS (○), DTAB (▽), and TTAB (▼).

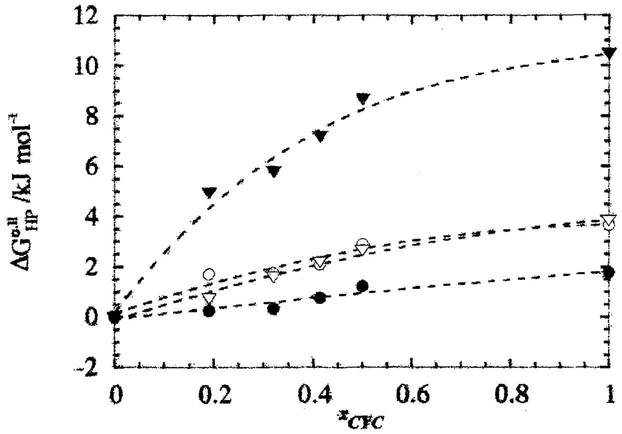

Fig. 3. Plot of $\Delta G^{\circ(\mathrm{II})}_{\mathrm{HP}}$ versus x_{CYC} for various surfactants. Symbols as for Fig. 2.

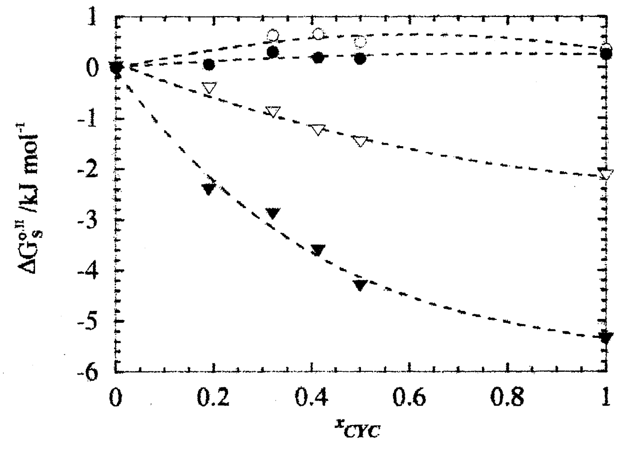

Fig. 4. Plot of $\Delta G^{\circ(\mathrm{II})}_{\mathrm{s}}$ versus x_{CYC} for various surfactants. Symbols as for Fig. 2.

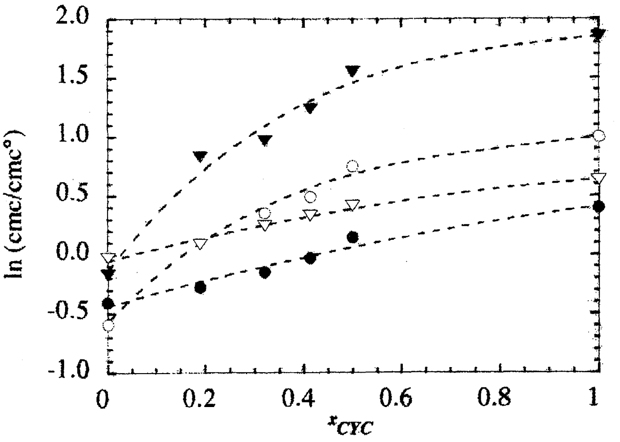

Fig. 5. Plot of ln (cmc/cmc°) versus x_{CYC} for various surfactants. Symbols as for Fig. 2.

the complex by electrostatic interactions. This can further help in the stabilization of the micelle due to the hydrophobic interactions which would help in the decrease in the cmc in comparison to the value in pure water. Such an effect is demonstrated by Fig. 5, in which ln (cmc/cmc°) is plotted against x_{CYC}. As can be seen, the reduced cmc in the presence of CR is significant negative value for SDeS and SDS, whereas it is very much close to zero for DTAB and TTAB. This shows that the micelles of anionic surfactants are being stabilized in the presence of CR, whereas micelles of cationic surfactants remain almost uneffected ($RT \ln X_{\mathrm{cmc}}$ for SDeS and SDS in CR+W are -21.467 and -23.633 kJ mol^{-1} in comparison to -18.720 and -22.139 kJ mol^{-1} in pure water respectively).

However, as we add CYC in the CR+W mixture, the micelles start denaturating, irrespective of the nature of the polar head group. This suggests that the strong hydrophobic interactions between the Na$^+$ counter ions and the CR cavity, which were responsible for the stabilization of SDeS and SDS micelles, are now no more effective in comparison to the strong hydrophobic interactions existing between the nonpolar tails of the respective surfactant and the CYC cavity. Therefore, it can be said that though CR is a strong micelle-stabilizing additive for SDeS and SDS, the addition of even a small amount of CYC is enough to destabilize the micelles, despite the fact that CR is always in large excess compared to CYC throughout the mole-fraction range of CYC studied.

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