Micelle Formation by Sodium Perfluorooctanoate and Decyltrimethylammonium Bromide in 18-Crown-6 + β-Cyclodextrin + Water Systems

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Abstract. The conductances of sodium perfluorooctanoate (SPFO) and decyltrimethylammonium bromide (DeTAB) have been determined in 18-crown-6 + water (CR + W), β-cyclodextrin + water (CD + W) and in CR + CD + W mixtures with a fixed 0.0151 mol dm^{-3} concentration of CR and varying amounts of CD with overall change in the mole fraction range of CD from 0.0 to 0.5 in CR + CD + W mixtures at 30 °C. From the conductivity data, the critical micellar concentration (cmc), the degree of counter-ion association (α), the free energy of transfer of the surfactant hydrocarbon chain from the medium to the micelle (ΔG^0_{HP}), and the free energy of transfer of surface contributions (ΔG^0_s) of SPFO and DeTAB have been computed. It has been found that the micelles of SPFO are stabilized in CR + W mixtures in comparison to pure water, whereas micelles of DeTAB remain comparatively unaffected upon addition of CR in water. On the other hand, micelles of SPFO and DeTAB are denatured upon addition of CD in CR + CD + W mixtures. The denaturation effect is stronger on the micelles of SPFO in comparison to that of DeTAB.

Key words: micelle formation, cationic surfactants, 18-crown-6, β-cyclodextrin, conductivity measurements.

1. Introduction

The aggregation of amphiphilic molecules involves contributions from both repulsive and attractive interactions. In particular, in ionic surfactants the repulsive forces originate primarily from electrostatic repulsions between the polar head groups [1, 2], whereas attractive interactions have generally been attributed to hydrophobic interactions [2, 3] between the nonpolar tails of the surfactant monomers. Therefore, a significant influence on the surfactant micellar properties of such surfactants can be observed by adding small amounts of various additives such as electrolytes [4, 5], and nonpolar [6] and polar organic liquids [7–10]. In the present study, such an additive effect on the micellisation of sodium perfluorooctanoate (SPFO) and decyltrimethylammonium bromide (DeTAB) has been examined in the presence of macrocyclic additives such as 18-crown-6 (CR) [11, 12] and β-cyclodextrin (CD) [13–15]. CR and CD belong to two different categories of macrocyclic compounds which undergo predominantly hydrophilic and hydropho-

bic interactions, respectively. They have many applications in the food industry, pharmacology and environmental chemistry. CRs are cyclic polyethers that interact mainly with a wide variety of cations [11, 12], whereas β-CD is an oligosaccharide which consists of seven glucose units [13]. CD has a unique configuration which makes the outer surface hydrophilic and the inner cavity hydrophobic in nature [16]. The most significant property of CR and CD is to form inclusion complexes with different kinds of guest molecules, ranging from ionic and neutral to organic or inorganic chemical species [11–13]. Factors such as geometric capability and the polarity of the guest molecule, the medium and the temperature greatly influence the stability of the inclusion complex formed [7, 8, 11–18].

Among the ionic surfactants, SPFO and DeTAB are of particular interest since they have oppositely charged polar head groups and different fluorocarbon and hydrocarbon nonpolar tails, respectively. They can interact with the CR and CD cavities simultaneously in a medium which contains both CR and CD molecules [19]. Hence, in view of such dual interactions of ionic surfactants, micellar properties have been evaluated from SPFO and DeTAB in CR + CD + W mixtures in order to discriminate the additive effect of CR and CD simultaneously on the micellisation of these surfactants.

2. Experimental

β-Cyclodextrin (CD) was a Sigma product. From several Karl Fischer analyses performed by using a Metrohm 655 Dosimat, it was found that the β-cyclodextrin contains 11% water. The partial molar volumes of β-cyclodextrin in water as a function of concentration were determined from repeated density measurements. These values were used to check the amount of water in the product before each measurement. This was due to the fact that β-cyclodextrin is quite hygroscopic in nature and hence it was kept continuously in an oven. 18-Crown-6 (CR), Sigma, was dried in a vacuum oven at 35 °C for at least 4 days before use.

Sodium perfluorooctanoate (SPFO) was prepared as reported elsewhere [20, 21]. Decyltrimethylammonium bromide (DeTAB), 99%, Sigma, was recrystallized from ethanol + ethyl acetate mixture. Both surfactants were dried in a vacuum oven at 60 °C for 2 days.

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

The precise conductance of SPFO and DeTAB in CR + W and CD + W containing 0.0151 mol dm^{-3} of each additive and in CR + CD + W ternary mixtures consisting of (CD : CR) fixed at 0.00356 : 0.0151, 0.00712 : 0.0151, 0.0107 : 0.0151 and 0.0151 : 0.0151 mole ratios between the concentration range of (1–8000) $\times$ 10^{-4} mol dm^{-3} were measured at 30 °C with an overall temperature variation of $\pm$0.01 °C. The procedure for the conductance measurements was basically similar to that reported in the literature [22]. The accuracy of the conductance measurements was $\pm$0.2%.
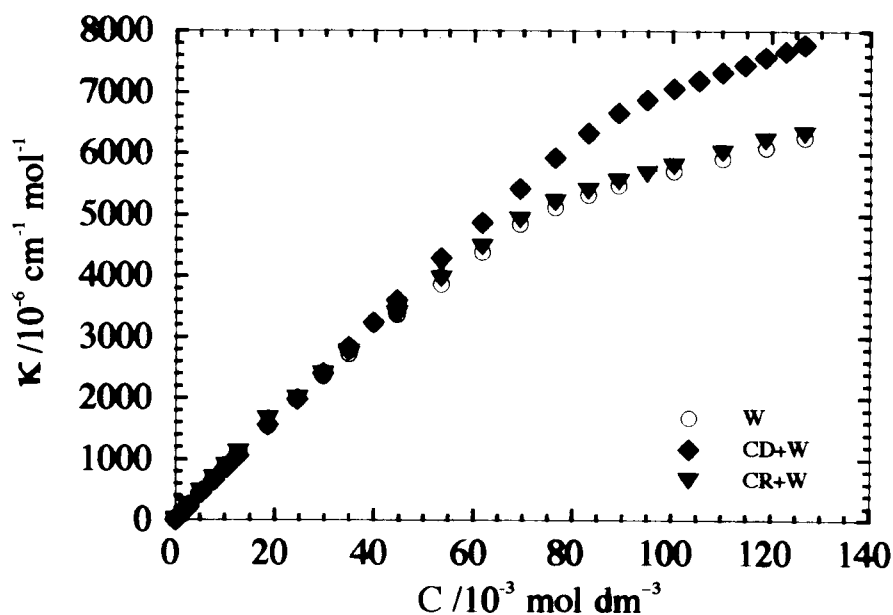
Figure 1. Plot of conductivity (κ) versus concentration (C) of SPFO in W, CR + W and CD + W mixtures.

3. Results

The conductivity (κ) is linearly correlated [23] with the surfactant concentration in both the pre-micellar and in the post-micellar regions, having a greater slope in the pre-micellar region than that in the post-micellar region. The intersection point between the two straight lines gives the cmc and the ratio between the slopes of the post-micellar region to that in the pre-micellar region gives the degree of counter-ion dissociation, (β), and, subsequently, the degree of counter-ion association ($\alpha = 1 - \beta$). Figure 1 shows such a variation of κ of DeTAB graphically in CR + W and CD + W binary mixtures consisting of 0.0151 mol dm^{-3} of each additive. In order to avoid the overcrowding of plots, κ values for DeTAB in CR + CD + W ternary mixtures are not shown.

The κ values for SPFO and DeTAB in all the systems in both the pre and the post micellar regions were fitted to a linear equation in order to evaluate the cmc and β,

$$\kappa = \kappa_0 + sC, \tag{1}$$

where κ_0 is the conductivity at infinite dilution, s is the slope in the pre- and post-micellar regions and C is the concentration (mol dm^{-3}) of the surfactant. The computed values for cmc and α, thus obtained for SPFO and DeTAB in binary and ternary mixtures are reported in Tables I and II respectively. According to Junquera et al. [24], the critical micellar concentration in the presence of additives such as

Table I. Critical micellar concentration (cmc)/mol dm^{-3}, degree of counter-ion association (α), free energy change for hydrophobic contributions (ΔG_{HP}^0)/kJ mol^{-1} and free energy change for surface contributions (ΔG_s^0)/kJ mol^{-1} for SPFO in CR + CD + W mixtures at corresponding mole fraction of CD (x_{CD})

x_{CD}	cmc	α	ΔG_{HP}^0	ΔG_s^0
0.0000	0.0135	0.68	−35.249	14.268
0.1905	0.0184	0.54	−31.096	10.904
0.3200	0.0220	0.45	−28.634	8.886
0.4138	0.0272	0.40	−26.893	7.683
0.5000	0.0305	0.37	−25.921	7.000
1.0000	0.0451	0.29	−23.137	5.201

Table II. Critical micellar concentration (cmc)/mol dm^{-3}, degree of counter-ion association (α), free energy change for hydrophobic contributions (ΔG_{HP}^0)/kJ mol^{-1} and free energy change for surface contributions (ΔG_s^0)/kJ mol^{-1} for DeTAB in CR + CD + W mixtures at corresponding mole fraction of CD (x_{CD})

x_{CD}	cmc	α	ΔG_{HP}^0	ΔG_s^0
0.0000	0.0643	0.71	−29.138	12.098
0.1905	0.0651	0.70	−28.914	11.906
0.3200	0.0668	0.69	−28.634	11.691
0.4138	0.0691	0.68	−28.322	11.464
0.5000	0.07115	0.67	−28.031	11.246
1.0000	0.0837	0.64	−26.856	10.480

CD is termed the apparent critical micellar concentration. This concentration is the sum of the free monomeric concentration at which the micellisation process occurs (essentially critical micellar concentration in water, cmc°) and the concentration of the surfactant associated with the CD. This is given by the following equation.

$$\text{cmc} = \text{cmc}° + C_{CD}/R \tag{2}$$

where R is the stoichiometry of the complex formed between the surfactant and β-CD and is defined as $R = [\beta\text{-CD/surfactant}]$. In the present study the critical
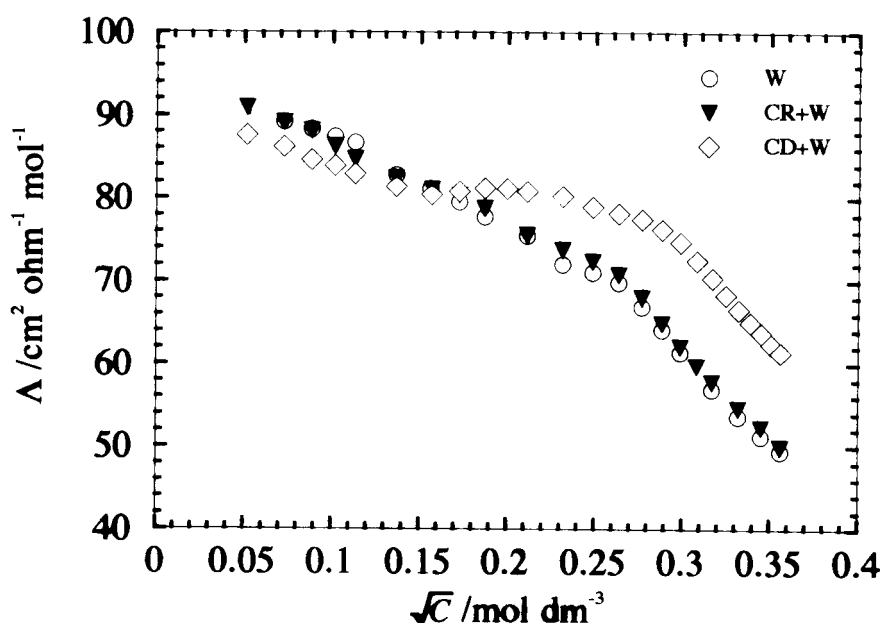
Figure 2. Plot of molar conductivity (Λ) versus concentration ($\sqrt{C}$) of SPFO in W, CR + W and CD + W mixtures.

micellar concentration for SPFO and DeTAB in 0.0151 mol dm^{-3} CD (C_{CD}) were 0.0451, and 0.0837 mol dm^{-3} and in water were 0.0281 and 0.0661 mol dm^{-3}, respectively. Using cmc and cmc° values for the present surfactants, values of R of 0.89 and 0.86 for SPFO and DeTAB were obtained, respectively, showing that a 1 : 1 complex [24, 25] is predominantly formed between both surfactants and CD.

From the κ values, the molar conductivities (Λ) for SPFO and DeTAB in W and CD + W were evaluated as usual for simple electrolytes by neglecting the hydrophobic nature of the surfactants [26, 27]. For comparison, such values for sodium decylsulphate (SDeS) have also been evaluated from our previous data [19]. These values were fitted to the Onsager equation [28] in the form

$$\Lambda = \Lambda_0 - (A\Lambda_0 + B)\sqrt{C}, \tag{3}$$

in order to determine the limiting molar conductivities at infinite dilution (Λ_0) in the pre-micellar region, as described previously [7, 26, 27].

From the Λ_0 values, the limiting ionic molar conductivities for Na$^+$ or Br$^-$ counter ions (λ_{Cl}^0) and that of each corresponding monomer (λ_{MN}^0) ion for each surfactant can be calculated using the limiting values of Na$^+$ and Br$^-$ ions in water, i.e. 56.58 and 85.86 S cm^2 mol^{-1}, respectively. These were obtained by interpolating the values at various temperatures by using literature data [28]. By subtracting the respective λ_{Cl}^0 value from 92.12, 77.35 and 97.85 S cm^2 mol^{-1}, the limiting molar conductivities for SPFO, SDeS and DeTAB in water at 30 °C,

one obtains 35.54, 20.77 and 11.99 S cm^2 mol^{-1} for the respective monomer. On the other hand, the Λ_0 value for these surfactants are considerably lower in CD + W in comparison to the values in pure water. In CD + W, the Λ_0 values obtained were 76.0, 73.9 and 91.37 S cm^2 mol^{-1}, respectively, for SPFO, SDeS and DeTAB. These values are 17.3, 4.5 and 6.6% lower than the respective values in pure water. Such a large decrease in the Λ_0 value of SPFO can be attributed to significantly stronger hydrophobic interactions in comparison to SDeS and DeTAB.

In the presence of additives, the free energy of micellisation consists of surfactant–surfactant interactions, additive–surfactant interactions and additive–additive interactions. These interactions can be divided into hydrophobic and hydrophilic contributions. In order to estimate both kinds of contributions, the thermodynamics of micelle formation, proposed by Evans and Ninham [29], has been taken into account, which gives

$$RT \ln X_{\mathrm{cmc}} = \Delta G_{\mathrm{HP}}^0 + \Delta G_s^0, \tag{4}$$

where ΔG_{HP}^0 is the hydrophobic free energy of transfer of the surfactant hydrocarbon chain from the medium to the interior of the micelle, and ΔG_s^0 corresponds to the energy associated with the surface contributions consisting of electrostatic interactions between the head groups and counter-ions and all other contributions due to specific interactions. The sum of these two terms is equivalent to the total Gibbs energy per surfactant molecule associated with the formation of micelles (ΔG_M^0), which is given by the following equation

$$\Delta G_M^0 = RT \ln X_{\mathrm{cmc}} \tag{5}$$

where X_{cmc} is the cmc in mole fraction units and is defined as $X_{\mathrm{cmc}} = C_{\mathrm{cmc}}/55.5$. In order to determine ΔG_s^0, the equilibrium model of Ueno et al. [30] can be employed, which is related to the degree of counter-ion binding to the electrostatic interactions between the surfactant head groups and counter ions [31]. This model also provides a measure of the free energy of transferring the nonpolar tail from the aqueous medium to the interior of the micelle. In the present study, Equation (6) can be used for the equilibrium between monomers, counter-ions and monodispersed micelles [29, 30]:

$$(n - p)C^+ + nS^- \Leftrightarrow M^{p-} \tag{6}$$

where C^+, S^- and M^{p-} stand for the counter-ion, surfactant monomer and micelles, respectively, for anionic surfactants and those of opposite polarities for cationic surfactants. The equilibrium constant can be written in terms of the standard free energy of micelle formation per monomer as [29, 30]:

$$\frac{\Delta G_M^0}{RT} = -(1/n) \ln C_{M^{p-}} + \ln C_{S^-} + \left(1 - \frac{p}{n}\right) \ln C_{C^+}. \tag{7}$$

For typical micelles ($n = 50$–100), the term M^{p^-} is small and insensitive to large errors in determining $C_{M^{p-}}$, and both C_{C^+} and C_{S^-} can be replaced by the cmc in the second and third terms in Equation (7) which becomes [29, 30]

$$\Delta G^0_{HP} = RT \ln X_{cmc} + RT \left(1 - \frac{p}{n}\right) \ln X_{cmc}, \tag{8}$$

where p/n is the degree of counter-ion dissociation (β). Comparing it with Equation (4) shows that in terms of the equilibrium model, ΔG^0_S is given by

$$\Delta G^0_S = -\alpha RT \ln X_{cmc}. \tag{9}$$

By using the ΔG^0_{HP} and ΔG^0_s values for each surfactant, the respective terms $\Delta G^{0(II)}_{HP}$ and $\Delta G^{0(II)}_s$, which represent the effect of an additive on micellisation, can be calculated by subtracting the value of the corresponding term in water from that in water + additive by means of the following general Equation (10) [7, 21, 32]:

$$\Delta G^{0(II)} = \Delta G^0 \text{ (in aqueous additive)} - \Delta G^0 \text{ (in H}_2\text{O)}. \tag{10}$$

The computed values for ΔG^0_{HP}, and ΔG^0_s, thus obtained for SPFO and DeTAB in CR + CD + W mixture are reported in Tables I and II, respectively.

4. Discussion

4.1. MICELLISATION OF SPFO IN CR + CD + W SYSTEMS

SPFO belongs to the category of anionic fluorosurfactants [33]. Table I and Figure 3 demonstrates the variation of cmc of SPFO in CR + CD + W mixtures with respect to the mole fraction of CD (x_{CD}). It can be seen that the cmc is significantly increased as the mole fraction of CD is increased up to $x_{CD} = 0.5$ in CR + CD + W mixture. This can be attributed to the removal of available monomers by CD upon complexation due to the hydrophobic interactions leading to the inclusion of the nonpolar tail of the surfactant monomer into the apolar cavity of CD. This is also responsible for the less negative value of ΔG^0_{HP} (Table I) and the large increase in $\Delta G^{0(II)}_{HP}$ value (Figure 4) which can be due to the change in properties of the surfactant solutions by transferring the amphiphilic molecules from monolayers to the bulk solvent upon additon of CD with the effect of which the total free energy is decreased. This decrease in free energy is the sum of the free energy upon inclusion complex formation and the free energy due to the destruction of the monolayers [34–36]. However, similar behaviour of other anionic surfactants, viz. sodium dodecyl sulphate and sodium decyl sulphate (SDeS), in CD + W has also been observed with the increase in concentration of CD in water [37, 38]. For comparison, such values for SDeS [19] have also been plotted in Figure 3 since the cmc value of SDeS in water (0.0330 mol dm^{-3}) is close to that of SPFO
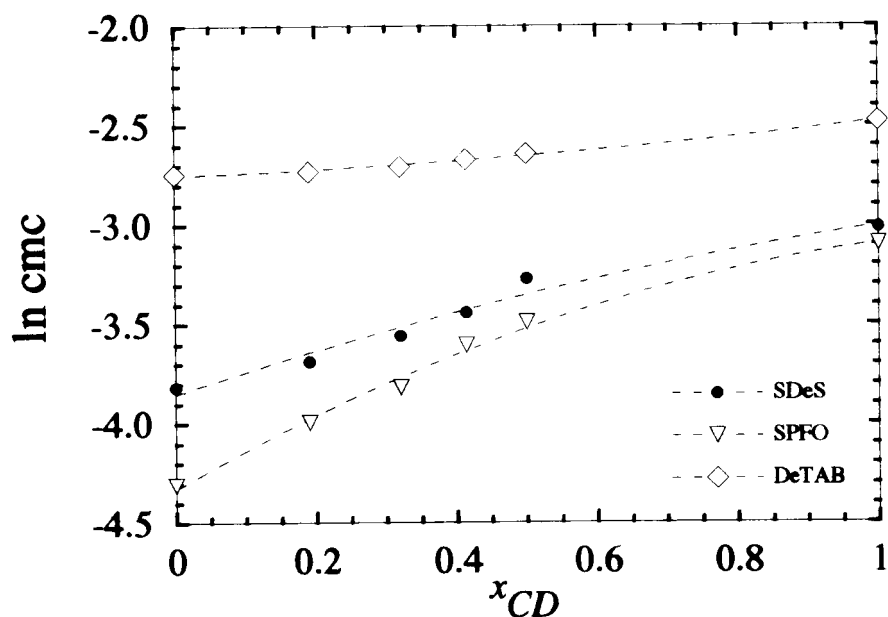
Figure 3. Plot of ln cmc versus x_{CD} for SPFO, SDeS and DeTAB.

(0.0281 mol dm^{-3}). On the other hand, however, a significant decrease in the α (Table I) and $\Delta G_s^{0(II)}$ values (Figure 5) can be attributed to the fact that the addition of CD in CR + W mixture enhances the repulsive interactions between the polar heads of SPFO at the micellar surfaces decreasing the α value and this decrease is also unfavourable to the micelle formation. Similar results have already been reported by Asakawa et al. [39] for the micelle formation of lithium perfluorononanoate in the presence of urea in water.

In view of the identical polar head groups and different nonpolar hydrophobic tails of SPFO (C$_8$) and SDeS (C$_{10}$), the additive effect of CD on the micellisation of SPFO which has a comparatively shorter hydrophobic tail, can be compared with that of SDeS in the CR + W mixture by plotting the reduced cmc (cmc/cmc^{CR+W}) versus x_{CD} in Figure 6. It is interesting to note that in spite of the shorter hydrophobic tail, the additive effect of CD is much stronger on the micellisation of SPFO than that of SDeS. However, it is already known [24, 25, 37, 38, 40, 41] that surfactant–CD interactions leading generally to 1 : 1 complexation depend mainly on two factors: the length of the hydrocarbon tail, and the polar head configuration. Palepu et al. [37] have shown that head group modifications makes less difference to the strength of the binding than does the nonpolar tail with the CD cavity. This is due to the fact that the alkyl chain of the surfactant and not the polar head is fitted into the CD cavity [41–43]. The binding constant is increased with the increase in the hydrophobicity [37]. However, this fact is true as far as the comparison between the hydrocarbon surfactants is concerned. On the other hand, when the fluorocarbon surfactants are compared with their hydrocarbon counterparts, it has
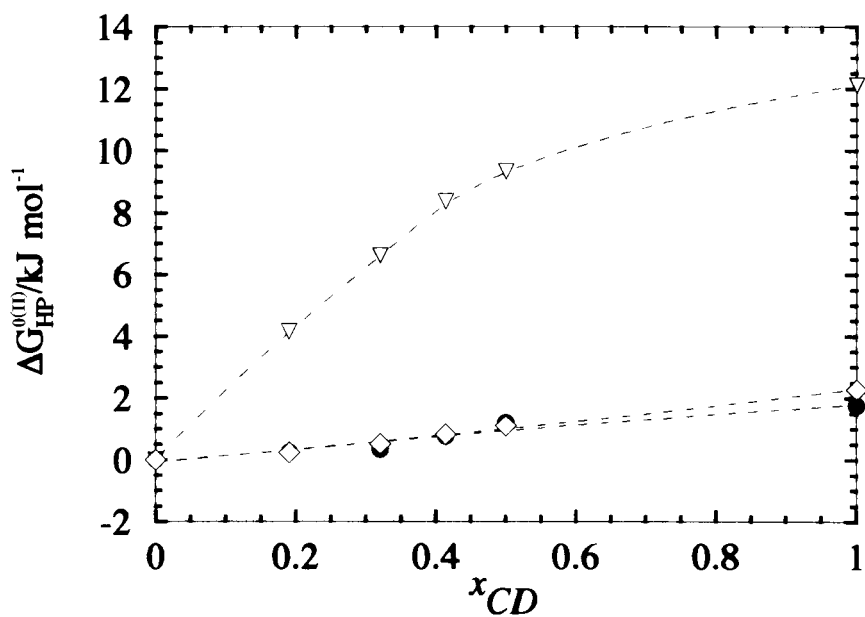
Figure 4. Plot of $\Delta G_{HP}^{0(II)}$ versus x_{CD} for various surfactants. Symbols as for Figure 3.
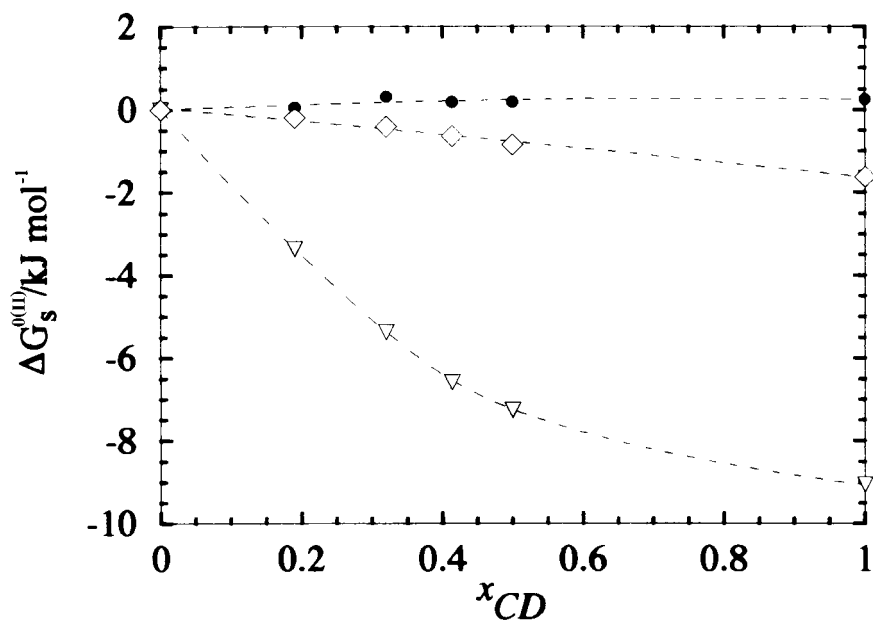

Figure 5. Plot of $\Delta G_s^{0(II)}$ versus x_{CD} for various surfactants. Symbols as for Fig. 3.
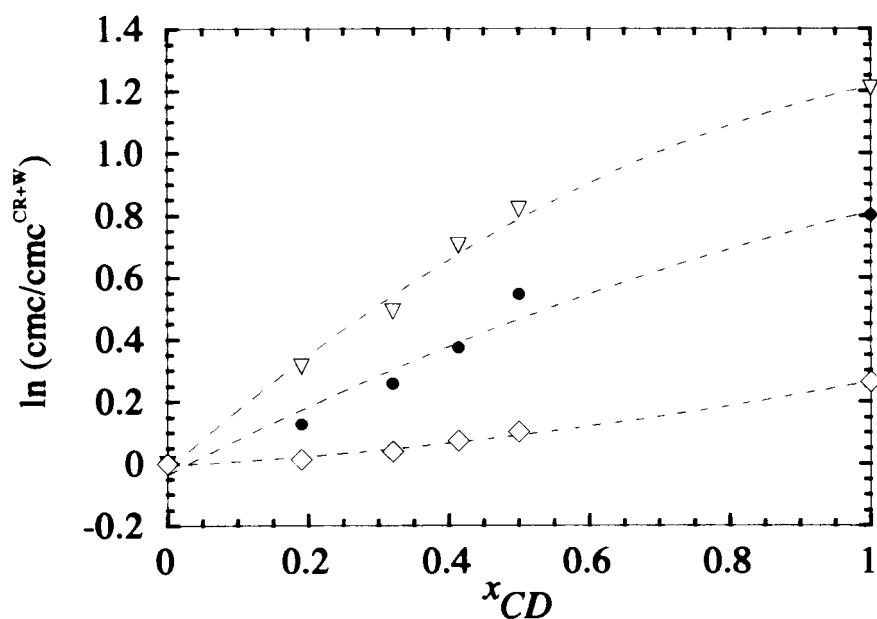
Figure 6. Plot of ln(cmc/cmc^{CR+W}) versus x_{CD} for various surfactants. Symbols as for Figure 3.

been found [24, 39] that the fluorocarbons are much more hydrophobic than their hydrocarbon counterparts, which is also responsible for their lower water solubility as well as the lower cmc value [44]. The partial molar volume changes of fluorocarbon surfactants are larger than those for hydrocarbon surfactants on micelle formation [45]. It can be seen (Figure 6) that, though the nonpolar tail of SPFO (C_8) is shorter than that of SDeS (C_{10}), the hydrophobic interactions are much stronger for the shorter fluorocarbon nonpolar tail in comparison to the longer hydrocarbon tail. Similar results have already been reported [39] for the micellisation of fluorocarbon and hydrocarbon surfactants consisting of identical polar head groups under the hydrophobic effect of urea in water.

4.2. MICELLISATION OF DeTAB IN CR + CD + W MIXTURES

DeTAB belong to a category of cationic surfactants in which Br^- ion is the counter-ion. Table I and Figure 3 show that the cmc of DeTAB increases with the increase in the amount of CD in CR + CD + W mixtures. Similar results have already been observed for a series of anionic and cationic surfactants upon complexation with CD [37, 38, 40]. On the other hand, this increase in cmc is also responsible for the decrease in ΔG_{HP}^0 (Table II) and the increase in $\Delta G_{HP}^{o(II)}$ (Figure 4). Herein, transfer of the amphiphilic molecules from monolayers to the bulk solvent by the addition of CD seems to effect the degree of Br^- counter-ion binding to the micelles (Table II). However, it is known that anions like Br^- counter-ions have

least affinity towards the CR cavity [11, 12]. Therefore, a small decrease in α with increasing x_{CD} (Table II) can be attributed to the solvation of Br$^-$ ions by the water molecules due to the structure breaking [46–48] properties of Br$^-$ ions. The structure has been created due to the strong hydrophobic interactions of the surfactant or surfactant–CD complex.

4.3. COMPARATIVE ADDITIVE EFFECT OF CR AND CD ON THE MICELLISATION OF SPFO AND DeTAB

The cmc is the result 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 surface of micelles. However, if the counter-ions are complexed by an additive like CR, this could lead to a decrease in micelle aggregation number as a result of which the cmc is decreased in comparison to the value in pure water. Such an effect is demonstrated by Figure 7, in which ln(cmc/cmc°) is plotted against x_{CD}. As can be seen, the reduced cmc in the presence of CR has a significant negative value for SPFO and SDeS, whereas it is very much close to zero for DeTAB. This shows that the micelles of anionic surfactants are stabilized in the presence of CR whereas micelles of cationic surfactants remain almost unaffected. This can be due to the noninteracting nature of Br$^-$ counter-ions with the CR cavity in the case of DeTAB. However, if we compare the micellar stability of SPFO with that of SDeS in CR + W mixtures, it can be seen that the micelles of SPFO are more stable than those of SDeS ($RT \ln X_{cmc}$ for SPFO and SDeS in CR + W are -20.97 and -21.47 kJ mol^{-1} in comparison to -19.12 and -18.72 kJ mol^{-1} in pure water respectively). It is known [11, 12, 49, 50] that the CR cavity undergoes strong electrostatic interactions with cations like Na$^+$ in order to form the inclusion complex. Therefore, the greater stability of SPFO micelles can be attributed to the stronger hydrophobic nature [31] of the SPFO monomer in comparison to that of SDeS. As a result, Na$^+$ can easily be dissociated from the monomer to form a complex with the CR cavity in the case of SPFO ($\beta_{SPFO} = 0.68$ and $\beta_{SDeS} = 0.60$ in CR + W) leading to the formation of loose aggregates with small aggregation numbers [3, 23, 39] in the CR + W mixture.

The purpose of studying such an additive effect of CD in CR + CD + W mixtures up to $x_{CD} = 0.5$ was to check the influence of CD on the micellisation of SPFO in CR + W rich region of the ternary mixtures. It shows that though micelles are being stabilized in the presence of CR, the addition of even a small amount of CD denatures the micelles, which increases further with the increase in concentration of CD (Table I). It seems that as we add CD to the CR + W mixture, the micelles start denaturing regardless of the nature of the polar head group, and the hydrophilic interactions, which were earlier guiding the micelle stability in the case of SPFO and SDeS, are now no longer effective in comparison to the strong hydrophobic
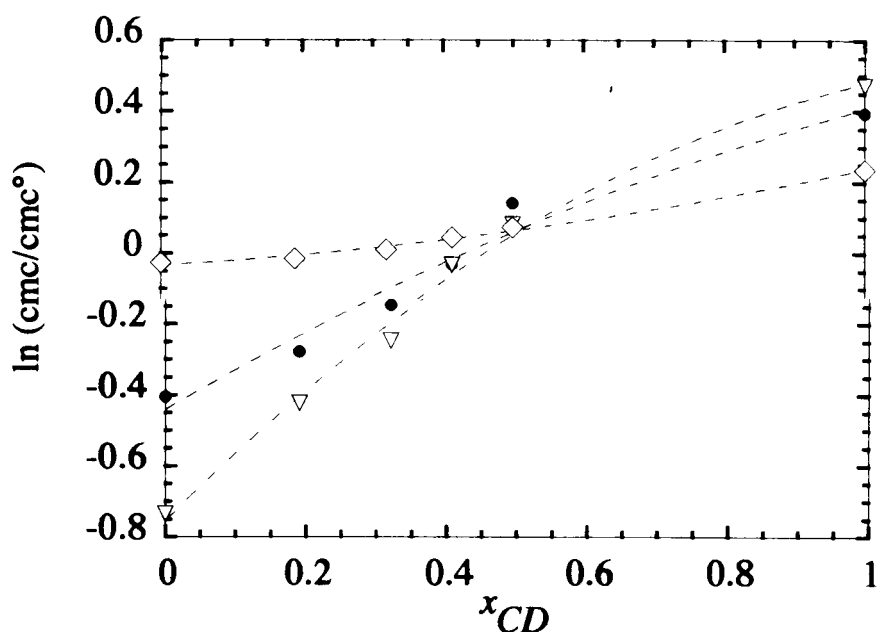
Figure 7. Plot of ln(cmc/cmc°) versus x_{CD} for various surfactants. Symbols as for Fig. 3.

interactions originating due to the strong complexation of the nonpolar tails of the respective surfactant with the CD cavity. Therefore, it can be said that though CR is a strong micelle stabilizing additive since it stabilizes the micelles by complexing with Na^+ counter-ions in the case of anionic surfactants, the addition of even a small amount of CD is enough to destabilize the micelles to some extent, though CR is always in large excess in comparison to CD throughout the mole fraction range of CD studied. However, it is also interesting to note in the case of SPFO and SDeS (Figure 7) that as the amount of CD is increased in CR + CD + W mixtures up to $x_{CD} = 0.5$, there is a continuing effect of the presence of CR on the micellar stability which decreases with the increase in amount of CD. Since the ln(cmc/cmc°) value remains negative up to $x_{CD} = 0.5$, it becomes almost zero at $x_{CD} = 0.5$, suggesting that CD needs an equal amount to that of CR in CR + CD + W mixtures in order to neutralize the effect of CR on the micellisation of anionic surfactants. However, bearing in mind the greater hydrophobicity of SPFO in comparison to that of SDeS, on the other hand, the comparatively weaker additive effect of CD on the micellisation of DeTAB (Figures 4 and 7) in comparison to that on SDeS in CR + CD + W mixtures suggests that in fact CR is enhancing the hydrophobic interactions between the nonpolar tail of the anionic surfactants with that of the CD cavity by complexing with Na^+ counter-ions. This leads to the decrease in electrostatic interactions between the polar head of the monomer and Na^+ counter-ion, making the monomer more vulnerable for complexing with the apolar cavity of CD. This effect, however, is absent in the case of DeTAB because

the additive effect of CD is quite weak, particularly in comparison to SDeS. Such results indicate that though the additive effect of CD in water should be similar [37, 40] on the micellisation of SDeS and DeTAB having identical carbon tails, but the presence of another hydrophilic additive like CR seems to help in enhancing the hydrophobic additive effect of CD on the micellisation of SDeS rather than DeTAB.

Acknowledgment

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