Investigation of the Properties of Polyoxyethylene (10) Lauryl Ether: $C_{12}E_{10}$ in Aquo-*n*-Alcohol Mediums

Kshatrapati Shivaji Sharma and Animesh Kumar Rakshit*

Department of Chemistry, Faculty of Science, The Maharaja Sayajirao University of Baroda,
Vadodara-390 002, Gujarat, India

Received May 6, 2004; E-mail: akrakshi@yahoo.co.in

The effect of the concentration and the nature of different *n*-alcohols (C_2–C_5) on the growth of $C_{12}E_{10}$ $[CH_3(CH_2)_{11}(OCH_2CH_2)_{10}OH]$ micelles has been studied by tensiometric, viscometric, and proton NMR techniques. Critical micelle concentrations (CMC) were determined by surface-tension measurements in the presence of different concentrations of *n*-alcohols (C_2–C_4) and at different temperatures. The Gibbs free energy, enthalpy, and entropy of micellization (ΔG°_m, ΔH°_m, ΔS°_m) and adsorption at an air/water interface (ΔG°_{ad}, ΔH°_{ad}, ΔS°_{ad}) were computed and discussed. An enthalpy–entropy compensation effect was observed at an isostructural temperature of about 300 K for both micellization and interfacial adsorption. The transfer enthalpies and heat capacities of the micelle from water to aqueous *n*-alcohol solutions were also computed. The intrinsic viscosity gave the hydrated micellar volume (V_h), volume of the hydrocarbon core (V_c), and the volume of the palisade layer of the OE unit (V_{OE}). The spin–lattice proton relaxation time (T_1) in the aqueous micellar region and ^{1}H NMR were also used to study the behavior of OE micelles in both the absence and presence of alcohols. There was a slight rise in the cloud point (CP) when using lower alcohols. However a decrease was seen for *n*-BuOH and *n*-PenOH.

Surfactant systems are characterized by a very wide variety of morphology of aggregates formed by the self assembly of surfactant molecules in aqueous solution to form micelles, where their properties are different from those of the non-aggregated monomer molecules. In other words, surfactants exhibit a very wide range of different phase structures. The study of these systems is a matter of serious scientific and technological interest from both theoretical as well as experimental points of view.

The aggregational and surface properties of a surfactant in solution are very sensitive, and are influenced or controlled by the solvent polarity and type, temperature, pressure, pH, and presence of various foreign substances (cosolvent).[1–12] The nature of a cosolvent determined the direction of changes in the cmc of surfactants. There are some organic cosolvents that when present in some greater amounts even cause a disappearance of micelles.[13,14] Electrolytes generally decrease the cmc and the cloud point.[13] On the other hand, nonelectrolytes may increase or decrease the cmc[6,9,15] and the cloud point.[13,16] Because hydrophobic association and water-structure destruction have a mutual correlation, they influence the solvent structure and dielectric constant, and can also undergo direct interactions with the surfactants.

The effect of different cosolvents having –OH group, such as PEG,[6,7,10,17] sucrose,[6,7,18] ethylene glycol,[19] and alcohols,[20–25] on the micellization process has been studied. However, there are some aspects that warrant further investigation. Intermediate chain alcohols are commonly added to surfactant solutions in order to change their characteristics. Candau and Zana[26] showed that alcohols may be distributed between the aqueous and micellar phases, and may accumulate both in a palisade layer and inside the micelle hydrophobic core, thus favoring stability of the system. Alcohols also exhibit some typical characteristics of surfactants,[27] thus earning the appellative of cosurfactants. Zana[28] and co-workers have reported extensive studies on the effect of linear chain length alcohols on the cmc, micellar molecular weight, degree of ionization and stability and diffusion coefficients of the micelle in cationic surfactant tetradecyl trimethyl ammonium bromide (TTAB), with particular emphasis on the Pentanol–TTAB system. They have shown that the incorporation of alcohol into the micelle produces a noticeable change in the micellar shape and its transport properties. On one hand, it causes micelle swelling; on the other hand, there is decrease in the micelle surface charge density and an increase in the degree of ionization. Also, it has been recognized that the partition coefficient of the neutral solute in a micellar solution can be computed with reasonable confidence from a cmc determination.[29] Moreover, a cmc-based method could be of great value in evaluating the effect of structure on the micellar solubilization of an additive.[6]

Most of the publications referred to above address the possible effect of alcohols on ionic surfactants, only a few are on nonionic surfactants. However, we have not seen a comprehensive thermodynamic and structural study of an oxyethylated nonionic, $C_{12}E_{10}$ surfactant in the presence of lower-to-medium chain alcohols. Nonionic surfactants of the polyoxyethylene type are chosen because of their wide use in detergency, cosmetics, emulsion formations, like shampoos, conditioners, and paints, as well as in pharmaceutical dosages and in drug delivery systems. This will continue in the future due to their higher solubility at low temperature. Hence, we report on the effect of *n*-alcohols (C_2–C_4) on the interfacial, thermodynamic, viscosity, cloud point, and ^{1}H NMR properties of $C_{12}E_{10}$. The thermodynamic activation parameters for viscous flow

Published on the web May 6, 2005; DOI 10.1246/bcsj.78.771

were evaluated using the Frenkel–Eyring equation. We also determined Traube's constant (σ) which is the rate of change of surface pressure per unit concentration. Viscosity studies were also carried out to determine the hydrated micellar volume (V_h), the volume of the hydrocarbon core (V_c), and the volume of the palisade layer of OE unit (V_{OE}). Transfer enthalpies, which are sensitive to the structure of a solvent, have been determined. Using ^{1}H NMR, we also studied the spin–lattice proton relaxation time (T_1) in an aqueous micellar solution and the change in the chemical shift in surfactant by *n*-alcohols.

Experimental

Materials. $C_{12}E_{10}$ [$CH_3(CH_2)_{11}(OCH_2CH_2)_{10}OH$], MW = 626.85, a commercially available product (Sigma, USA), was used without any further purification. Ethanol (EtOH), 1-propanol (*n*-PrOH), 1-butanol (*n*-BuOH), and 1-pentanol (*n*-PenOH) were purified by refluxing AR-grade alcohols (Merck, India) over calcium oxide for 12 h, and then fractionally distilling and keeping them over molecular sieves before use. For physicochemical properties, all solutions were prepared by using triple-distilled deionized water, showing electric conductance values of 2–3 $\mu S\,cm^{-1}$ at 303 K. The solvent D_2O (aldrich, USA) of 99.96% purity has been used for ^{1}H NMR experiments.

Methods. The cmc was determined by surface tension (γ) measurements using a du-Nouy ring tensiometer (S. C. Dey and Co., Calcutta, India) at different temperatures viz. 303, 308, 313, and 318 K and *n*-alcohols (C_2–C_4), concentration (v/v) viz. 0.05, 0.1, 0.25, 0.5, 0.75, and 1.0%. The temperature was maintained constant (±0.1 K) by circulating thermostated water through a jacketed vessel containing the solution. Other conditions were the same as reported in our recent papers.[6,30–33] Representative plots of surface tension (γ) against $\log_{10} C$ are shown in Fig. 1. The reproducibility of the surface tension vs concentration curve was checked by duplicate runs; in the cmc it was found to be less then ±1.0%, calculated from the experimental cmc data obtained from at least two runs.

The flow times of the surfactant solution and water were measured with the help of a Ubbelohde suspended level viscometer.[30] The temperatures (308, 313, and 318 K) were maintained within ±0.1 K in a thermostated bath. Samples were carefully filtered before injection into the viscometer. The density of the surfactant solution was determined with a pyknometer at a given temperature. The change in the viscosity of the surfactant solution (5% w/v) at 0.1, 0.5, and 1.0% (v/v) concentration of *n*-alcohols (C_2–C_4) was studied. Three consecutive flow times, agreeing within ±0.02 s, were taken and the mean flow time was considered.

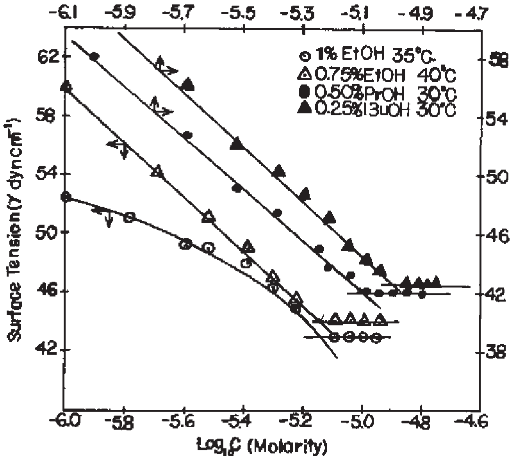

Fig. 1. Representative plots of surface tension (γ) vs $\log_{10} C$ (molarity) in presence of *n*-alcohols at different temperature.

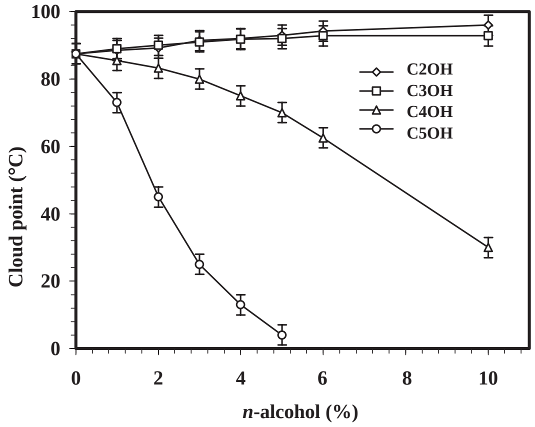

Fig. 2. Variation of Cloud point of $C_{12}E_{10}$ (1%) with weight % of *n*-alcohols.

The intrinsic viscosity, $|\eta|$, was calculated using the relation

$$|\eta| = \lim_{c \to 0} \frac{(\eta_r - 1)}{C}, \tag{1}$$

where the limit to zero concentration indicates that intermolecular interactions were absent, and η_r indicates the relative viscosity of the surfactant solution. Some researchers[34] have taken $|\eta|$ to be equal to $(\eta_r - 1)/C$ without the condition of limiting concentration. It has been defined as the shape factor, and is expected to have a value of between 2.5 and 4 $cm^3\,g^{-1}$ for globular particles.[35] In the present work, we calculated $|\eta|$ without taking the zero concentration limit, as we did earlier.[30]

The cloud points (CP) of $C_{12}E_{10}$ in presence of *n*-alcohols (C_2–C_5) were determined by an experimental method described elsewhere.[36] The surfactant concentration was 1% (w/v) and the alcohols were in 1, 2, 3, 4, 5, and 6% (v/v). The CPs can be seen in Fig. 2. These are the averages of the appearance and disappearance temperatures of the cloud, the difference being not greater than 0.4 °C under constant stirring. The error in CP was less than ±2%.

Proton NMR measurements were carried out in a deuterium oxide solvent at room temperature (25 ± 0.5 °C). The solution for the spectra was prepared by taking a 0.1 M $C_{12}E_{10}$ solution mixed with *n*-alcohols (surfactant:alcohol 1:1 w/v); the densities of alcohols used were taken from the standard literature. Proton NMR spectra were recorded with Brucker DPX 200 MHz and 300 MHz FT NMR spectrometers. ^{1}H NMR chemical shifts were referred to the internal TMS. The spin–lattice relaxation time (T_1) was measured by an inversion recovery technique with a (180°–τ–90°, FID) pulse sequence. The relaxation times were calculated by the nonlinear least squares fitting using the instrument's inbuilt software.[6]

Results and Discussion

The surface tension is a fast, nondestructive, and dependable means to determine the cmc.[37] The cmc values of $C_{12}E_{10}$ in both the absence and in presence of EtOH, *n*-PrOH, and *n*-BuOH are presented in Table 1. It can be seen from the table that the cmc values of $C_{12}E_{10}$ were found to decrease with an

Table 1. The cmc of $C_{12}E_{10}$ in the Aqueous Solution in the Presence of *n*-Alcohols at Various Temperatures

n-Alcohol	Critical micelle concentration/μm[a]											
	EtOH				*n*-PrOH				*n*-BuOH			
(% v/v)	303 K	308 K	313 K	318 K	303 K	308 K	313 K	318 K	303 K	308 K	313 K	318 K
0.0[a]	12.8 ± 0.13	11.8 ± 0.12	10.0 ± 0.10	8.9 ± 0.09	—	—	—	—	—	—	—	—
0.05	—	—	—	—	—	—	—	—	10.7 ± 0.11	12.0 ± 0.12	13.8 ± 0.14	14.6 ± 0.15
0.10	—	—	—	—	—	—	—	—	10.0 ± 0.10	11.2 ± 0.11	13.2 ± 0.13	14.1 ± 0.14
0.25	8.1 ± 0.08	9.1 ± 0.09	10.9 ± 0.11	13.3 ± 0.13	9.1 ± 0.09	10.0 ± 0.10	11.2 ± 0.11	11.2 ± 0.11	9.7 ± 0.10	10.5 ± 0.11	12.0 ± 0.12	13.2 ± 0.13
0.50	6.6 ± 0.07	8.5 ± 0.09	10.0 ± 0.10	13.2 ± 0.13	8.1 ± 0.08	9.1 ± 0.09	9.5 ± 0.10	13.1 ± 0.13	—	—	—	—
0.75	6.4 ± 0.06	7.2 ± 0.07	9.8 ± 0.09	11.2 ± 0.11	6.9 ± 0.07	8.5 ± 0.09	9.3 ± 0.09	13.1 ± 0.13	—	—	—	—
1.0	6.0 ± 0.06	7.1 ± 0.07	9.1 ± 0.09	12.0 ± 0.12	6.6 ± 0.07	7.2 ± 0.07	9.1 ± 0.09	13.2 ± 0.13	—	—	—	—

a) These values are low than expected probably because this commercial sample is not very pure (Ref. 41).

increase in temperature in the absence of any alcohols. This is generally observed in the case of a nonionic surfactant, and was also observed earlier.[38] However, in the presence of *n*-alcohols, the cmcs increased with increasing temperature in all of the systems reported in this study. This was observed earlier in the presence of different additives.[6,7,39] That the cmc increases with an increase in temperature (in the presence of different additives) is a characteristic of an ionic surfactant.[40] The cmc value without any additive, at a particular temperature, is in good agreement with our earlier value.[7] However, we must mention that the cmc values are very low compared to the expected values, probably because we used a commercial sample supplied by Aldrich.[41]

At the cmc micelles are formed as a result of a hydrophobic interaction,[42] supplemented with the London dispersion force of attraction.[43] In the case of a nonionic surfactant without any additive, the cmc decreases with increasing temperature due to dehydration of the hydrophilic moiety of the surfactant molecule; it is also due to breaking of the water structure. In the presence of additives, however, the reverse situation is seen, which indicates that these molecules significantly alter the micellization process. As shown in Table 1, as the hydrocarbon chain length increases from EtOH to *n*-BuOH the cmc values increase. As we can see from the Table 1, the addition of alcohol, in general, decreases the cmc value of the surfactant. This is because the presence of alcohol decreases the hydration of the surfactant, and hence the cmc decreases. However, as the temperature is increased the cmc increases in the presence of alcohols. Alcohols interact through hydrogen bonding, or otherwise with water, and forms a structured solvent system that is different from that of water. As the temperature rises, the solvent system becomes less structured and the hydration of the surfactant increases; the cmc therefore rises. Moreover, it is to be noted that the presence of any additive will destroy the water structure, but can also form a different structured system, particularly in the presence of hydroxy groups. This results in an antagonistic effect on micelle formation. Hence, the overall values of the obtained cmc are the result of these above-mentioned effects.

The Gibbs free energy of micellization ($\Delta G^\circ_\mathrm{m}$) for a nonionic surfactant is directly proportional to the ln cmc (cmc in mole fraction scale) at constant temperature according to the following relation:[44]

$$\Delta G^\circ_\mathrm{m} = RT \ln \mathrm{cmc}, \tag{2}$$

where R and T have the usual significance. The initial standard state is a hypothetical state where the surfactant molecules are in a hypothetical unit mole fraction, behaving as if they are at infinite dilution, and the final state is the micelle, itself. In Table 2 the changes in the Gibbs free energy ($\Delta G^\circ_\mathrm{m}$), enthalpy ($\Delta H^\circ_\mathrm{m}$), and entropy ($\Delta S^\circ_\mathrm{m}$) of micellization at the standard state of the unit mole fraction are reported for cases in the presence of various amounts of *n*-alcohols. It can be noted that in the absence of additives, the free energy of micellization becomes more negative with increasing temperature. That is, the formation of micelles becomes relatively more spontaneous at higher temperature. Even in the presence of alcohols, the variation is similar, though the cmcs increase with temperature. The reason for such an observation was suggested earlier

Table 2. Free Energy ($\Delta G^\circ_{\mathrm{m}}$), Enthalpy ($\Delta H^\circ_{\mathrm{m}}$), Entropy ($\Delta S^\circ_{\mathrm{m}}$), Heat Capacity ($\Delta C^\circ_{\mathrm{p.m.}}$), Transfer Enthalpy ($\Delta H^\circ_{\mathrm{m.tr.}}$), and Transfer Heat Capacity ($\Delta C^\circ_{\mathrm{p.m.tr.}}$), of Micellization of $C_{12}E_{10}$ Aqueous Solution in Presence of *n*-Alcohols at 40 °C

n-Alcohols (%)	$-\Delta G^\circ_{\mathrm{m}}$ /kJ mol^{-1}	$\Delta H^\circ_{\mathrm{m}}$ /kJ mol^{-1}	$\Delta S^\circ_{\mathrm{m}}$ /J mol^{-1} K^{-1}	$\Delta C^\circ_{\mathrm{p.m.}}$ /kJ mol^{-1} K^{-1}	$-\Delta H^\circ_{\mathrm{m.tr.}}$ /kJ mol^{-1}	$\Delta C^\circ_{\mathrm{p.m.tr.}}$ /J mol^{-1} K^{-1}
EtOH						
0.0	40.4	21.0	196	−0.12	—	—
0.25	40.2	−25.8	46.0	−0.02	46.8	0.10
0.50	40.4	−37.3	10.0	−0.01	58.2	0.11
0.75	40.5	−29.9	34.0	−0.02	50.8	0.10
1.0	40.7	−36.3	14.0	−0.01	57.3	0.11
n-PrOH						
0.25	40.1	−34.0	19.5	−0.01	54.9	0.12
0.50	40.6	−36.3	13.7	−0.03	57.3	0.09
0.75	40.6	−32.5	26.0	−0.03	53.5	0.10
1.0	40.7	−38.2	8.0	−0.03	59.2	0.09
n-BuOH						
0.05	39.6	−22.3	55.3	−0.02	43.3	0.10
0.10	39.7	−17.8	70.0	−0.01	38.8	0.11
0.25	39.9	−17.4	72.0	−0.01	38.3	0.12

to be that changes in the magnitude of the logarithm of the cmc are more than compensated by changes in the values of R and T.[7] However, $\Delta G^\circ_{\mathrm{m}}$ in the presence of *n*-BuOH is less spontaneous than that in the presence of EtOH and *n*-PrOH. The standard enthalpy of micellization ($\Delta H^\circ_{\mathrm{m}}$) and the standard entropy of micellization ($\Delta S^\circ_{\mathrm{m}}$) were computed from reasonably linear $\Delta G^\circ_{\mathrm{m}}$ vs T plots, the slope being $\Delta S^\circ_{\mathrm{m}}$. $\Delta H^\circ_{\mathrm{m}}$ was then computed by using the following equation:[44]

$$\Delta H^\circ_{\mathrm{m}} = \Delta G^\circ_{\mathrm{m}} + T\Delta S^\circ_{\mathrm{m}}. \tag{3}$$

The enthalpy of micellization is endothermic, though it becomes exothermic in the presence of *n*-alcohols. The exothermicity may be due to the additive-surfactant attractive interaction,[43] which shows the stability of the system, and is expected to increase upon an increase in the concentration of alcohols. However, the values for EtOH and *n*-PrOH systems are lower than that in the *n*-BuOH system. The exothermic and endothermic characteristics of micellization are specific to the surfactant, the additive and the temperature of micellization, though it is independent of temperature in the present system.[10,17,44] The entropy of micellization ($\Delta S^\circ_{\mathrm{m}}$) is positive, indicating that the micellization process is somewhat entropy-dominated. However, it should be noted that micellization process is exothermic in these systems, and therefore the formation of a micelle is very much favoured in the presence of alcohols. Shaw[45] suggested that the high entropy change may be due to the freedom of movement of the hydrocarbon chain in the core of the micelle. However, it is not very clear how this movement of hydrocarbon chains in the core of the micellar aggregates can have a dominating effect on $\Delta S^\circ_{\mathrm{m}}$, which is a macroscopic property.[7] Rosen[38] has stated that the presence of hydrated OE groups of the surfactant introduces structure in the liquid phase, and that removal of the surfactant via micellization results in an increase in the overall randomness,[46] and hence an increase in entropy. Micelle formation also makes water molecules free due to the absence of a hydrophobic interaction.

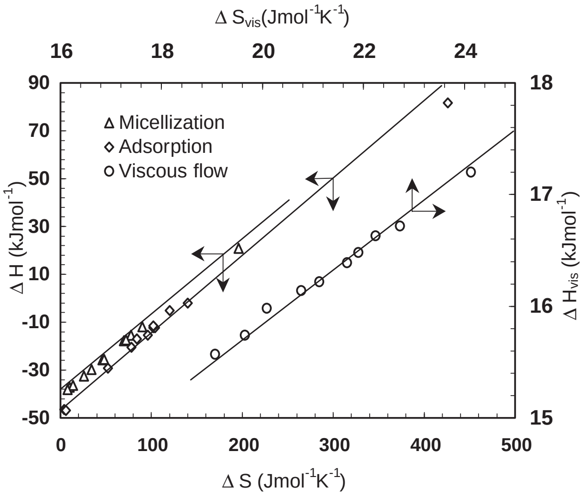

Fig. 3. Enthalpy–entropy compensation plot for all systems taken together.

A linear correlation between $\Delta H^\circ_{\mathrm{m}}$ and $\Delta S^\circ_{\mathrm{m}}$ was seen in all of these systems (Fig. 3) taken together. Such a compensation phenomenon was suggested by Lumry et al.[47] The slope of the line, i.e., the compensation temperature (T_{C}), was found to be 308 K, which is close to the expected values of an aqueous medium[48] at 270 to 294 K. The observed value is slightly higher from the suggested values due to additive effects. The small variations that we observe here as well as those observed earlier[11] may be due to differences in the bulk structural property of the solution from that of water.

The heat capacities for micelle formation ($\Delta C^\circ_{\mathrm{p.m.}}$) were also evaluated from a plot of $\Delta H^\circ_{\mathrm{m}}$ vs T, the slope being $\Delta C^\circ_{\mathrm{p.m.}}$ (Table 2). The variation in the heat capacities with concentration of the additives, in all cases, did not show any regularity; this was also observed earlier by calorimetric studies.[49] The transfer enthalpies ($\Delta H^\circ_{\mathrm{m.tr.}}$) and transfer heat capacities ($\Delta C^\circ_{\mathrm{p.m.tr.}}$) of a micelle from water to an aqueous solution were obtained using the relations

$$\Delta H^{\circ}_{\text{m.tr.}} = \Delta H^{\circ}_{\text{m}}(\text{aq.additive}) - \Delta H^{\circ}_{\text{m}}(\text{aq.}), \quad (4)$$

$$\Delta C^{\circ}_{\text{p.m.tr.}} = \Delta C^{\circ}_{\text{p.m.}}(\text{aq.additive}) - \Delta C^{\circ}_{\text{p.m.}}(\text{aq.}). \quad (5)$$

The transfer enthalpies of micelle were found to be negative (Table 2). Such negative transfer enthalpies were also reported for the transfer of NaCl and amino acids from water to aqueous urea solutions.[50] This shows that the transfer of hydrophilic groups (OE) from water to aqueous solutions is exothermic, the strong OE–*n*-alcohols interaction being the dominating cause. The transfer heat capacities of micellization ($\Delta C^{\circ}_{\text{p.m.tr.}}$) for the transfer of a micelle from water to an additive-containing solution are positive, indicating increased hydration of the micelles due to a greater extent of interaction between OE and *n*-alcohol present in the solution. $\Delta C^{\circ}_{\text{p.m.tr.}}$ show a maximum for all systems as a function of the concentration of *n*-alcohols, which was also observed by other workers.[19,51] It is probably due to changes in the micellar structure.

It was shown by Treiner[53] that for dilute solutions of polar additives in an aqueous surfactant solution at cmc, the following general form of the classical Stechenow equation is well obeyed:[53]

$$\log(\text{cmc}_{\text{w}}/\text{cmc}_{\text{w+A}}) = K_{\text{M}}m', \quad (6)$$

where cmc_{w} and $\text{cmc}_{\text{w+A}}$ are the cmc values of the surfactant in both the absence and presence of additives, K_{M} is a constant and m' is the molality of the additive. In a dilute solution, with respect to a polar additive, the constant K_{M} takes the form

$$K_{\text{M}} = 1/2[k_{\text{s}}^{\text{N}} + qM/2.303 \times 1000], \quad (7)$$

where k_{s}^{N} is the familiar Stechenow constant, or salting-out constant, q is the ideal partition coefficient of the solute between the micelle and water, and M is the solvent molecular weight. The salting-out constant is calculated by the empirical relationship[53]

$$k_{\text{s}}^{\text{N}} = 0.637 - 0.014n(\text{CH}_2) - 0.1464r, \quad (8)$$

where $n(\text{CH}_2)$ is the number of methylene groups in the linear hydrocarbon chain of the surfactant ($C_{12}E_{10}$) and r is the hard-sphere diameter of the additives calculated from the van der Waal's volumes. The r values for EtOH, *n*-PrOH, and *n*-BuOH are 4.66 Å, 5.12 Å, and 5.84 Å respectively.[54]

The thus-calculated k_{s}^{N} values for all of the three additives are negative, indicating a salting-in effect in an aqueous surfactant solution. Also, the K_{M} values obtained at all ratios of alcohols are given in Table 3. Equation 6 does not seem to be true for all systems studied at higher temperatures of 313 and 318 K. Though in most cases a straight line was obtained, they do not pass through the origin, and hence those results are not shown.

The thus-calculated ideal partition coefficient (q) using the K_{M} and k_{s}^{N} values tend to zero for all systems. Such a q value suggests that additives do not penetrate the micelle, i.e., the additives are not partitioned between the micelle and the solvent. This is generally observed in predominantly hydrophilic solutes, as shown by the increase in cmc.[55] The variation of the cmc with the addition of these solutes may be entirely ascribed to the effect of these additives on the bulk solvent properties. Therefore, the additives, by interacting with both the surfactant monomers and the solvent molecules, induce a shift of the equilibrium between the micelles and the surfactant monomers in favor of the later. Since these additives are nonpenetrating ones (i.e., they are not partitioned between micelles and the bulk solvent), they can probably be assumed to locate themselves at the micelle-solvent interface. In other words, many of the additives are present in the solvent, which are in contact with the hydrophilic group of the surfactant. However, Manabe et al.[23] have shown that the partition of alcohols increases between an ionic surfactant micelle and the solvent water as the alcohol chain length increases. We also made a similar observation, since *n*-pentanol seems to become partitioned between nonionic surfactant micelles and water (Rakshit et al. unpublished work).

Table 3. Value of Constant K_{M} (L mol^{-1}) for $C_{12}E_{10}$ in Presence of *n*-Alcohols (C_2–C_4) at 303 and 308 K

n-Alcohol	303 K	308 K
EtOH	1.65	0.67
n-PrOH	1.44	1.09
n-BuOH	4.26	1.38

The air/water interface of a surfactant solution is well populated[48] by the adsorbed molecules. Accordingly, it has been shown that the concentration of the surfactant is always more at the air/water interface than that in the bulk. The surface excess concentration (Γ_{max}) can be calculated by Gibbs adsorption equation,[56]

$$\Gamma_{\text{max}}\ (\text{mol cm}^{-2}) = (-1/nRT)(\mathrm{d}\gamma/\mathrm{d}\ln C), \quad (9)$$

where Γ_{max}, γ, R, T, and C are the surface excess, surface tension, gas constant, absolute temperature, and concentration respectively; n is a constant and for nonionic surfactant is taken to be 1. The slope of the tangent at the given concentration of the γ vs $\log C$ plot was used to calculate Γ_{max}. This was obtained by using curve fitting to a polynomial of the form $y = ax^2 + bx + c$ in the Microsoft Excel program. The R^2 (Regression coefficient) value of the fit lies between 0.9783 and 0.9997. The slope was then calculated. The surface excess is an effective measure of the molecular adsorption at the air/liquid interface. The Γ_{max} values are presented in Table 4. From the surface excess quantity it is possible to calculate the minimum area per molecule (A_{min}) by the relation

$$A_{\text{min}}(\text{nm}^2) = 10^{14}/N\Gamma_{\text{max}}, \quad (10)$$

where N is Avogadro's number. In general, the surface excess quantity increases with an increase in temperature. This is because as the temperature increases, the hydration of the OE segment of the nonionic surfactant decreases, and hence the tendency to locate at the air/water interface is higher. The magnitude of A_{min} is very low, suggesting that the air/water interface is a close-packed one, and therefore the orientation of the surfactant molecule is almost perpendicular to the surface.

The effectiveness of a surface-active molecule is measured by the surface pressure (π_{cmc}) at the cmc, i.e., $\pi_{\text{cmc}} = \gamma_{\text{o}} - \gamma_{\text{cmc}}$, where γ_{o} and γ_{cmc} are the surface tension of water and the surface tension at the cmc, respectively.

The value of the free energy of adsorption at an air/water interface ($\Delta G^{\circ}_{\text{ad}}$) was calculated using the relation[57]

Table 4. Maximum Surface Excess ($\Gamma_{\max}$) of $C_{12}E_{10}$ in the Presence of *n*-Alcohols at Different Temperatures

n-Alcohols (%)	$\Gamma_{\max} \times 10^{10}/\text{mol cm}^{-2}$											
	EtOH				*n*-PrOH				*n*-BuOH			
	303 K	308 K	313 K	318 K	303 K	308 K	313 K	318 K	303 K	308 K	313 K	318 K
0.0	2.3	2.4	3.3	3.6	—	—	—	—	—	—	—	—
0.10	—	—	—	—	—	—	—	—	2.54	2.83	3.13	2.32
0.05	—	—	—	—	—	—	—	—	1.92	3.59	3.30	3.13
0.25	3.17	3.66	3.24	2.74	3.66	2.19	2.85	4.1	4.37	3.20	2.18	3.09
0.50	2.93	3.39	3.24	3.16	2.51	3.86	5.06	2.87				
0.75	3.45	2.87	2.86	2.57	3.21	2.71	4.22	3.80				
1.0	1.17	1.70	1.11	2.93	2.29	2.97	3.94	2.39				

Table 5. Free Energy ($\Delta G^\circ_{\text{ad}}$), Enthalpy ($\Delta H^\circ_{\text{ad}}$), Entropy ($\Delta S^\circ_{\text{ad}}$) of Adsorption and Effect of Alcohol on Micellization and Adsorption of $C_{12}E_{10}$ Aqueous Solution at 40 °C

n-Alcohols (%)	$-\Delta G^\circ_{\text{ad}}$ /kJ mol^{-1}	$\Delta H^\circ_{\text{ad}}$ /kJ mol^{-1}	$\Delta S^\circ_{\text{ad}}$ /J mol^{-1} K^{-1}	$\Delta G^\circ_{\text{m}} - \Delta G^\circ_{\text{ad}}$ /kJ mol^{-1}	$\Delta H^\circ_{\text{m}} - \Delta H^\circ_{\text{ad}}$ /kJ mol^{-1}	$T(\Delta S^\circ_{\text{m}} - \Delta S^\circ_{\text{ad}})$ /kJ mol^{-1}
EtOH						
0.0	54.5	81.6	426	14.1	−60.6	−72.0
0.25	44.5	−12.3	102	4.3	−13.5	−17.5
0.50	45.6	−15.5	96	5.2	−21.8	−26.9
0.75	45.0	−12.4	104	4.5	−17.5	−21.9
1.0	46.0	−2.1	140	5.3	−34.2	−39.4
n-PrOH						
0.25	46.6	−29.3	55	6.5	−4.7	−11.2
0.50	46.1	−25.3	66	5.5	−11.0	−11.5
0.75	43.8	−20.5	78	3.2	−12.0	−16.3
1.0	44.7	−25.5	61	4.0	−12.7	−16.7
n-BuOH						
0.05	43.5	−16.9	84	3.9	−5.4	−2.0
0.10	44.3	−5.2	120	4.6	−12.0	−15.6
0.25	44.1	−11.5	102	4.2	−5.9	−9.4

$$\Delta G^\circ_{\text{ad}} = RT \ln \text{cmc} - N\pi_{\text{cmc}}A_{\min}, \tag{11}$$

Table 5 gives the thermodynamic parameters of adsorption, i.e., $\Delta G^\circ_{\text{ad}}$, $\Delta H^\circ_{\text{ad}}$, and $\Delta S^\circ_{\text{ad}}$ of $C_{12}E_{10}$ in the presence of EtOH, *n*-PrOH, and *n*-BuOH at an air/water interface.

It can be observed from Table 5 that the standard free energy of adsorption ($\Delta G^\circ_{\text{ad}}$) values are negative throughout, indicating that the adsorption of the surfactant at the air/water interface takes place spontaneously in the presence of *n*-alcohols. The standard entropy ($\Delta S^\circ_{\text{ad}}$) and enthalpy ($\Delta H^\circ_{\text{ad}}$) of adsorption were obtained from the slope of the $\Delta G^\circ_{\text{ad}}$–$T$ plot, the slope being $\Delta S^\circ_{\text{ad}}$. $\Delta H^\circ_{\text{ad}}$ was calculated by Eq. 3 at a given temperature.

As expected, the values of the free energy of adsorption ($\Delta G^\circ_{\text{ad}}$) are more negative than their corresponding free energy of micellization ($\Delta G^\circ_{\text{m}}$), indicating that when a micelle is formed, work has to be done to transfer the excess surfactant molecules present in the monomeric form at the surface to the micellar stage through the aqueous medium. Under this condition, the air/solution interface is saturated with monomeric surfactant molecules.

Both in the presence and in the absence of additives, $\Delta G^\circ_{\text{ad}}$ becomes more negative, in general, with an increase in temperature, suggesting that adsorption at higher temperature is more facile. $\Delta H^\circ_{\text{ad}}$ in a pure aqueous solution is positive, as is $\Delta H^\circ_{\text{m}}$. However, in the presence of *n*-alcohols, the results are different. This indicates that these additives interact with a surfactant's hydrophilic group, which is exothermic, as was shown earlier for NaCl by Jha and Ahluwalia[50] from calorimetric measurements. The standard entropy change of adsorption ($\Delta S^\circ_{\text{ad}}$) in a pure aqueous solution is positive, which is also the case in the presence of *n*-alcohols. This may be ascribed to a larger freedom of motion of the hydrocarbon chain at the interface, and also due to the mixing of surfactant monomers with additive molecules. The $\Delta S^\circ_{\text{ad}}$ values are all positive and higher than the $\Delta S^\circ_{\text{m}}$ values for the same system. This reflects the greater freedom of motion of the hydrocarbon chain at the planner air/aqueous solution interface compared to that in the relatively cramped interior beneath the convex surface of the micelle. This is reasonable, since groups at the micellar surface would not experience the space restriction imposed upon the groups extending into the interior. The values of $\Delta H^\circ_{\text{ad}}$ are more than those of $\Delta H^\circ_{\text{m}}$, which indicates that strong bond formation occurs between OE and aqueous alcohol molecules in the processes of adsorption at an air/aqueous solution interface than in the micellization process. A linear correlation between $\Delta H^\circ_{\text{ad}}$ and $\Delta S^\circ_{\text{ad}}$ was observed while taking all systems together (Fig. 3) with $T_{\text{c}} = 300$ K.

From Eqs. 2 and 11, it follows that[57]

Table 6. Values of Traube's Constant ($\sigma \times 10^{-7}$) for $C_{12}E_{10}$ in Presence of *n*-Alcohols (C_2–C_4) at Different Temperatures

n-Alcohols	EtOH				*n*-PrOH				*n*-BuOH			
(%)	303 K	308 K	313 K	318 K	303 K	308 K	313 K	318 K	303 K	308 K	313 K	318 K
0.0	5.5	6.8	12.5	25.7								
0.05	—	—	—	—	—	—	—	—	2.1	1.7	1.8	2.1
0.1	—	—	—	—	—	—	—	—	3.3	2.6	2.5	3.0
0.25	2.8	2.5	2.6	2.1	2.3	14.9	6.0	1.7	2.5	2.6	2.3	2.0
0.5	4.9	4.3	4.1	3.5	9.6	2.5	4.9	2.9				
0.75	3.8	3.3	3.2	3.0	2.4	9.7	2.0	2.7				
1.0	5.1	4.2	4.7	4.7	6.2	3.8	2.0	2.6				

$$N\pi_{\mathrm{cmc}}A_{\mathrm{cmc}} = (\Delta G^\circ_{\mathrm{m}} - \Delta G^\circ_{\mathrm{ad}}), \tag{12}$$

i.e., the $\pi_{\mathrm{cmc}}A_{\mathrm{cmc}}$ product expresses the work involved in transferring the surfactant molecule from a monolayer at zero surface pressure to the micelle. The $\Delta G^\circ_{\mathrm{m}} - \Delta G^\circ_{\mathrm{ad}}$ values are listed in Table 5. It is apparent that the "work of transfer", which measures the ease of adsorption to form a monolayer at zero surface pressure relative to the ease of micellization, shows a change in the presence of *n*-alcohols. The positive values for this work of transfer stem from two sources: 1) a greater positive entropy change upon adsorption than upon micellization and 2) a smaller positive enthalpy change upon adsorption than upon micellization. Table 5 also lists $\Delta H^\circ_{\mathrm{m}} - \Delta H^\circ_{\mathrm{ad}}$ and $T(\Delta S^\circ_{\mathrm{m}} - \Delta S^\circ_{\mathrm{ad}})$ values. It can be seen that the contribution of entropy to $\Delta G^\circ_{\mathrm{m}} - \Delta G^\circ_{\mathrm{ad}}$ is higher than enthalpy. As reported earlier,[57] the steric factors inhibit micellization more than they inhibit adsorption at the air/aqueous solution interface. Also, a greater dehydration of an OE chain is required for micellization than for adsorption at an air/aqueous solution interface. This implies that the space available to the hydrophilic group at the surface of the micelle is more restricted than at the planar air/aqueous solution interface.

It has been suggested by Weiner and Zografi[58] that

$$\Delta G^\circ_{\mathrm{ad}} = -RT\ln\sigma, \tag{13}$$

where "σ" is known as Traube's constant,[59] and is defined by the relation

$$\sigma = (\partial\pi/\partial C)_{c\to 0} = -(\partial\gamma/\partial C)_{c\to 0}. \tag{14}$$

This means that σ is the rate of change of the surface pressure per unit concentration change at infinite dilution. The σ values are given in Table 6. It can be noted that the σ of pure $C_{12}E_{10}$ is similar to the data given in Table 4 of Meguro et al.,[60] thereby suggesting that our adsorption data are reasonable. We computed the effect of different aliphatic *n*-alcohols on σ (Table 6). It seems that there is not much difference in the σ values as a function of *n*-alcohol, probably because the *n*-alcohol concentrations are not very high.

Cloud points (CP) are a manifestation of the solvation/desolvation phenomenon in a non-ionic surfactant solution. The desolvation of the hydrophilic group of the surfactant leads to the formation of a cloud in the surfactant solution. For a $C_{12}E_{10}$ (1%) solution, the CP is 88 °C.[36,38] EtOH and *n*-PrOH slightly increase the CP, because they help in the solvation of hydrophilic group of $C_{12}E_{10}$. A higher cloud point has been observed, indicating that the micelles are much hydrated. On the other hand, *n*-BuOH and *n*-PenOH are not very hydrophilic (solubility decreases with increase in alkanol chain length) and the CP sharply decreases. This results in an attraction between the OE micelles with these cosolvents, and thus increasing their aggregation and thereby raising the cloud point. CP is also a manifestation of an intermicellar interaction. It has been suggested that water is present in between the micelles as some type of bridge.[22] If the hydrophilic additives replace this bridge water, then the CP may or may not increase. However, if BuOH or PenOH are present in place of a bridge water, then the CP is expected to decrease. We observed the same phenomenon (Fig. 2).

The structural and dynamic properties can be elucidated by the viscous flow. The intrinsic viscosity ($|\eta|$) decreases with an increase in temperature (Table 7), indicating pronounced micellar dehydration. This is anticipated as the micelles become compact with an increase in temperature due to dehydration of the OE chains.[61] In the presence of alcohol, a similar behaviour with respect to the temperature was observed. However, the $|\eta|$ value increased due to cosolubilization upon increasing the concentration as well as increasing the chain length of alcohols. From the intrinsic viscosity, the hydrated micellar volume (V_{h}) has been computed by the relation[30,62]

$$V_{\mathrm{h}} = |\eta| M_{\mathrm{m}}/2.5N, \tag{15}$$

where N is Avogadro's number and M_{m} is the micellar molecular weight of the OE chain, which is calculated by[62]

$$M_{\mathrm{m}} = A_{\mathrm{n}}M = (1025/n - 5.1)M, \tag{16}$$

where A_{n} is the aggregation number and M is the molecular weight of $C_{12}E_n$. The micellar molecular weight evaluated here, where $n = 10$ by Eq. 16, is 6.1×10^4.

The volume of the hydrocarbon core (V_{c}) and the volume of the paliasde layer of ethylene oxide units (V_{OE}) were calculated using

$$V_{\mathrm{c}} = A_{\mathrm{n}}V = 10^{24}A_{\mathrm{n}}M_{\mathrm{c}}/dN \tag{17}$$

and

$$V_{\mathrm{OE}} = V_{\mathrm{h}} - V_{\mathrm{c}}, \tag{18}$$

where V is the volume of the alkyl chain length in a single $C_{12}E_n$ molecule, M_{c} is the molecular weight (170) and d is the density (0.802 g/cm^3) of the corresponding liquid *n*-alkane at 25 °C.[7,12] Both the hydrated micellar volume (V_{h}) and the volume of the palisade layer of the OE (V_{OE}) units increase as the concentration of *n*-alcohol increases. This may be because the *n*-alcohol, which is somewhat identical to the OE part of a nonionic surfactant, assumes itself to be part of it.[63]

Table 7. Intrinsic Viscosity, Micellar Hydration Volume (V_h), and Volume of the Oxyethylene Chain (V_{OE}) of $C_{12}E_{10}$ (5% w/v) in the Presence and Absence of *n*-Alcohols (C_2–C_4) at Different Temperatures

n-Alcohols (% w/v)	308 K			313 K			318 K		
	$\lvert\eta\rvert$ /cm^3 g^{-1}	V_h /$\times10^4$ Å^3	V_{OE} /$\times10^4$ Å^3	$\lvert\eta\rvert$ /cm^3 g^{-1}	V_h /$\times10^4$ Å^3	V_{OE} /$\times10^4$ Å^3	$\lvert\eta\rvert$ /cm^3 g^{-1}	V_h /$\times10^4$ Å^3	V_{OE} /$\times10^4$ Å^3
EtOH									
0.0	7.10	28.75	25.32	6.85	27.75	24.32	6.77	27.41	23.98
0.1	7.37	29.84	26.41	6.94	28.10	24.89	6.80	27.53	24.10
0.5	7.38	29.89	26.46	7.13	28.87	25.44	7.07	28.62	25.19
1.0	7.57	30.25	26.82	7.41	30.00	26.57	7.20	29.15	25.72
n-PrOH									
0.1	7.20	29.15	25.72	7.02	28.43	25.00	6.95	28.14	24.71
0.5	7.58	30.69	27.26	7.13	28.88	25.45	7.10	28.75	25.32
1.0	8.09	32.76	29.33	7.69	31.15	27.72	7.57	30.65	27.22
n-BuOH									
0.1	7.38	29.88	26.45	7.05	28.54	25.11	6.95	28.14	24.71
0.5	7.84	31.75	28.32	7.47	30.24	26.81	7.01	28.38	24.95
1.0	8.09	32.76	29.33	7.97	32.28	28.85	7.75	31.38	27.95

Table 8. Thermodynamic Activation Parameters for Viscous Flow of $C_{12}E_{10}$ (5% w/v) in the Presence and Absence of *n*-Alcohols

n-Alcohols (% w/v)	$\Delta G^{\#}_{vis}$ (308 K) /kJ mol^{-1}	$\Delta H^{\#}_{vis}$ /kJ mol^{-1}	$\Delta S^{\#}_{vis}$ /J mol^{-1} K^{-1}
EtOH			
0.0	9.68	15.7	20
0.1	9.72	16.7	23
0.5	9.72	16.2	21
1.0	9.74	16.1	21
n-PrOH			
0.1	9.70	15.6	19
0.5	9.74	16.5	22
1.0	9.78	16.6	22
n-BuOH			
0.1	9.72	16.4	22
0.5	9.77	17.2	24
1.0	9.79	16.0	20

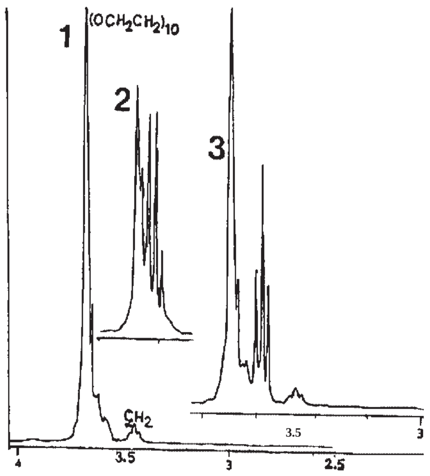

Fig. 4. ^{1}H NMR spectra of 1) 0.1 M $C_{12}E_{10}$, 2) $C_{12}E_{10}$:PrOH 1:1, 3) $C_{12}E_{10}$:*n*-PenOH 1:1 in D_2O at 25 °C and 300 MHz.

A similar behaviour was suggested in the presence of PEG 400.[7] Upon increasing the temperature, both V_h and V_{OE} decrease. This is because water and the aquo-*n*-alcohol media become a poorer solvent at higher temperatures. Viscosity measurements also support the presence of non-spherical aggregates (Table 7).

The thermodynamic activation parameters for the viscous flow were evaluated using the Frenkel–Eyring eqation,[30,64]

$$\ln(\eta V/Nh) = \frac{\Delta H^{\#}_{vis}}{RT} - \frac{\Delta S^{\#}_{vis}}{R}, \tag{19}$$

where V, N, h, and R are the molar volumes, Avogadro number, Plank constant, and the universal gas constant, respectively. From the slope and the intercepts of the straight line obtained by plotting $\ln(\eta V/Nh)$ against $1/T$, the activation enthalpy ($\Delta H^{\#}_{vis}$) and the activation entropy ($\Delta S^{\#}_{vis}$) for the viscous flow were calculated.

All of the thermodynamic activation parameters for the systems are presented in Table 8. In all of these systems, $\Delta G^{\#}_{vis}$ is positive, indicating nonspontaneous viscous flow. All alcohols seem to have almost the same effect on $\Delta G^{\#}_{vis}$. The $\Delta H^{\#}_{vis}$ values indicate that the system accepts energy for the viscous flow, which is expected. The entropies of activation of the viscous flow ($\Delta S^{\#}_{vis}$) are positive in all cases, indicating disorderliness in these flowing systems.

NMR studies of the surfactant solution in the presence of alcohols were conducted to determine the electronic atmosphere around the protons and the additive effects on the atmosphere. Peak assignments were made for CH_3–$C_\beta H_2$–$(CH_2)_n$–$C_\alpha H_2$–$(OCH_2CH_2)_m$–OH[6,65] with the 3.69 ppm peak corresponding to the oxyethylene $(OCH_2CH_2)_m$ moiety, 3.45 for $C_\alpha H_2$, 1.57 for $C_\beta H_2$, 0.88 for CH_3, and 1.29 ppm peak for methylene protons $(CH_2)_n$. The changes in the chemical shifts due to the addition of alcohols were monitored, and the chemical shifts due to the oxyethylene group showed a significant change compared to other peaks (Fig. 4). The proton spin–lattice relaxation time (T_1) was measured for a pure micellar system in D_2O. The T_1 value varies, depending on the chemical environment. The T_1 values of the surfactant in the absence of any additives was found to be as follows OE: 0.47, $C_\alpha H_2$ 0.37, $(CH_2)_n$ 0.45, CH_3 0.97, and $C_\beta H_2$ 0.39 (second). There is small down-field chemical shift of OE units signals from 3.69 to 3.71 ppm, which show that these hydrophilic molecules interact with micelles through intermolecular hydrogen bonding. The extent of intermolecular H-bonding was decreased by dilution with a nonpolar solvent and with an increase of temperature; this effect is seen in the viscosity data. These results show that surfactant aggregates grow in size. Figure 4 illustrates that the main OE signal become broader, and also spit when the [surfactant] to [alcohols] ratio was 1:1. This means that the micelles grow and their shape changes. This is also shown by an increase in the intrinsic viscosity. A NMR study indicates that the alcohols effect the hydrophilic group, i.e., OCH_2CH_2 and the electronic atmosphere of the OCH_2CH_2 group at the palisade layer are also affected. However, in *n*-PenOH it seems that the alcohol molecules have entered the micellar core. We have not conducted more quantitative studies.

University Grants Commission-Department of Atomic Energy (UGC-DAE) Consortium for Scientific Research (Formerly: Inter University Consortium-for Department of Atomic Energy (IUC-DAE) Facilities), Government of India, Bhabha Atomic Research Centre (BARC), Mumbai, is gratefully acknowledged for financial support [IUC/CRS/M-70/2000/346]. Dr. R. V. Jasra, Dy. Director, Central Salt and Marine Chemical Research Institute (CSMCRI), Bhavnagar India deserves our grateful thanks for NMR measurements.

References

1 M. J. Schick, "Nonionic Surfactant, Physical Chemistry," Marcel Dekker, New York (1987), Vol. 23.

2 L. Magid, "Solution Chemistry of Surfactant," ed by K. L. Mittal, Plenum, New York (1979), Vol. 1, p. 427.

3 K. Shinoda, "Colloidal Surfactant," ed by K. Shinoda, T. Nakagawa, B. Tamamushi, and T. Isemura, Academic Press, New York (1963), p. 1.

4 P. Mukerjee and A. Roy, *J. Phys. Chem.*, **67**, 190 (1963).

5 A. Holtzer and M. F. Emerson, *J. Phys. Chem.*, **73**, 26 (1969).

6 S. B. Sulthana, P. V. C. Rao, S. G. T. Bhat, and A. K. Rakshit, *J. Phys. Chem.*, **102**, 9653 (1998).

7 S. B. Sulthana, S. G. T. Bhat, and A. K. Rakshit, *Langmuir*, **13**, 4562 (1997).

8 S. P. Moulik, *Curr. Sci.*, **714**, 5 (1996).

9 M. Mao, J. Huang, B. Zhu, and J. Ye, *J. Phys. Chem.*, **106**, 219 (2002).

10 B. G. Sharma and A. K. Rakshit, "Surfactant in Solution," ed by K. L. Mittal, Plenum, New York (1989), Vol. 7.

11 B. G. Sharma and A. K. Rakshit, *J. Colloid Interface Sci.*, **129**, 139 (1989).

12 A. K. Rakshit and B. Sharma, *Colloid Polym. Sci.*, **281**, 45 (2003).

13 K. Meguro, M. Ueno, and K. Esumi, "Nonionic Surfactant, Physical Chemistry," Marcel Dekker, New York (1987), p. 151.

14 K. Deguchi, T. Mizuno, and K. Meguro, *J. Colloid Interface Sci.*, **48**, 474 (1974).

15 J. E. Adderson and G. C. Butler, *J. Pharm. Pharmacol.*, **24**, 130 (1972).

16 M. J. Schick and A. H. Gilbert, *J. Colloid Interface Sci.*, **20**, 464 (1965).

17 A. H. Saiyad, S. G. T. Bhatt, and A. K. Rakshit, *Colloid Polym. Sci.*, **276**, 913 (1998).

18 T. Kawaguchi and T. Hanandka, *J. Colloid Interface Sci.*, **151**, 41 (1992).

19 K. Mukherjee, C. Mukherjee, and S. P. Moulik, *J. Phys. Chem.*, **98**, 4713 (1994); A. Callaghan, R. E. Alexander, and R. Palepu, *Langmuir*, **9**, 34 (1993).

20 R. De Lisi, S. Milioto, and A. Inglese, *J. Phys. Chem.*, **95**, 3322 (1991).

21 A. Moller, P. Lang, and G. H. Findenegg, *J. Phys. Chem.*, **102**, 8258 (1998).

22 A. K. Rakshit and R. M. Palepu, *Recent Dev. Coll. Inter. Res.*, **1**, 203 (2003).

23 M. Manabe, M. Koda, and K. Shirahama, *Bull. Chem. Soc. Jpn.*, **48**, 3553 (1975).

24 M. Manabe, H. Kawamura, A. Yamashita, and S. Tokunaya, *J. Colloid Interface Sci.*, **115**, 147 (1987).

25 M. Manabe and M. Koda, *J. Colloid Interface Sci.*, **77**, 189 (1980).

26 S. Candau and R. Zana, *J. Colloid Interface Sci.*, **84**, 206 (1981).

27 M. Kahlweit and G. Bosse, *J. Phys. Chem.*, **95**, 5580 (1991).

28 R. Zana, S. Yiu, C. Satrazielle, and P. Lianos, *J. Colloid Interface Sci.*, **80**, 208 (1981).

29 C. Treiner, "Solubilization in Surfactant Aggregates," ed by S. D. Christian and J. F. Scamehorn, Marcel Dekker, New York (1995).

30 K. S. Sharma and A. K. Rakshit, *J. Surfactant Deterg.*, **7**, 305 (2004).

31 K. S. Sharma, S. R. Patil, A. K. Rakshit, K. Glenn, M. Doiron, R. M. Palepu, and P. A. Hassan, *J. Phys. Chem. B*, **34**, 12804 (2004).

32 K. S. Sharma, C. Rodgers, R. M. Palepu, and A. K. Rakshit, *J. Colloid Interface Sci.*, **262**, 482 (2003).

33 K. S. Sharma and A. K. Rakshit, *Indian J. Chem.*, **43A**, 265 (2004).

34 M. Corti, C. Minero, and V. Degeorgio, *J. Phys. Chem. B*, **88**, 309 (1994).

35 H. H. Kohler and J. Strnad, *J. Phys. Chem. B*, **9**, 7628 (1990).

36 K. S. Sharma, S. R. Patil, and A. K. Rakshit, *Colloids Surf., A*, **219**, 67 (2003).

37 F. M. Menger and J. S. Keiper, *Angew. Chem., Int. Ed.*, **39**, 1906 (2000).

38 M. J. Rosen, "Surfactants and Interfacial Phenomena," John Wiley, New York (1988).

39 S. B. Sulthana, P. V. C. Rao, S. G. T. Bhat, T. Y. Nakano, G. Sugihara, and A. K. Rakshit, *Langmuir*, **16**, 980 (2000); S. B. Sulthana, S. G. T. Bhat, and A. K. Rakshit, *Colloids Surf.*, **111**, 57 (1996).

40 K. Shinoda, *Adv. Colloid Interface Sci.*, **41**, 81 (1992).

41 A. Berthod, S. Tomer, and J. G. Dorsey, *Talanta*, **55**, 69 (2001).

42 S. Schito, "Nonionic Surfactant, Physical Chemistry," Marcel Dekker, New York (1987), p. 885.

43 J. M. delRio, C. Pombo, G. Ptieto, F. Sarmiento, V. Mosquera, and M. N. Jones, *J. Chem. Thermodyn.*, **26**, 879 (1994).

44 D. Atwood and A. T. Florence, "Surfactant System, Their Chemistry Pharmacy and Biology," Champman and Hall, London

(1983).

45 D. J. Shaw, "Introduction to Colloid and Surface Chemistry," 4th ed, Herworths-Heinmann, London (1992).

46 J. Marrignan, P. Basserau, and F. Delord, *J. Phys. Chem.*, **90**, 645 (1986).

47 P. Lumry and S. Rajender, *Biopolymer*, **9**, 1125 (1970).

48 J. H. Clint, "Surfactant Aggregation," Blakie, London (1992), p. 6.

49 R. DeLisi, G. Calogero, and T. L. V. Nvenzo, *J. Colloid Interface Sci.*, **95**, 428 (1983).

50 R. Jha and J. C. Ahluwalia, *J. Chem. Soc., Faraday Trans.*, **89**, 3465 (1993).

51 S. Causi, R. DeLisi, and S. Milioto, *J. Phys. Chem.*, **95**, 5664 (1990).

52 C. Treiner, *J. Colloid Interface Sci.*, **93**, 33 (1983).

53 C. Treiner, *J. Colloid Interface Sci.*, **118**, 244 (1987).

54 J. T. Edward, *J. Chem. Educ.*, **47**, 261 (1970).

55 C. Treiner, *J. Colloid Interface Sci.*, **90**, 444 (1982).

56 A. W. Adamson, "Physical Chemistry of Surface," 2nd ed (1967), p. 90.

57 M. J. Rosen, W. Cohen, M. Dahanayake, and Y. Hua, *J. Phys. Chem.*, **86**, 541 (1982).

58 N. D. Weiner and G. Zografi, *J. Pharm. Sci.*, **54**, 436 (1965).

59 I. Traube, *Ann. Chem.*, **265**, 271 (1891).

60 M. Ueno, Y. Takasawa, H. Miyashige, Y. Tabata, and K. Meguro, *Colloid Polym. Sci.*, **259**, 761 (1981).

61 P. Bahadur and K. Pandya, *Langmuir*, **8**, 2666 (1992).

62 K. Saito, M. Abe, and T. Sato, *J. Am. Oil Chem. Soc.*, **70**, 717 (1993).

63 I. J. Lin and J. A. Metzu, *J. Phys. Chem.*, **75**, 3000 (1971).

64 R. Joseph, S. G. Devi, and A. K. Rakshit, *Polym. Int.*, **1**, 25 (1991).

65 A. A. Ribeiro and A. Dennis, *J. Phys. Chem.*, **81**, 959 (1977).