Chapter VI

Investigation of the Properties of Polyoxyethylene (10) lauryl ether: $C_{12}E_{10}$ in Aquo Alcohols-rich Region.

SYNOPSIS

The effect of 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 NMP techniques. Critical micelle concentrations (CMC) were determined by the surface tension measurement in presence of n-alcohols (C_2-C_4) at different concentrations and temperatures. The Gibbs free energy, enthalpy and entropy of micellization (ΔG_m^o, ΔH_m^o, ΔS_m^o) and adsorption at air/water interface ($\Delta G_{ad}^o, \Delta H_{ad}^o, \Delta S_{ad}^o$) have been computed and discussed. An enthalpy-entropy compensation effect has been observed with an isostructural temperature of about 300K for micellization and interfacial adsorption. The transfer enthalpies and heat capacities of micelle from water to aqueous n-alcohols solution were also computed. Intrinsic viscosity gives the hydrated micellar volume (V_h), volume of the hydrocarbon core (V_c) and the volume of the palisade layer of OE unit (V_{OE}). Viscosity data support the formation of non-spherical micelle of $C_{12}E_{10}$ in absence and presence of n-alcohols. The spin-lattice proton relaxation time (T_1) in aqueous micellar region and ^1H NMR was also used to study the behaviour of OE micelles in absence and presence of alcohols. There was slight rise in the cloud point (CP) by lower alcohols. However a decrease was seen for n-BuOH and n-PenOH.

INTRODUCTION

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 micelle, where there properties are different from those of the non-aggregated monomer molecules. In other words, the surfactants exhibit a very wide richness of different phase structures. The study of these systems is a matter of serious scientific and technological interests from both the theoretical as well as experimental points of view.

The aggregational and surface properties of surfactant in solution are very sensitive and are influenced or controlled by solvent polarity and type, temperature, pressure, pH and presence of various foreign substances (cosolvent) [1-12].The nature of cosolvent decides the direction of the changes in the cmc of the surfactants. There are some organic cosolvents which when present in some greater amounts even cause disappearance of the 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]. As the hydrophobic association and water structure destruction have a mutual correlation, they influence solvent structure and dielectric constant and can also undergo direct interaction 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]etc on the micellization process has been studied. However there are some aspects, which warrant further investigation. Intermediate chain alcohols are commonly added to surfactant solutions in order to improve their characteristics. One reason for this is that alcohols oppose the strong hydrophilicity of these surfactants molecules. Candau et.al [26] show that alcohols may be distributed between aqueous and micellar phase and may accumulate both in palisade layer and inside the micelle hydrophobic core, thus favoring the stability of the system. Alcohols also exhibit the 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 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 noticeable change in micellar shape and its transport properties. On the one hand, it causes the micelle swelling and on the other hand, there is decrease of micelles surface charge density and increase of the degree of ionization. Also it has been recognized that the partition coefficient of the neutral solute in micellar solution can be computed with reasonable confidence from cmc determination[29]. Moreover, cmc-based method could be of great value in the evaluation of the effect of structure on the micellar solubilization of additive[6].

Most of publications referred above address the possible effect of alcohols on ionic surfactant, only few are on nonionic surfactant. However, we have not seen a comprehensive thermodynamic and structural study of oxyethylated nonionic, $C_{12}E_{10}$ surfactant in presence of lower to medium chain alcohols. Nonionic surfactant of the polyoxyethylene type are chosen because of their wide used in detergency, cosmetics, emulsion formation like shampoo, conditioners, paints as well as in pharmaceutical dosages and in drug delivery system etc. and will continue in the future due to their higher solubility at low temperature. Hence, we report the effect of n-alcohols (C_2-C_4) on interfacial, thermodynamic, viscosity, cloud point and 1H NMR properties of $C_{12}E_{10.}$ The thermodynamic activation parameters for the viscous flow were evaluated using the Frenkel-Eyring equation. We also determined the Traube's constant (σ) which is the rate of change of surface pressure per unit concentration. Intrinsic viscosity also gives the hydrated micellar volume (V_h), 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 solvent have been determined. By NMR, we also studied the spin lattice proton relaxation time (T_1) in aqueous micellar solution and 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[30]. For physicochemical properties, all solutions were prepared by using triple distilled deionized water, having electric conductance 2-3 μScm^{-1} at 303K. The solvent D_2O of 99.96% purity, have been used for ^1H NMR experiments.

Methods: The cmc was determined by the Surface tension (γ) measurement using a du-Nouy ring tensiometer (S.C.Dey and Co. Calcutta, India) at different temperatures of 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 temperatures were maintained (±0.1K) constant by circulating thermostated water through a jacketed vessel containing the solution. The concentration of solution was varied by adding aliquots of stock solution of known concentration to the known volume of solution in the vessel by using a Hamilton microsyringe.

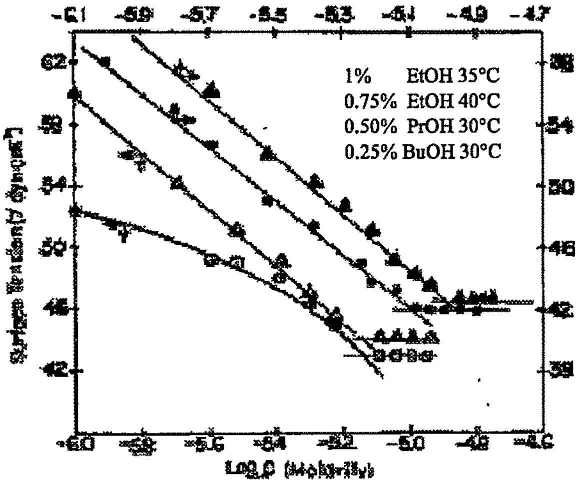

Figure 1. Representative plots of surface tension (γ) vs $Log_{10}C$ (Molarity) in presence of n-alcohols at different temperature.

For each set of experiments the ring was cleaned by heating it in alcohol flame. The standard deviation of the mean in γ was ±0.5%. The measured surface tension values were plotted as a function of the log of surfactant concentration[31]. Representative plots of surface tension (γ) against log concentration of surfactant in solution ($Log_{10}C$) are shown in Figure 1. The reproducibility (standard deviation of the mean) of the surface tension vs concentration curve was checked by duplicate runs and in the cmc it was found to be less then ±1.0%, calculated from the experimental cmc data from at least two runs.

The flow time of surfactant solution and water were measured with the help of Ubbelohde suspended level viscometer[32,33]. The temperatures were 308, 313 and 318 K and were maintained within ± 0.01K in a thermostated bath. Samples were carefully filtered before injection into viscometer. Density of surfactant solution has been determined with a pyknometer at a given temperature. The change in the viscosity of surfactant solution (5% w/v) at 0.1, 0.5 and 1.0% (v/v) concentration of n-alcohols (C_2-C_4) were studied. Three consecutive flow times agreeing within ± 0.02s were taken and the mean flow time was considered.

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

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

where limit to zero concentration indicates that intermolecular interactions are absent. 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 between 2.5-4 cm^3 g^{-1} for globular particles[35]. In this article we have calculated $|\eta|$ without taking the zero concentration limit as we did earlier[36].

Cloud points (CP) of $C_{12}E_{10}$ ether in presence of n-alcohols (C_2-C_5) were determined by the experimental method described earlier[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 Figure 3. These are the averages of the appearance and disappearance temperatures of the cloud, the difference being no greater than 0.4°C under constant stirrings. The error in CP is less than ± 2 %.

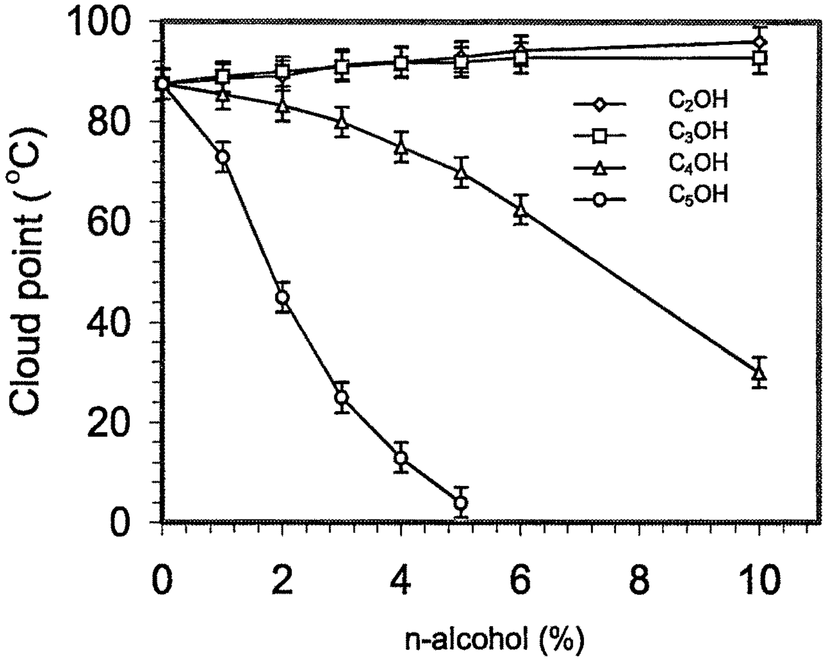

Figure 3. Variation of Cloud point of $C_{12}E_{10}$ (1%) with weight % of n- alcohols.

Proton NMR measurements were carried out in deuterium oxide (D_2O, 99.96 atom % D, Aldrich USA) solvent at room temperature ($25^{\circ}C \pm 0.5$). The solution for spectra were prepared by taking 0.1M $C_{12}E_{10}$ solution mixed with n-alcohols ratio of 1:1(w/v), density of alcohols taken as standard at room temperature. Proton NMR spectra were recorded with Brucker Advance DPX 200 MHz and 300 MHz FT NMR spectrophotometer. ^1H NMR chemical shifts were referred to internal TMS. The spin-lattice relaxation time, T_1 was measured by inversion recovery technique with a (180°-τ-90°, FID) pulse sequence. The relaxation times were calculated by the nonlinear least square fit using the instruments inbuilt software[6].

RESULTS AND DISCUSSION

Surface tension is a fast, nondestructive to the surfactant molecules and dependable means to determine cmc[37]. Below cmc surfactant molecules position themselves in both at air/water interface and in the bulk and thus lower the surface tension. Above cmc, any added surfactant joins a micelle in the bulk. At this point the interface is saturated with surfactant molecules. The cmc values of $C_{12}E_{10}$ in 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 increase in temperature in absence of any alcohols. This is generally seen in case of nonionic surfactant and was observed earlier also[38]. But in presence of n- alcohols the cmcs increase with increasing temperature in all cases studied. This was observed earlier in presence of different additives[6,7,39]. The cmc increase with the increase in temperature in the presence of different additives, which is generally the characteristic of 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 cmc values are very low from the expected values probably because we are using commercial sample supplied by Aldrich.[41]

At cmc the micelles are formed as a result of hydrophobic interaction.[41] supplemented with the London dispersion force of attraction.[43] In the case of nonionic surfactant without any additive the cmc decrease with increasing temperature due to the dehydration of the hydrophilic moiety of the surfactant molecule as also due to breaking of water structure. In the presence of additive however the reverse is seen, which indicate 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. This indicates the interaction between the surfactant molecules and n-alcohols, which is possible due to the interaction between the head groups of the surfactants through hydration and a small repulsive interaction between the OE units of surfactant and OH group of n-alcohols. Alcohols also form intermolecular hydrogen bonds with solvent water molecules and there by promote the water structure, which is also promoted by the hydrophobic group of the surfactant molecules due to hydrophobic interaction. The above are the reasons for decrease in the cmc values of the surfactant.[38] In the presence of additives, as the temperature increases the solvent structure is broken and hence the cmc increases. Also on increasing temperature the dehydration of surfactant molecule takes place, i.e. the hydrophilicity decreases or hydrophobicity increases and hence the cmcs of nonionic surfactant decreases.

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

Alcohol (% v/v)	Critical Micelle Concentration (μm)*											
	EtOH				n-PrOH				n-BuOH			
	303	308	313	318	303	308	313	318	303	308	313	318K
0.0*	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	-	-	-	-

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

Table 2. Free energy (ΔG_m^o), Enthalpy (ΔH_m^o), Entropy (ΔS_m^o), Heat Capacity ($\Delta C_{p.m.}^0$), Transfer Enthalpy ($\Delta H_{m.tr.}^0$), and Transfer Heat Capacity ($\Delta C_{p.m.tr.}^0$), of Micellization of $C_{12}E_{10}$ Aqueous Solution in Presence of n-Alcohols at 40°C.

n-alcohols % EtOH	$-\Delta G_m^o$ (kJmol^{-1})	ΔH_m^o (kJmol^{-1})	ΔS_m^o (Jmol^{-1}K^{-1})	$\Delta C_{p.m.}^0$ (kJmol^{-1}K^{-1})	$-\Delta H_{m.tr.}^0$ (kJmol^{-1})	$\Delta C_{p.m.tr.}^0$ (Jmol^{-1}K^{-1})
0.0	40.4	20.95	196	-0.120	-	-
0.25	40.2	-25.80	46.0	-0.018	46.75	0.102
0.50	40.4	-37.27	10.0	-0.012	58.22	0.108
0.75	40.5	-29.86	34.0	-0.02	50.81	0.100
1.0	40.7	-36.32	14.0	-0.012	57.27	0.108
n-PrOH						
0.25	40.1	-34.00	19.5	-0.004	54.90	0.116
0.50	40.6	-36.30	13.7	-0.03	57.30	0.090
0.75	40.6	-32.46	26.0	-0.024	53.52	0.096
1.0	40.7	-38.19	8.0	-0.03	59.14	0.090
n-BuOH						
0.05	39.6	-22.30	55.3	-0.024	43.30	0.096
0.10	39.7	-17.79	70.0	-0.002	38.74	0.112
0.25	39.9	-17.36	72.0	-0.006	38.31	0.114

The Gibbs free energy of micellization (ΔG_m^o) for a nonionic surfactant is directly proportional to the ln cmc (cmc in mole fraction scale) at constant temperature by the following relation [44]

$$\Delta G_m^o = RT \ln cmc \tag{2}$$

where R and T are usual constants. The initial standard state being a hypothetical sate where the surfactant molecules are in hypothetical unit mole fraction behaving as if they are at infinite dilution and the final state being the micelle itself. In Table 2 the Gibbs free energy (ΔG_m^o), enthalpy (ΔH_m^o) and entropy (ΔS_m^o) of micellization at the standard state of unit mole fraction are reported in 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 become relatively more spontaneous at higher temperature. Even in the presence of alcohols the variation is similar though the cmc increase with temperature. The reason for such observation was suggested earlier as the changes in the magnitude of the logarithm of the cmc is more than compensated by the change in the values of RT.[7] However the ΔG_m^o in presence of n-BuOH is less spontaneous than in presence of EtOH and n-PrOH. The standard enthalpy of micellization (ΔH_m^o) and the standard entropy of micellization (ΔS_m^o) were computed from the reasonably linear ΔG_m^o vs T plots, the slope being ΔS_m^o.

The ΔH_m^o was then computed by using the following equation [44]

$$\Delta H_m^o = \Delta G_m^o + T\Delta S_m^o \tag{3}$$

The enthalpy of micellization is endothermic though it becomes exothermic in the presence of n-alcohols. The exothermicity may be due to additive-surfactant attractive interaction[43], which show the stability of system and was expected to increase on increase in the concentration of alcohols. However the values for EtOH and n-PrOH systems are lower than 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 (ΔS_m^o) 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 micelle is very much favoured in presence of alcohols. Shaw[45] has suggested that the high entropy change may be due to the freedom of movement of the hydrocarbon chain in the core of the micelle. Rosen[38] has stated that the presence of hydrated OE groups of the surfactant introduces structure in the liquid phase and that the removal of the surfactant via micellization result 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 hydrophobic interaction.

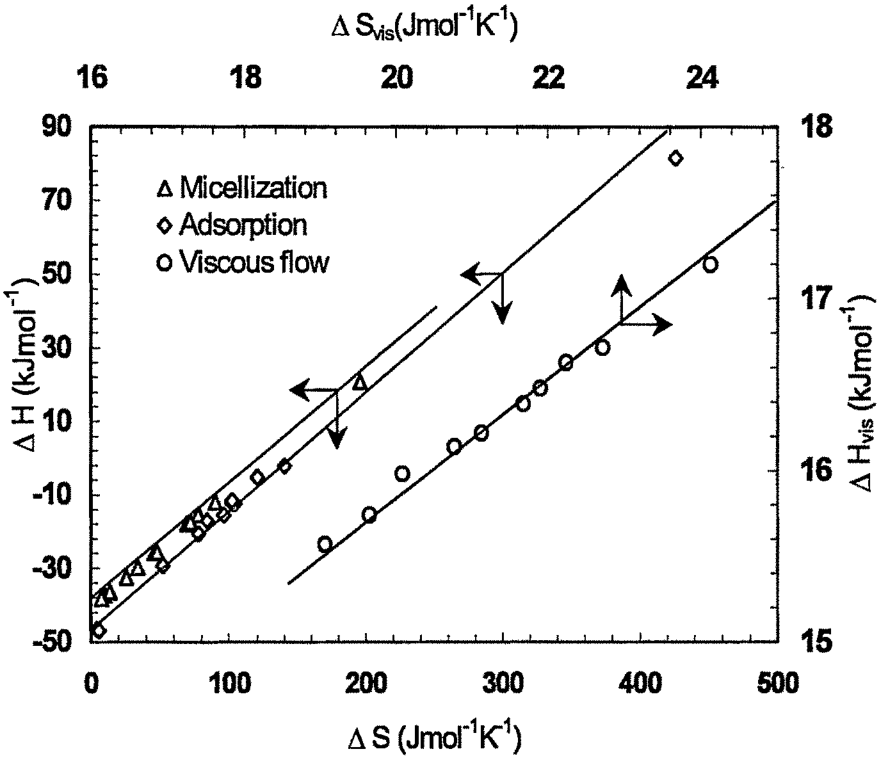

Figure 2.Enthalpy-entropy compensation plot for all systems together.

A linear correlation between ΔH_m^o and ΔS_m^o was seen in all these system (Figure 2) 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. It was close to the expected values of aqueous medium[48] 270 to 294 K. The observed value is a little higher from the suggested values due to additive effects. The small variations, we observe here as well as those observed earlier[11] may be due to the difference of the bulk structural property of the solution from that of water.

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

$$\Delta H^{0}_{m.tr.} = \Delta H^{0}_{m}(aq.additive) - \Delta H^{0}_{m}(aq.) \qquad (4)$$

$$\Delta C^{0}_{p.m.tr.} = \Delta C^{0}_{p.m.}(aq.additive) - \Delta C^{0}_{p.m.}(aq.) \qquad (5)$$

The transfer enthalpies of micelle were found to be negative (Table 2). Such negative transfer enthalpies were also reported from the transfer of NaCl and amino acids from water to aqueous urea solution [50], It shows that transfer of hydrophilic groups (OE) from water to aqueous solution is exothermic where as that of hydrophobic group is endothermic, the strong OE-n-alcohols interaction being the dominating cause. The transfer heat capacities of micellization $\Delta C^{0}_{p.m.tr.}$ for the transfer of micelle from water to additive containing solution are positive indicating increased hydration of micelles due to greater extent of hydrogen bonding between OE and n-alcohol present in the solution. $\Delta C^{0}_{p.m.tr.}$ show a maximum for all system as a function of concentration of n-alcohols, and was observed by other workers also [19, 51,52] and is probably due to micellar structure changes.

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

$$\log cmc_w / cmc_{w+A} = K_M m' \tag{6}$$

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

$$K_M = \frac{1}{2}\left[k_s^N + \frac{qM}{2.303 \times 1000}\right] \tag{7}$$

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

$$k_s^N = 0.637 - 0.014n(CH_2) - 0.1464r \tag{8}$$

where n (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 Vander Waals volumes. The r values for EtOH, n-PrOH and n-BuOH are 4.66 Å, 5.12 Å and 5.84Å respectively[54].

Table 3 Constant K_M ($Lmol^{-1}$) for $C_{12}E_{10}$ in Presence of n-Alcohols (C_2-C_4)at 303 and 308K.

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

The k_s^N values thus calculated for all the three additives are negative indicating a salting-in effect in 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 temperature of 313 and 318 K. Though in most cases a straight line was obtained but they do not pass through the origin and hence those results are not shown.

The ideal partition coefficient q thus obtained using the K_M and k_s^N values tend to Zero for all the 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. There for, the additives by interacting with both the surfactant monomers and the solvent molecules induce a shift of the equilibrium between the micelles and surfactant monomers in favor of the later. Since these additives are nonpenetrating ones (i.e. they are not partitioned between micelles and bulk solvent), they can probably be assumed to locate themselves at the micelle-solvent interface. In other words, a large amount of the additives are present in the solvent, which are in contact with the hydrophilic group of the surfactant.

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

alcohols (%)	$\Gamma_{max} \times 10^{10} (molcm^{-2})$											
	Et OH				n-Pr OH				n-Bu OH			
	303	308	313	318	303	308	313	318	303	308	313	318K
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				

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 surface than that in the bulk. The surface excess concentration ($\Gamma_{\max}$) can be calculated by Gibbs adsorption equation [56]

$$\Gamma_{\max}(molcm^{-2}) = \left(-1/nRT\right)\left(d\gamma/d\ln C\right) \tag{9}$$

where $\Gamma_{\max}$, 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. This was obtained by using curve fitting to a polynomial of the form $y = ax^2 + bx + c$ in 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 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.

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

where N is Avogadro's number. In general the surface excess quantity increases with 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 much less than 1.5 nm^2, 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.

Table 5. Free energy ΔG^o_{ad}), Enthalpy (ΔH^o_{ad}), Entropy (ΔS^o_{ad}) of Adsorption and n-Alcohol Structural Effect on Micellization and Adsorption of $C_{12}E_{10}$ Aqueous Solution at 40°C.

n-alcohols % EtOH	$-\Delta G^o_{ad}$ (kJmol^{-1})	ΔH^o_{ad} (kJmol^{-1})	ΔS^o_{ad} (Jmol^{-1}K^{-1})	$\Delta G^o_m - \Delta G^o_{ad}$ (kJmol^{-1})	$\Delta H^o_m - \Delta H^o_{ad}$ (kJmol^{-1})	$T(\Delta S^o_m - \Delta S^o_{ad})$ (kJmol^{-1})
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	55.3	6.5	-4.7	-11.2
0.50	46.1	-25.3	66.5	5.5	-11.0	-11.5
0.75	43.8	-20.5	78.0	3.2	-12.0	-16.3
1.0	44.7	-25.5	61.3	4.0	-12.7	-16.7
n-BuOH						
0.05	43.5	-16.9	84.0	3.9	-5.4	-2.0
0.10	44.3	-5.24	120	4.6	-12.0	-15.6
0.25	44.1	-11.5	102	4.2	-5.9	-9.4

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

The value of free energy of adsorption at air/water interface (ΔG^o_{ad}) was calculated using the relation [57]

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

In table 5 the thermodynamic parameters of adsorption i.e. ΔG^o_{ad}, ΔH^o_{ad} and ΔS^o_{ad} of $C_{12}E_{10}$ in presence of EtOH, n-PrOH and n-BuOH at air/water interface are presented.

It is observed from Table 5 that the standard free energy of adsorption (ΔG^o_{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 (ΔS^o_{ad}) and enthalpy (ΔH^o_{ad}) of adsorption were obtained from the slope of the ΔG^o_{ad} –T plot, the slope being ΔS^o_{ad}. ΔH^o_{ad} was calculated by eqn. 3 at a given temperature.

As expected the free energy of adsorption, ΔG^o_{ad} are more negative than their corresponding free energy of micellization ΔG^o_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, ΔG^o_{ad} becomes more negative, in general, with increase in temperature, suggesting that the adsorption at higher temperature is more facile. ΔH^o_{ad} in pure aqueous solution is positive as well as ΔH^o_m. But 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 Ahluwalia et. al [50] from calorimetric measurements. The standard entropy change of adsorption (ΔS^o_{ad}) in pure aqueous solution is positive, so is the case in 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 ΔS^o_{ad} values are all positive and higher than the ΔS^o_m values for the same system. This may reflect 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 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 value of ΔH^o_{ad} are more than ΔH^o_m which indicate that strong bonds formation between OE and aqueous alcohol molecule in the processes of adsorption at air/aqueous solution interface than in the micellization process. A linear correlation between ΔH^o_{ad} and ΔS^o_{ad} was observed taking all systems together (Figure 2) with $T_c = 300$ K.

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

$$N\pi_{cmc}A_{cmc} = \left(\Delta G^o_m - \Delta G^o_{ad}\right) \tag{12}$$

i.e. the $\pi_{cmc}A_{cmc}$ product expresses the work involved in transferring the surfactant molecule from a monolayer at zero surface pressure to the micelle. $\Delta G^o_m - \Delta G^o_{ad}$ 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, show change in presence of n-alcohols. The positive values for this work of transfer stem from two sources: 1) the greater positive entropy change upon adsorption than upon micellization 2) the smaller positive enthalpy change upon adsorption than upon micellization. Table 5 also lists $\Delta H^o_m - \Delta H^o_{ad}$ and $T\left(\Delta S^o_m - \Delta S^o_{ad}\right)$ values. It can be seen that the contribution of entropy to $\Delta G^o_m - \Delta G^o_{ad}$ 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 OE chain is required for micellization than for adsorption at the 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,

$$\Delta G^o_{ad} = -RT \ln \sigma \tag{13}$$

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

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

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

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

%	Et OH				n-Pr OH				n-Bu OH			
n-alcohols	303	308	313	318K	303	308	313	318K	303	308	313	318K
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				

Cloud points (CP) are the manifestation of the solvation/desolvation phenomena in non-ionic surfactant solution. The desolvation of the hydrophilic group of the surfactant leads to the formation of cloud in the surfactant solution. For $C_{12}E_{10}$ (1%) solution the CP is 88°C [38,61].

Most of the studies of CP are with 1% (w/v) surfactant solutions and we have also done the same. EtOH and n-PrOH slight increases the CP, because they help in the solvation of hydrophilic group of $C_{12}E_{10}$. They have the property of breaking water structure as well as making it. A higher cloud point is 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 attraction between OE micelles with these cosolvents and thus increasing their aggregation and thereby raising the cloud point. CP is the manifestation of intermicellar interaction. It is known[34] that water is present in between the micelles as some type of a bridge. If the hydrophilic additives replaces this bridge water, then the CP may or may not increase. However if BuOH or PenOH are present in place of bridge water, then the CP is expected to decrease and we see the same phenomenon (Figure 3).

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			313			318K		
% Et OH	$\|\eta\|$ (cm^3/g)	V_h (x10^4 Å^3)	V_{OE} (x10^4 Å^3)	$\|\eta\|$ (cm^3/g)	V_h (x10^4 Å^3)	V_{OE} (x10^4 Å^3)	$\|\eta\|$ (cm^3/g)	V_h (x10^4 Å^3)	V_{OE} (x10^4 Å^3)
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-Pr OH									
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-Bu OH									
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

Structural and dynamic properties can be elucidated by viscous flow. The intrinsic viscosity [η] decreases with increase in temperature (Table 7) indicating pronounced micellar dehydration. This is anticipated as micelles become compact with an increase in temperature due to dehydration of OE chains [62]. In presence of alcohol similar behaviour with respect to temperature was observed. However $|\eta|$ value increase due to the cosolubilization on increasing the concentration as well as increasing the chain length of alcohols. From intrinsic viscosity, the hydrated micellar volume (V_h) have been computed by the relation [63]

$$V_h = |\eta| M_m / 2.5N \tag{15}$$

where N is Avogadro number and M_m is the micellar molecular weight of the OE chain which is calculated by [63]

$$M_n = A_n M = (1025/n - 5.1)M \tag{16}$$

where A_n is the aggregation number and M is the molacular weight of $C_{12}E_n$. The micellar molecular weight evaluated here where n=10 by eq 16 is 6.1 x 10^4

The volume of the hydrocarbon core (V_c) and the volume of the paliasde layer of ethylene oxide units (V_{OE}) have been calculated using the following equations

$$V_c = A_n V = 10^{24} A_n M_c / dN \tag{17}$$

and

$$V_{OE} = V_h - V_c \tag{18}$$

where V is the volume of alkyl chain length in a single $C_{12}E_n$ molecule, M_c is the molecular weight (170) and d is the density (0.802g/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 OE (V_{OE}) units increase as the concentration of n-alcohol increases. This may be because the n-alcohol which is somewhat identical to OE part of nonionic surfactant assume them selves to be part of it[64]. Similar behaviour was suggested in presence of PEG 400[7]. On increasing temperature both

V_h and V_{OE} decrease. This was because of water and the aquo-n-alcohol medium become poorer solvent at higher temperature. Viscosity measurements also support the presence of non-spherical shape aggregates. The shape factor for aggregate calculated from intrinsic viscosity has been found to be same obtained independently from the axial ratios obtained from SANS measurement. SANS measurement could not observe the effect of alcohol on micelle of $C_{12}E_{10}$. Only n-PenOH among the alcohols used seems to be going into the micelle core.

The thermodynamic activation parameters for the viscous flow have been evaluated using the Frenkel-Eyring eqation [65]

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

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 $\ln\left(\eta V/_{Nh}\right)$ against $1/_{T}$, activation enthalpy ($\Delta H^{\#}_{vis}$) and activation entropy ($\Delta S^{\#}_{vis}$) for the viscous flow were calculated.

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

Conc. of n-alcohol % EtOH	$\Delta G^{\#}_{vis}$ (308K) (kJmol^{-1})	$\Delta H^{\#}_{vis}$ (kJmol^{-1})	$\Delta S^{\#}_{vis}$ (Jmol^{-1}K^{-1})
0.0	9.68	15.74	19.65
0.1	9.72	16.72	22.72
0.5	9.72	16.22	21.12
1.0	9.74	16.14	20.77
n-PrOH			
0.1	9.70	15.57	19.06
0.5	9.74	16.48	21.90
1.0	9.78	16.63	22.24
n-BuOH			
0.1	9.72	16.39	21.67
0.5	9.77	17.20	24.13
1.0	9.79	15.98	20.08

All the thermodynamic activation parameters for the system are presented in Table 8. In all these system $\Delta G^{\#}_{vis}$ is positive indicating nonspontaneous viscous flow. All alcohols seem to have almost same effect on $\Delta G^{\#}_{vis}$. $\Delta H^{\#}_{vis}$ values indicate that the system accept energy for the viscous flow which is expected. Entropies of activation of the viscous flow ($\Delta S^{\#}_{vis}$) are positive in all cases indicating that there are ordered structures when the solutions flow and the order is almost similar.

The NMR studies of the surfactant solution in presence of alcohols were done to determine the electronic atmosphere around the protons and the additive effects on the atmosphere. The peak assignments were done for CH_3-$C_\beta H_2$- $(CH_2)_n$-$C_\alpha H_2$-$(OCH_2CH_2)_m$-OH [6,66] 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 chemical shifts due to the addition of alcohols were monitored and chemical shifts due to oxyethylene group showed a significant change compared to other peaks (Figure 4). The protron spin-lattice relaxation time (T_1) was measured for pure micellar system in D_2O. T_1 value varies, depending on the chemical environment. T_1 values of the surfactant in absence of any additives was found 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 3.71ppm which show that these hydrophilic molecules interact with micelle through intermolecular hydrogen bonding. The extent of intermolecular H-bonding was decreased by dilution with a nonpolar solvent and with increase of temperature, this effect is seen in viscosity data. These results show that surfactant aggregates grow in size. Figure 4 shows the main OE signal gets broader and also spitted when the [surfactant] to [alcohols] ratio was 1:1. This means that the micelles grow and there shapes change.

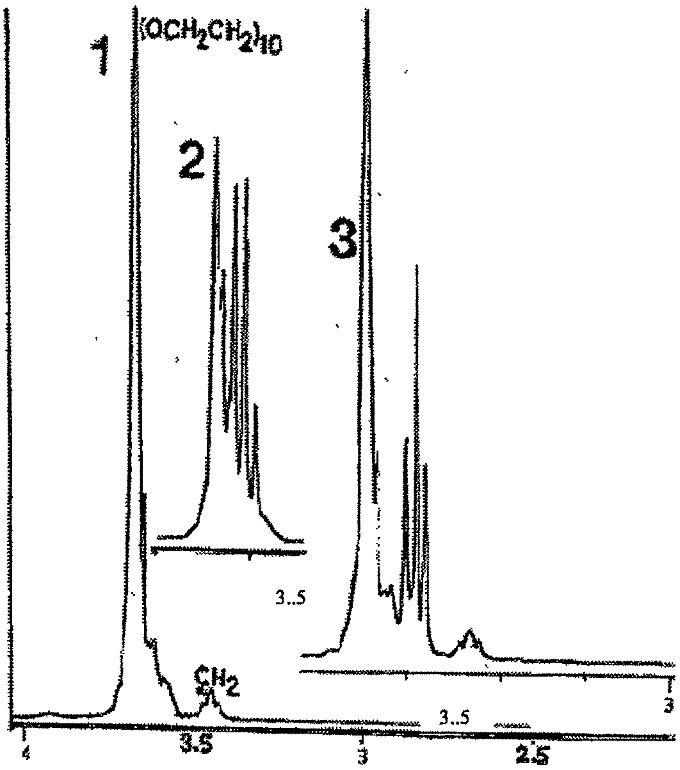

Figure 4. ^{1}H NMR spectra of 1) 0.1 M $C_{12}E_{10}$ 2) $C_{12}E_{10}$: PrOH 1:1
3) $C_{12}E_{10}$: n-PenOH 1:1 in D_2O at 25°C and 300 MHz

This is also shown by increase in intrinsic viscosity study of same system. The NMR study indicates that the alcohols are effecting the hydrophilic group i.e. OCH_2 CH_2. and the electronic atmosphere of the OCH_2CH_2 group at the palisade layer are getting affected. However in n-PeOH it seems that the alcohol molecules have entered the micellar core. We have not done more quantitative studies.

CONCLUSIONS

The thermodynamic properties of micellization and adsorption at air/solution interface of decaoxyethylenemonododecyl ether in presence of n-alcohols (C_2-C_4) at various concentrations and different temperatures were determined. The micellization process was exothermic in presence of n-alcohols and endothermic in pure aqueous solutions. A linear correlation between ΔH^o_m and ΔS^o_m as well as ΔH^o_{ad} and ΔS^o_{ad} was observed in these systems, which suggests that micellization as well as adsorption at air/water interface are dependent on the bulk structure of the solvent. Large positive ΔS^o_{ad} values in the presence of additives reflect greater freedom of motion of the hydrocarbon chain at the planar air/solution interface. The heat capacity of micellization was also determined which reflect the micellar structural transition. The transfer of OE group from water to aqeous solution is exothermic, whereas that of hydrophobic group is endothermic. Increase in the cloud point of $C_{12}E_{10}$ in presence of EtOH or n-PrOH show solvation of the micelle by water or by hydrophilic EtOH or n-PrOH and hence requirement of high temperature for CP, while in presence of n-BuOH or n-PeOH where hydrophilicity is low i.e. less solvation of micelle, the intermicellar interaction becomes dominant and the cloud point shows reverse effect. The ideal partition coefficient found to be zero for all system. Viscosity also shows that micelle become compact with increase in temperature due to dehydration of OE chain. The positive value for the work of transfer suggests the greater positive entropy change upon adsorption than upon micellization. The effect of the nature of chain length of n-alcohols (C_2-C_5) on the micellar structure of $C_{12}E_{10}$ have been studied using ^{1}H NMR. NMR and transfer enthalpy of micelles show strong intermolecular H-bonding between OE and n-alcohols.

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