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1) Thermodynamics of Micellization of a Nonionic Surfactant Myrj 45 : Effect of Additives.
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2) Studies of the Effect of Additives of the Surface and Thermodynamic Properties of Poly[oxyethylene (10)] Lauryl Ether in Aqueous Solution.
Shireen B Sulthana, S.G.T. Bhat and A.K. Rakshit ***Langmuir***, **13**, 4562, 1997.

3) Interfacial and Thermodynamic Properties of Mixed Anionic / Nonionic Binary Surfactant System.
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Thermodynamics of micellization of a non-ionic surfactant Myrj 45: effect of additives

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Abstract

Critical micelle concentrations of the non-ionic surfactant Myrj 45 in aqueous solution at various temperatures (35, 40, 45 and 50°C) were determined by the iodine solubilization method. A few systems were also studied by direct surface tension measurement. The effect of additives, e.g PEG 400, sucrose, acetamide and urea, on the CMC was studied The free energy, enthalpy and entropy of micellization were determined A negative free energy and a positive entropy of micellization were observed for all the systems The micellization process was exothermic in all cases except in aqueous solution without additives, where the process was endothermic. An enthalpy–entropy compensation effect was observed for all the systems Transfer enthalpies and heat capacities were evaluated from enthalpy of micellization data. The transfer enthalpy $\Delta H_{\mathrm{m,tr}}$ was negative throughout, indicating the transfer of hydrophilic groups from water to the aqueous additive solutions. A maximum observed in the plot of $\Delta C_{\mathrm{p,m,tr}}$–concentration of additives was ascribed to a micellar structural transition.

Keywords: Critical micelle concentration; Micellization; Myrj 45; Non-ionic surfactants; Thermodynamic properties

1. Introduction

In last few years, extensive structural, kinetic and thermodynamic studies have been performed on surfactant–water systems [1] including the effect of additives on micellization [2–10]. The formation of micelles by ionic and non-ionic surfactants is a well-established fact, and thermodynamic data of micellization under varying conditions are required in order to understand the phenomenon.

The aggregation and surface properties of surfactants in solutions are dependent on the nature and amount of additives. The effect of different additives having an OH group, such as PEG [4–6], *n*-alcohols [11,12], sucrose [7,8], ethylene glycol [9,10], etc. on the micellization process of both ionic and non-ionic surfactants has been studied. Similar studies with DMF and DMSO [13], acetamide [4], urea [14,15], cyclohexane and dioxane [9,16] have also been reported. Although there are a reasonably large number of such studies on non-ionic surfactants like Brij 35, Triton X-100, alkyl poly(ethylene oxides), dodecyl (polyoxyethylene) glycol ethers etc. [4–7,16,17] based on the effect of additives, we have not found such a detailed study of Myrj 45 (polyoxyethylene(8) monostearate) in aqueous solution in the literature. However, in pursuance of our interest in non-ionic surfactants [5,18–21], we decided to study the thermodynamics of micellization of Myrj 45 in aqueous solution in the presence of additives such

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as PEG 400, sucrose, acetamide and urea, as we are interested in various other properties including the microemulsion formation of Myrj 45.

The additives were chosen by keeping some wide-ranging properties in mind. For example PEG is a short-chain, low-molecular-weight, water-miscible oligomer, extensively used in the preparation of cosmetics and pharmaceuticals Acetamide has a peptide linkage, i.e. a –CONH group, and is very highly polar [5]. Sucrose is not ionic. The effects observed for PEG and sucrose will only be chemical in nature and not electrochemical [8]. Urea is a strong protein denaturant and a known water-structure breaker [17]. Hence we presumed that studies of the effect of these additives on the process of micellization should be of wide interest.

2. Materials and method

Myrj 45 (Sigma), PEG 400 (Merck, India), sucrose (AR; 99.9%; Qualigens, India), urea (99%; Merck, Germany) were used without any pretreatment. Acetamide (BDH, India; 98.5%) was recrystallized from benzene before use. Myrj 45 ($H(OC_2H_4)_8\ OOC(CH_2)_{16}CH_3$) is polyoxyethylene(8) monostearate with an average molar mass of 636. The purity of PEG 400 and Myrj 45 was not given by the supplier.

Iodine (AR; Sarabhai Chemicals, India) was resublimed before use. Water was doubly distilled from KOH and $KMnO_4$. A Bausch and Lomb Spectronic 20 colorimeter was used for determining the CMCs by the iodine solubilization method [22]. A Du Nouy tensiometer (S.C. Dey & Co. Calcutta, India) was used to determine the surface tension. Solvents were prepared by adding the required amount of water by volume to weighed additives in a volumetric flask. The stock solution of iodine had an 80% transmittance (T) at a λ_{max} of 370 nm. A series of surfactant solutions of various concentrations were prepared by dilution using this iodine mixture as solvent. These solutions were kept in a thermostatted bath for sufficient time, and the percentage transmittance (%T) was measured at 360 nm. Log %T was plotted against log C (i.e. surfactant concentration) and the breakpoint in the plot was taken as the CMC. Some representative plots are shown in Fig. 1A. The transmittance was measured at least twice for each solution to check on the reproducibility. Moreover, experiments were repeated with fresh samples. The error in the CMC was found to be less than 1%. The probability of iodine reacting with the additives was checked previously [4,5,7] as well as at this time, and no change in the transmittance of the additive–iodine systems was observed for 2 h at least. Moreover, for a few systems only, direct surface tension measurements were used to determine the CMC (Fig. 1B). As was observed earlier [7], the CMC values obtained by the iodine solubilization method and by surface tension measurements were the same. The CMC values obtained by surface tension measurements are given in Tables 1–4 in parentheses.

The cloud points of 0.1% Myrj 45 solution in the presence of all the additives were determined by slowly heating the solution in a test tube under constant stirring. At the point of appearance of a cloud, the temperature was noted. It was then allowed to cool. The temperature at the disappearance of the cloud was also noted The average of the cloud appearance and disappearance temperatures is the reported cloud point

3. Results

The CMCs of Myrj 45 in water and also in aqueous additive solutions at 35, 40, 45 and 50°C are presented in Tables 1–4. It can be seen from these tables that the CMC decreases with increase of temperature in aqueous systems, whereas in the presence of additives the CMC continues to increase with increase of temperature. The effect of the additives depends upon both the nature and the concentration of the additives. The cloud points of 0.1% (w/v) Myrj 45 in each of the solutions were also determined and are presented in Tables 1–4. In general, the cloud point decreases with the addition of PEG 400 and sucrose, whereas the cloud point increases with the addition of urea and acetamide

Various thermodynamic quantities like the free energy ΔG_m, the enthalpy ΔH_m, and the entropy ΔS_m of micellization were obtained by using the

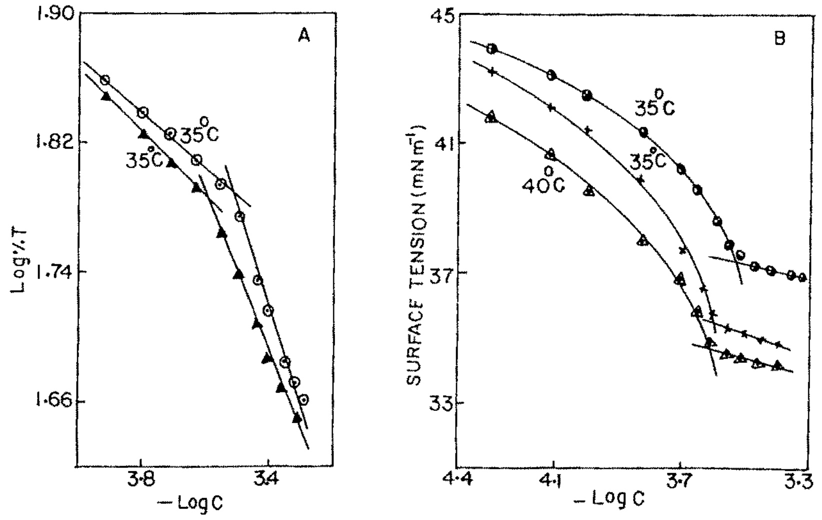

Fig 1 (A) Representative plots of log % T vs log C ◉, 0.5% Sucrose. ▲, 0.3% acetamide (B) Representative plots of surface tension vs log C ◑, 0.05% Urea, △, no additive, ×, 0.5% sucrose

Table 1
CMC values for Myrj 45 in aqueous solution in the presence of PEG 400 at different temperatures, and the cloud points of 0.1% Myrj 45 at different concentrations of PEG 400 (see text)

Concentration of PEG 400 (%)	CMC (mM)				Cloud point (°C)
	35°C	40°C	45°C	50°C	
0.0	0.286	0.245 (0.245)[a]	0.202	0.157	67.7
0.05	0.255	0.270	0.286	0.305	65.1
0.1	0.264	0.273	0.289	0.302	62.1
0.3	0.286	0.305	0.324	0.333	58.0
0.5	0.160	0.169	0.179 (0.180)[a]	0.185	56.1
0.7	0.273	0.298	0.321	0.330	58.1
1.0	0.192	0.207	0.223	0.236	56.8

[a] Values in parentheses were obtained by surface tension measurements

following relationships

$$\Delta G_{\mathrm{m}} = RT \ln(\mathrm{CMC})$$

$$\Delta H_{\mathrm{m}} = -RT^2 \, \mathrm{d} \ln(\mathrm{CMC})/\mathrm{d}T$$

$$\Delta S_{\mathrm{m}} = (\Delta H_{\mathrm{m}} - \Delta G_{\mathrm{m}})/T$$

where the CMC was on the mole fraction scale. The rate of change of ΔH_{m} with temperature, i.e. the specific heat of micellization $\Delta C_{\mathrm{p,m}}$ was also computed for all the systems. These values are presented in Tables 5–8. As expected, the free energy of micellization is negative. The micellization process is exothermic in the presence of all the additives, although in pure water it is endothermic. The ΔS_{m} is positive in all cases, indicating the formation of more disordered systems on micellization and in pure water the value is more than double the values obtained for other systems.

4. Discussion

From Tables 1–4 it is seen that the CMC of Myrj 45 decreases with increasing temperature in

Table 2
CMC values for Myrj 45 in aqueous solution in the presence of surcrose at different temperatures, and the cloud points of 0.1% Myrj 45 at different concentrations of sucrose (see text)

Concentration of sucrose (%)	CMC (mM)				Cloud point (°C)
	35°C	40°C	45°C	50°C	
0.05	0.233	0.276	0.305	0.321	66.7
0.1	0.236	0.273	0.308	0.317	66.7
0.3	0.236	0.273	0.305	0.317	66.2
0.5	0.245 (0.251)[a]	0.279	0.308 (0.305)[a]	0.327	65.2
0.7	0.292	0.308	0.321	0.339	64.4
1.0	0.314	0.333	0.352	0.365	63.3

[a] Values in parentheses were obtained by surface tension measurements

Table 3
CMC values for Myrj 45 in aqueous solution in the presence of acetamide at different temperatures, and the cloud points of 0.1% Myrj 45 in the presence of different concentrations of acetamide (see text)

Concentration of acetamide (%)	CMC (mM)				Cloud point (°C)
	35°C	40°C	45°C	50°C	
0.005	0.283	0.302	0.314	0.330	–
0.01	–	0.321	0.327	0.333	–
0.05	0.308	0.324	0.333	0.333	68.4
0.1	0.279	0.277 (0.278)[a]	0.281	0.286	69.2
0.3	0.311	0.317	0.333	0.336	70.6
0.5	0.311	0.314	0.333	0.336	71.6
0.7	0.311	0.314	0.327	0.333	71.8
1.0	0.308	0.318	0.327	0.333	73.0

[a] Values in parentheses were obtained by surface tension measurements.

Table 4
CMC values for Myrj 45 in aqueous solution in the presence of urea at different temperatures, and the cloud points of 0.1% Myrj 45 in the presence of different concentrations of urea (see text)

Concentration of urea (%)	CMC (mM)				Cloud point (°C)
	35°C	40°C	45°C	50°C	
0.05	0.295 (0.295)[a]	0.308	0.317	0.330	73.4
0.1	0.298	0.311	0.321	0.330	74.4
0.3	0.302	0.314	0.327	0.333	76.2
0.5	0.305	0.317	0.330	0.336	78.0
0.7	0.308	0.324	0.333	0.339	80.2
1.0	0.314	0.327	0.336	0.343	82.6

[a] Values in parentheses were obtained by surface tension measurements

water when no additive is present. It is well known that the breaking of the water structure, the formation of icebergs of water surrounding the solute as well as the presence of the cloud point are responsible for lowering the CMC [23]. However, when PEG 400 and sucrose were added there was an initial decrease in the CMC at all temperatures with an increase on further addition of the additives. However, for urea and acetamide, the CMC starts increasing with the addition of the first aliquot of the additives.

It has already been pointed out by us [4,5,7] that the addition of additives breaks the water matrix. Moreover, there will be a formation of structure between the free water molecules and the additives, particularly those having hydrogen-bond-forming groups. Moreover, cosolubilization as well as mixed micelle formation are possible. Both PEG 400 and sucrose are capable of forming hydrogen bonds. Hence there is an interplay of both water–structure–breaking and water–structure–forming phenomena. On the addition of the first aliquot of both PEG 400 and sucrose, the system becomes less structured than water and the CMC decreases. The further addition of additives provides a greater possibility of hydrogen bonding and the system becomes relatively more structured and the CMC increases. However, we would like to stress that the CMC values obtained in 0.1% acetamide and in 0.5, 0.7 and 1.0% PEG 400 are quite unexpected, and we have not been able to

Table 5
Free energy (ΔG_m), enthalpy, (ΔH_m), entropy (ΔS_m), heat capacity ($\Delta C_{p,m}$), transfer enthalpy ($\Delta H_{m\,tr}$) and heat capacity ($\Delta C_{p\,m\,tr}$) of micellization of Myrj 45 in aqueous solution in the presence of PEG 400 at 40°C

Concentration of PEG 400 (%)	$-\Delta G_m$ (kJ mol^{-1})	ΔH_m (kJ mol^{-1})	ΔS_m (J mol^{-1} K^{-1})	$\Delta C_{p,m}$ (kJ mol^{-1} K^{-1})	$\Delta H_{m\,tr}$ (kJ mol^{-1})	$\Delta C_{p,m\,tr}$ (kJ mol^{-1} K^{-1})
0.0	32.08	30.54	200.09	0.196	–	–
0.05	31.83	−10.13	69.32	−0.065	40.67	−0.262
0.1	31.80	−7.52	76.71	−0.048	38.06	−0.245
0.3	31.52	−12.78	81.04	0.836	43.32	0.639
0.5	33.04	−7.46	82.83	0.425	38.0	0.229
0.7	31.57	−12.89	77.75	0.572	43.43	0.375
1.0	32.52	−14.85	74.48	0.808	45.39	0.612

Table 6
Free energy (ΔG_m), enthalpy, (ΔH_m), entropy (ΔS_m), heat capacity ($\Delta C_{p\,m}$) transfer enthalpy ($\Delta H_{m\,tr}$) and heat capacity ($\Delta C_{p\,m\,tr}$) of micellization of Myrj 45 in aqueous solution in the presence of sucrose at 40 C

Concentration of sucrose (%)	$-\Delta G_m$ (kJ mol^{-1})	ΔH_m (kJ mol^{-1})	ΔS_m (J mol^{-1} K^{-1})	$\Delta C_{p,m}$ (kJ mol^{-1} K^{-1})	$\Delta H_{m\,tr}$ (kJ mol^{-1})	$\Delta C_{p,m\,tr}$ (kJ mol^{-1} K^{-1})
0.0	32.08	30.54	200.09	0.196	–	–
0.05	31.80	−21.66	32.40	1.807	−52.20	1.610
0.1	31.80	−20.96	34.64	1.617	−51.50	1.420
0.3	31.80	−21.33	33.46	1.937	−51.87	1.741
0.5	31.74	−19.77	38.24	1.301	−50.31	1.104
0.7	31.49	−8.55	73.29	−0.054	−39.09	−0.251
1.0	31.29	−9.39	69.97	0.324	−39.93	0.128

Table 7
Free energy (ΔG_m), enthalpy, (ΔH_m), entropy (ΔS_m), heat capacity ($\Delta C_{p,m}$) transfer enthalpy ($\Delta H_{m,tr}$) and heat capacity ($\Delta C_{p\,m,tr}$) of micellization of Myrj 45 in aqueous solution in the presence of acetamide at 40°C

Concentration of acetamide (%)	$-\Delta G_m$ (kJ mol^{-1})	ΔH_m (kJ mol^{-1})	ΔS_m (J mol^{-1} K^{-1})	$\Delta C_{p\,m}$ (kJ mol^{-1} K^{-1})	$\Delta H_{m,tr}$ (kJ mol^{-1})	$\Delta C_{p\,m,tr}$ (kJ mol^{-1} K^{-1})
0.0	32.08	30.54	200.09	0.196	–	–
0.005	31.56	−8.14	74.81	−0.052	−38.68	−0.249
0.01	31.38	−3.49	89.10	−0.022	−34.03	−0.218
0.05	31.36	−5.97	81.11	0.736	−36.51	0.539
0.1	31.72	−1.49	96.83	−0.0093	−32.03	−0.205
0.3	31.41	−4.12	87.19	−0.034	−34.66	−0.230
0.5	31.41	−5.43	83.00	−0.035	−35.97	−0.232
0.7	31.40	−4.28	86.62	−0.027	−34.82	−0.224
1.0	31.42	−4.88	84.77	−0.096	−35.42	−0.1002

find a proper coherent explanation. We have checked and rechecked our data, including changing the bottle of PEG, but the CMC values were reproducible within 1%.

The water-structure-breaking property of urea is well known [24]. The effects of an increase in temperature and the addition of urea should therefore be similar. However, it is seen in Table 4 that the CMC increases on the addition of urea; this was observed in other surfactant systems also

Table 8
Free energy (ΔG_m), enthalpy, (ΔH_m), entropy (ΔS_m), heat capacity ($\Delta C_{p,m}$) transfer enthalpy ($\Delta H_{m,tr}$) and heat capacity ($\Delta C_{pm,tr}$) of micellization of Myrj 45 in aqueous solution in the presence of urea at 40°C

Concentration of urea (%)	$-\Delta G_m$ (kJ mol^{-1})	ΔH_m (kJ mol^{-1})	ΔS_m (J mol^{-1} K^{-1})	$\Delta C_{p,m}$ (kJ mol^{-1} K^{-1})	$\Delta H_{m,tr}$ (kJ mol^{-1})	$\Delta C_{p,m,tr}$ (kJ mol^{-1} K^{-1})
0.0	32.08	30.54	200.09	0.196		
0.05	31.49	−5.97	81.53	−0.038	−36.51	−0.235
0.1	31.46	−6.11	83.74	0.233	−36.65	0.036
0.3	31.44	−6.51	79.65	0.368	−37.05	0.172
0.5	31.42	−8.59	72.99	0.643	−39.13	0.446
0.7	31.37	−6.11	80.70	0.506	−36.65	0.310
1.0	31.34	−5.23	83.42	0.243	−35.77	0.046

[25,26]. Urea is known to be a strong protein denaturant and hence its demicellization property (i.e. higher CMC) is probably a manifestation of that [17]. It has also been suggested that the monomers of the surfactants become stabilized in aqueous urea solutions, and therefore the micellization occurs at higher concentrations [27]. Therefore, the interplay of various antagonistic properties like the breaking of the water structure (i.e. a decrease in the CMC) and demicellization, monomer stability, solvation of hydrophilic groups (i.e. an increase in the CMC) actually determine the overall experimentally obtained result.

The effect of acetamide as an additive on the CMC of Myrj 45 is similar to that of urea. However, acetamide is less interactive than urea as one NH_2 group of urea is replaced by a CH_3 group. It was observed earlier by us [4] that acetamide increases the CMC of the non-ionic surfactant Brij 35. The effect on Myrj 45 is much greater (125 μM) than in Brij 35 (19 μM) at 45°C for 1 M acetamide.

Cloud points are the manifestation of the solvation/desolvation phenomena in non-ionic surfactant solutions. The desolvation of the hydrophilic groups of the surfactant leads to the formation of cloud in the surfactant solution. By being water-structure breakers, urea and acetamide help in the solvation of hydrophilic groups of Myrj 45. Hence higher temperatures are required for desolvation, i.e. a higher cloud point. On the other hand, PEG 400 and sucrose are sufficiently hydrophilic to interact with water and hence the surfactant hydrophilic groups are relatively less solvated than in water. Therefore, a lower temperature would suffice for the desolvation of hydrophilic groups and hence a lower cloud point. Moreover, urea and acetamide probably form mixed charged micelles. Therefore the cloud points would be higher. However, for unchanged molecules like PEG 400 or sucrose, the cloud point need not be higher.

Thermodynamic quantities of micellization are reported in Tables 5–8. As expected, the free energy of micellization in all cases is negative. The variation of free energy with concentration of additives is somewhat irregular for PEG 400. As we mentioned earlier, we have no proper explanation for this. In all other cases, the variation of ΔG_m with concentration of the additives was regular.

The micellization process in the presence of additives in most cases is exothermic. This was also observed for Triton X-100 in aqueous ethylene glycol [28] and for Brij 35 in aqueous PEG solutions [5]. The variation of ΔH_m with both temperature and concentration of the additives may probably be due to changes in the hydration of the oxyethylene groups on micellization. The entropies of micellization (ΔS_m) for all systems are high, indicating that the process is associated with some type of phase separation [7]. In aqueous systems, in the absence of additives, a positive ΔH_m and a negative ΔG_m lead to large positive entropies. This is attributed to (a) water-structure breakdown on micellization; and (b) increased randomness due to the freedom of the hydrophobic chain in the relatively non-polar interior of the micelle compared to the aqueous environment [29]. However, in the presence of the additives, ΔS_m, though positive, is relatively small because of the comparative weakness of the hydrophobic bond in these cases [4] Micellization is the manifestation of hydrophobic forces. Therefore, a weakness of this force requires the addition of more surfactant molecules for micelle formation [13,22], and therefore the CMC increase for the urea systems.

A linear correlation between enthalpy and entropy of micellization was observed for all systems (correlation coefficient 0.999), and this is shown in Fig. 2. Such an enthalpy–entropy compensation effect was observed earlier in many physicochemical processes including micellization [4,5,7] and monolayer formation [30]. The slope of the curve is 315 K, which is not far away from the suggested value of 270–294 K for water systems [31]. This implies that the phenomenon of micellization in all the systems studied here, is governed by the same structural property of water [7], i.e. at 315 K, the micellization process is totally independent of structural changes in the system and is dependent on enthalpic forces. The heat capacities for micelle formation ($\Delta C_{p,m}$) were also evaluated from the plot of ΔH_m vs. T, the slope being $\Delta C_{p,m}$ (Tables 5–8). The variation of $\Delta C_{p,m}$ with concentration of the additives in all cases did not show any regularity; this was also observed earlier in calorimetric studies [32].

The transfer enthalpies ($\Delta H_{m,tr}$) and transfer heat capacities ($\Delta C_{p,m,tr}$) of micelles from water to aqueous additive solutions were obtained using the following relationships

$$\Delta H_{m,tr} = \Delta H_m(\text{aq.additive}) - \Delta H_m(\text{aq})$$

and

$$\Delta C_{p,m,tr} = \Delta C_{p,m}(\text{aq.additive}) - \Delta C_{p,m}(\text{aq})$$

The transfer enthalpies of the Myrj 45 micelle as calculated using the above relationships were found to be negative (Tables 5–8). Such negative transfer enthalpies were reported for the transfer of NaCl and amino acids from water to aqueous urea solutions [17]. It can be concluded that the transfer of hydrophilic groups from water to aqueous solutions is exothermic, whereas that of hydrophobic groups is endothermic, the strong hydrophilic group–additive interaction being the dominating cause.

The structure-changing properties of both hydrophobic (water-structure making) and hydrophilic (water-structure breaking) groups decrease in a less structured medium. This results in their opposing contributions to the $\Delta H_{m,tr}$ quantity. The decrease in the structure around the monomers

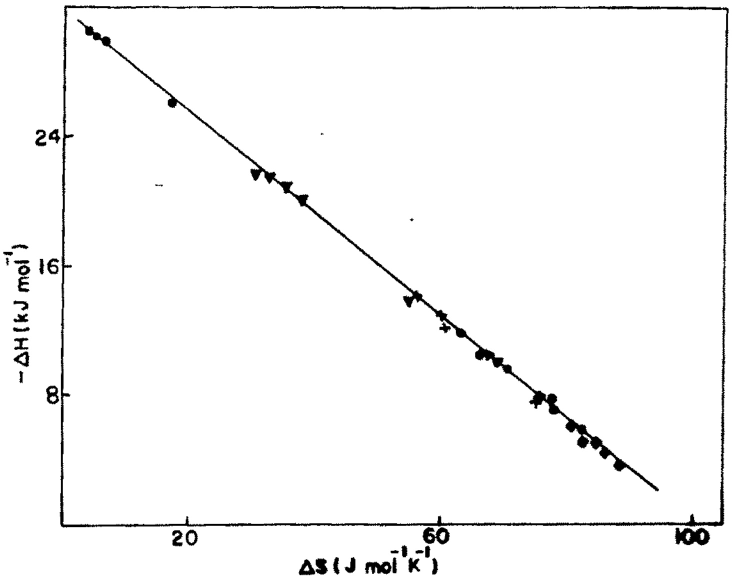

Fig 2 Enthalpy-entropy compensation plot for all the systems ●. 35°C; ▲, 40°C; ■, 45°C; ×, 50°C

in their solutions, reflecting a greater structure-breaking ability of these groups, may also be the reason for negative $\Delta H_{m,tr}$ values.

The transfer heat capacities of micellization $\Delta C_{p,m,tr}$ for the transfer of micelles from water to additive-containing solutions are positive for most of the systems, indicating increased hydration of micelles in these solutions due to the greater extent of hydrogen bonding between ethylene oxide groups and additives present in the solution. Negative $\Delta C_{p,m,tr}$ values can be attributed to a less structured medium compared to pure water [17]. However, $\Delta C_{p,m,tr}$ shows a maximum for all systems as a function of the concentration of additives; this was observed by other workers also [11,33,34]. This maximum has been attributed to micellar structural transitions [33,34].

5. Conclusion

The CMC of Myrj 45, a non-ionic surfactant, in water as well as in aqueous solutions of PEG 400, sucrose, acetamide and urea was determined. It was observed that the CMC is dependent upon temperature and the nature of the additive as well as on the concentration of the additive. The micellization process, in general, is exothermic, although in water it is endothermic. The entropy of micellization is very highly positive in water. In the presence of additives, ΔS_m is positive, although it is less than half of that in water. These values indicate the formation of a new phase. An enthalpy–entropy compensation effect was also observed, with 315 K as the compensation temperature.

The heat capacity of micellization was also determined. No clear relationship to the additive concentration was obtained. The enthalpy of transfer of the micelle from aqueous systems to additive solutions as well as the heat capacity of transfer were determined. A maximum was observed in the $\Delta C_{p,m,tr}$ quantities as a function of concentration, which was ascribed to micellar structural transitions.

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Studies of the Effect of Additives on the Surface and Thermodynamic Properties of Poly(oxyethylene(10)) Lauryl Ether in Aqueous Solution

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The interfacial and thermodynamic properties of a nonionic surfactant, poly(oxyethylene(10)) lauryl ether [$C_{12}H_{25}(OCH_2CH_2)_{10}OH$], in aqueous solution in the presence and the absence of both polyethylene glycol 400 and sucrose have been investigated. Critical micelle concentrations (cmc's) were determined by surface tension measurements at different additive concentrations and temperatures using a du Noüy tensiometer. From the surface tension data, the surface excess concentration (Γ), the minimum area per molecule (A_{min}), and the surface pressure at the cmc (Π_{cmc}) were evaluated. Thermodynamic parameters of adsorption and micellization were evaluated and discussed. An enthalpy–entropy compensation effect was observed in all solvent systems. Transfer enthalpies of micellization from water to additive solutions which are sensitive to the solvent structure have been computed using the enthalpy of micellization data. $\Delta\Delta H_m^{\circ,tr}$ data were all large and negative, indicating hydrophilic group–additive interaction. The other solution properties of this surfactant like the cloud point, viscosity, foaming, and wetting have been determined in the presence of different concentrations of PEG 400 and sucrose.

Introduction

The investigation of interfacial and thermodynamic properties of surfactants in solutions, both in the presence and in the absence of additives, can provide a wealth of information about solute–solute and solute–solvent interactions of the surfactant in solution. Further, these studies are of relevance for enhanced oil recovery and in froth floatation processes for metal ore concentration.[1] The interfacial and micellar properties of these solutions are governed by a delicate balance of hydrophobic and hydrophilic interactions. These characteristics can be modified in two ways: (i) through specific interactions with the surfactant molecules and (ii) by changing the nature of the solvent.[2] Such studies on the effect of cosolvents on the aggregational and other physicochemical properties of surfactants are of fundamental and industrial interest.[3] Because of the present day importance of nonionic surfactants in industry and in understanding the micellization process as well as our own intense interest in these types of compounds,[4–8] we decided to study the thermodynamics of micellization of poly(oxyethylene(10)) lauryl ether particularly in the presence of additive molecules which can have a significant influence on the system, namely polyethylene glycol 400 (PEG 400) and sucrose. PEG 400 is a water soluble low molecular weight oligomer. Sucrose is also highly hydrophilic and nonionic like PEG 400. Therefore the influence of these two additives would be purely chemical and not electrochemical.[9,10]

In this paper we report the effect of these additives on the various solution properties, such as the critical micelle concentration (cmc), cloud point, foaming, viscosity, and wetting of the nonionic surfactant $C_{12}H_{25}(OCH_2CH_2)_{10}OH$, poly(oxyethylene(10)) lauryl ether, in aqueous media at different temperatures.

To have a better understanding of the properties of surfactants in the aqueous solutions containing these additives,[11,12] thermodynamic parameters of micellization and adsorption at the air/water interface including the surface excess (Γ), minimum area per molecule (A_{min}), and surface pressure (Π_{cmc}), which measures the effectiveness of surface tension reduction, were determined. Transfer enthalpies, which are sensitive to the structure of the solvent, were also determined.

Materials and Experimental Methods

Poly(oxyethylene(10)) lauryl ether ($C_{12}H_{25}(OCH_2CH_2)_{10}OH$, $C_{12}E_{10}$, SIGMA), molar mass = 626, was used without any further purification. The surface tension concentration plot did not show any minimum. PEG 400 (Merck, India) and sucrose (AR, 99.9%, Qualigens, India) were used without any pretreatment. All solutions were prepared in doubly distilled water (distilled from KOH and $KMnO_4$). The purity of PEG 400 and $C_{12}E_{10}$ was not mentioned by the supplier.

Critical Micelle Concentration Measurement. The critical micelle concentration (cmc) was obtained by the surface tension method using a du Noüy tensiometer (S.C. Dey & Co., Calcutta, India). Measurements were made at 35, 40, 45, and 50 °C. The temperature was maintained constant by circulating thermostated water through a jacketed vessel containing the solution. Surface tension (γ) decreases quite rapidly with increasing surfactant concentration before reaching a near plateau region. The concentration of solution was varied by adding aliquots of concentrated stock solution to the known volume of solution in the jacketed vessel by means of a 5 μL

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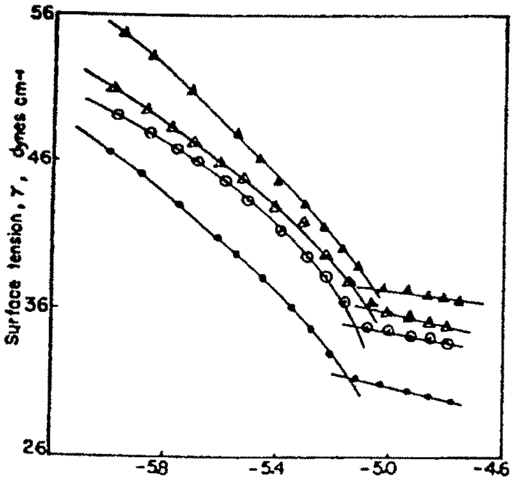

Figure 1. Representative plots of surface tension vs log *C* in various solvents (concentration in molarity): △, 0.3% PEG at 50 °C; ⊙, 0.3% PEG at 45 °C; ▲, water at 45 °C; ●, 0.3% sucrose at 40 °C.

Table 1. Critical Micelle Concentration of Poly(oxyethylene(10)) Lauryl Ether in Aqueous Solution in the Presence and Absence of PEG 400 and Sucrose at Different Temperatures

conc of additive (% PEG 400 (w/v))	cmc (μM) 35 °C	40 °C	45 °C	50 °C	cloud point[a] (°C)
0.0	11.8	10.0	8.9	7.1	93.0
0.05	5.6	7.9	8.0	8.4	88.0
0.1	5.7	7.1	8.0	8.2	86 9
0.3	5.5	6.6	7.4	8.0	85.1
0.5	5.7	6.9	7.8	8.3	83.8
0.7	5.6	7.1	7.9	8.4	82 9
1.0	5.9	6 5	7.6	8.5	81 8

% sucrose	cmc (μM) 35 °C	40 °C	45 °C	50 °C	cloud point[a] (°C)
0.1	5.9	6.8	7.4	8.3	90.6
0.3	6.4	7.1	7.9	8.5	89.5
0.5	6.6	7.6	8.1	8 9	88 2
0.7	6.8	7.8	8.3	9.1	87.2
1.0	6.8	7.6	8.5	9.3	86.4

[a] The cloud point is for a 1% (w/v) surfactant solution.

Hamilton microsyringe. The ring was cleaned between each measurement of surface tension. The standard deviation of the mean in γ was 0.5%.

The measured surface tension values were plotted as a function of the logarithm of surfactant concentration, and the cmc was estimated from the break point in the resulting curve. The experiments were repeated in which aqueous solutions of the additives were used as solvent instead of water. Representative plots of surface tension vs logarithm of surfactant concentration (M) are shown in Figure 1. The reproducibility of the surface tension–concentration curves was checked by duplicate runs. The reproducibility of individual points was, in general, very good. The reproducibility (standard deviation of the mean) in the cmc was found to be ±0.9%, calculated from the experimental cmc data from at least two runs.

Cloud Points. Cloud points of poly(oxyethylene(10)) lauryl ether in all experimental solutions were determined. The surfactant concentration was 1% (w/v). The experimental method has been described earlier.[13] The cloud points are presented in Table 1. These are the averages of the appearance and disappearance temperatures, this difference being no greater than 0.6 °C, of the cloudiness under constant stirring.

Contact Angle (θ) Measurements. The contact angles of the surfactant solutions with Teflon tape were measured with the help of a contact '*θ*' meter[14] obtained as a gift from Department of Color Chemistry, Leeds University, Leeds, U.K. For this purpose a strip of polytetrafluoroethylene (PTFE) (Samson, India) was washed with chromic acid and water, rinsed in acetone, and dried before use. The surfactant solution was placed as a drop on the PTFE surface using a microsyringe. Contact angles were determined, and the averages of at least four determinations are reported. The error in the contact angle is ±1°. All measurements were carried out at room temperature (~27 °C). The contact angles of surfactant solutions in the presence of PEG 400 and sucrose at different concentrations were also determined (Figure 4).

Viscosity Measurements. The viscosities of the surfactant solutions (5% w/v) were measured with the help of an Ubbelohde viscometer[14,15] at temperatures of 35, 40, and 45 °C. The changes in the viscosities of surfactant solutions at 0.1, 0.5, and 1.0% (w/v) concentrations of PEG 400 and sucrose were also studied.

Foaming Measurements. The foaming efficiency of the surfactant was determined by measuring the initial foam height. The Ross–Miles method[16] was used. The effect of PEG 400 and sucrose of different concentrations on the initial foam heights of the surfactant solutions was also determined. The concentration of surfactants was 0.01% (w/v), the reproducibility of the initial foam heights was within ±2%.

Results and Discussion

The critical micelle concentrations (cmc's) of poly(oxyethylene(10)) lauryl ether in water as well as in aqueous solutions of PEG 400 and sucrose at different temperatures are presented in Table 1. It is obvious from the tabulated data that in water as the temperature increases, the cmc decreases. This was observed earlier also[17] and may be taken as a typical characteristic of a nonionic surfactant within the limited temperature region being used here. However this characteristic does not seem to hold in the presence of additives,[18] particularly structure-forming additives like PEG 400 and sucrose. The cmc increases with the increase in temperature in the presence of the additives, which is generally the characteristic of ionic surfactants.[19] Nevertheless the presence of PEG 400 or sucrose lowers the cmc significantly.

The formation of the micelle is the result of hydrophobic interaction.[20] It is also known that the London dispersion force is the main attractive force helping in the formation of the micelle.[21] In the case of nonionic surfactants, the cmc decreases with the rise in temperature due to the dehydration of the polyoxyethylene moiety of the surfactant molecule. In the presence of additives however the reverse is seen, which indicates that the micellization process is significantly altered by these molecules. The additives PEG 400 and sucrose may form hydrogen bonds with solvent water molecules and thereby promote the water structure. The hydrophobic group of the surfactant also promotes water structure. These two reasons together decrease the cmc of the surfactant.[16] In the presence of additives as the temperature increases the solvent structure is broken and hence the cmc increases.

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Table 2. Standard Free Energy (ΔG°_m), Enthalpy (ΔH°_m), and Entropy (ΔS°_m) of Micellization in the Presence of PEG 400 in Aqueous Solution at Different Temperatures[a]

conc of PEG 400 (% (w/v))	$-\Delta G^\circ_m$ (kJ mol^{-1}) 35 °C	40 °C	45 °C	50 °C	ΔH°_m (kJ mol^{-1})	ΔS°_m (J mol^{-1} K^{-1})
0.0	39.3	40.4	41.4	42.6	27	220
0.05	41.2	41.4	41.7	42.2	−21	66
0.10	41.2	41.3	41.8	42.3	−20	69
0.3	41.3	41.5	41.9	42.3	−21	67
0.5	41.2	41.4	41.7	42.2	−21	66
0.7	41.2	41.3	41.7	42.2	−22	61
1.0	41.1	41.6	41.8	42.1	−21	66

[a] The maximum error in ΔG°_m is 0.1%; that in ΔH°_m is 25%; and that in ΔS°_m is 26%.

Table 3. Standard Free Energy (ΔG°_m), Enthalpy (ΔH°_m), and Entropy (ΔS°_m) of Micellization in the Presence of Sucrose in Aqueous Solution at Different Temperatures[a]

conc of sucrose (% (w/v))	$-\Delta G^\circ_m$ (kJ mol^{-1}) 35 °C	40 °C	45 °C	50 °C	ΔH°_m (kJ mol^{-1})	ΔS°_m (J mol^{-1} K^{-1})
0.1	41.1	41.4	41.9	42.2	−18	76
0 3	41.0	41.3	41.7	42.1	−18	74
0.5	40.8	41.1	41.6	42.0	−15	80
0.7	40.8	41.1	41.6	42.0	−15	80
1.0	40.8	41.1	41.5	41.9	−18	74

[a] The maximum error in ΔG°_m is 0.1%; that in ΔH°_m is 11%; and that in ΔS°_m is 11%.

In Table 1 we also present the cloud points for 1% (w/v) surfactant solutions in the presence and absence of various amounts of additives. It is obvious that as the concentration of additive increases, the cloud point decreases. This indicates that additives remove water from near the micelle and thereby help the micelles to approach each other easily. It was stated by Kjellander et al.[22] that the appearance of the cloud point is entropy dominated. The ethylene oxide group is highly hydrated, and the nonionic micelles are expected to have water deep inside the micelle. As additives are added, the water of hydration of the micelles decreases because the additives compete for the water molecules with the micelles. Now with two relatively less hydrated micelles approaching each other, the hydration spheres overlap and some water molecules are freed to increase the entropy of the system. At the cloud point, the water molecules get totally detached from the micelles. The overall entropy is high, and hence the free energy change is relatively more negative[13] and the appearance of the cloud point is facile.

The free energy of micellization (ΔG°_m) for a nonionic surfactant is directly proportional to the ln cmc (cmc in mole fraction scale) by the following relation.[23]

$$\Delta G^\circ_m = RT \ln \text{cmc} \qquad (1)$$

In Tables 2 and 3, ΔG°_m values are reported for different temperatures in the presence of various amounts of additives. The transfer process here indicates the formation of micelles in the solvent from the solvated free monomer of unit mole fraction. 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. Even in the presence of additives the variation is similar though the cmc increases with temperature. This is obvious, as the change in the magnitude of the logarithm of the cmc is more than compensated by the change in the values of RT. The temperature variation of the cmc can be used to compute the enthalpy of micellization ΔH°_m and hence the entropy of micellization ΔS°_m. The following relations have been used for these computations[23]

$$\Delta H^\circ_m = -RT^2 \frac{d \ln \text{cmc}}{dT} \qquad (2)$$

$$\Delta S^\circ_m = \frac{\Delta H^\circ_m - \Delta G^\circ_m}{T} \qquad (3)$$

The (ln cmc)−T plot was linear in both PEG and sucrose solutions. Hence d(ln cmc)/dT was computed from the slope of the line. The error in ΔH°_m is of the order of 25% and 10% in PEG and sucrose solutions, respectively, and hence average values are given in Tables 2 and 3.

The data in Tables 2 and 3 indicate that the micellization process is endothermic though it becomes exothermic in the presence of both sucrose and PEG 400, which was observed earlier also for PEG 400.[8] However, in the presence of sucrose the micellization process was endothermic in the case of Brij 35 for most concentrations of additives.[8] The exothermic and endothermic characteristics of micellization are specific to the surfactant, the additive, and the temperature of micellization.[8,9,24,25] It should also be mentioned here that the ΔH°_m values calculated from eq 2 may be somewhat different from the calorimetrically determined data. The calorimetric data are in general scarce, and we have not been able to locate any for this system for comparison. It has been mentioned earlier[26] that the ΔH°_m for a nonionic surfactant is independent of the number of oxyethylene groups when the number is over six, and the value is ~32 kJ mol^{-1} (cf. 27.3 kJ mol^{-1} in this work) at 20 °C. It is to be noted that the enthalpy of micellization ΔH°_m is almost independent of temperature in the presence of both PEG and sucrose (Tables 2 and 3). This independence can be attributed to the fact that there does not occur a remarkable change in the environment surrounding the hydrocarbon chain of the surfactant molecule in the presence of both PEG and sucrose[21] as the temperature is changed. Further addition of additives does not change ΔH°_m to a large extent, and this means that the environment surrounding the molecules does not change any further with additional amounts of additives. However this independence may also be due to the error associated with ΔH°_m.

The entropy of micellization (ΔS°_m) is positive, indicating that the micellization process is somewhat entropy dominated particularly for the systems where the entropy changes are high. High-entropy changes are generally associated with a phase change. Hence it can be assumed that the micelles are separate phases in these systems. Shaw[27] 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. 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 ΔS°_m, which is a macroscopic property. Rosen[16] has stated that the presence of the hydrated oxyethylene groups of the surfactant introduces structure in the liquid water phase and that the removal of the surfactant via

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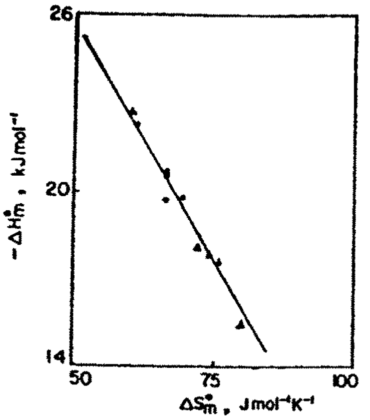

Figure 2. Enthalpy–entropy plot for all systems together: ●, PEG; ▲, sucrose.

micellization results in an increase in the overall randomness[28] and hence an increase in entropy. In the presence of additives, the entropy changes are not large because the additives still control the formation of the three-dimensional water structure.

A linear correlation between ΔH_m° and ΔS_m° was seen in these systems (Figure 2), which was suggested by Lumry et al.[29] The slope of the line was found to be 312 K. It was suggested earlier[29] that this value for water was expected to be between 270 and 294 K. Our observed value of 312 K is very near to these values. Therefore we feel that the micellization is a property dependent upon the bulk structure of the solvent. Additives do not have much effect on the process. However, the small variations that we observe here as well as those observed earlier[10] may be due to the difference of the bulk structural property of the solution from that of the water. It should be clear though that the linearity in ΔH_m°–ΔS_m° plots should not be overinterpreted,[30] though this linearity is quite often seen.

It is also possible to calculate the change in enthalpy of micellization, i.e. the so-called transfer quantities[31–34] defined by

$$\Delta\Delta H_m^{\circ,\mathrm{tr}} = \Delta H_m^\circ(\mathrm{soln}) - \Delta H_m^\circ(\mathrm{water}) \qquad (4)$$

This computation can be easily done, and $\Delta\Delta H_m^{\circ,\mathrm{tr}}$ was found to be negative for all systems, as was observed earlier.[18] Negative transfer enthalpies were observed for the transfer of amino acids and NaCl from water to aqueous urea.[35] It was concluded that the hydrophilic group transfer from water to aqueous solutions was exothermic whereas for hydrophobic groups it was endothermic. The overall exothermicity of the transfer process in the present case indicates that the additive–oxyethylene group (of the surfactant) interaction will be a very dominating one. Moreover the structure-breaking ability of the solutes may be another reason for the negative $\Delta\Delta H_m^{\circ,\mathrm{tr}}$ values.

Table 4. Surface Excess ($\Gamma \times 10^{10}$ mol cm^{-2}) in the Presence of PEG 400 and Sucrose at Different Temperatures (See Text)

conc of additive	surface excess							
	PEG 400				sucrose			
(% (w/v))	35 °C	40 °C	45 °C	50 °C	35 °C	40 °C	45 °C	50 °C
0.0	2.3	2.4	3.3	3.6				
0.05	5.2	5.2	3.7	2.7				
0.1	4.8	4.6	3.1	3.0	3.0	2.2	2.1	2.0
0.3	4.8	3.5	2.7	2.4	3.5	3.1	2.0	1.6
0.5	3.4	3.4	2.3	3.4	3.0	2.7	1.9	1.5
0.7	2.6	2.3	2.3	1.2	2.5	2.1	2.4	2.1
1.0	2.1	3.1	2.8	2.6	2.7	2.6	1.7	1.5

It is well-known that the air–solution interface of a surfactant solution is well populated[36] by the adsorbed molecules. Accordingly it has been shown that the concentration of the surfactant is always more at the surface due to adsorption over and above the concentration of surfactant in the bulk.

The Gibbs equation[37] (in dilute systems)

$$\Gamma = -\frac{1}{RT}\frac{\mathrm{d}\gamma}{\mathrm{d}\ln C} \qquad (5)$$

where Γ, γ, R, T, and C are surface excess, surface tension, gas constant, absolute temperature, and concentration, respectively, can be used to determine the surface excess. The slope of the tangent at the given concentration of the γ vs ln C plot was used to calculate Γ. The curve of the γ − log C plot was fitted to a second-order polynomial equation around the point log $C = -5.4$. The coefficients of the polynomial were then computed, and hence Γ was calculated. The maximum error in γ (between calculated and experimental) around the point log $C = -5.4$ was around 7%. The maximum error in dγ/d log C around that point was found to be ~4%. We have also computed Γ_{cmc} (=$\Gamma_{\max}$), where Γ_{cmc} indicates the maximum surface excess concentration of the surfactants. The surface excess is an effective measure of the Gibbs adsorption at the liquid/air interface. In Table 4 the calculated surface excess quantities are presented (at log $C = -5.4$). The surface excess quantity increases with an increase in temperature (for systems without additive). This is because as the temperature increases, the hydration of the ethoxy segment of the nonionic surfactant decreases and hence the tendency to locate at the air/water interface. However for systems where additives (both sucrose and PEG 400) are present, the value in general decreases as temperature increases. That is, the increase in temperature hinders the adsorption of surfactants at the air/liquid interface. This is because of (i) the changed nature of water because of the presence of additives, (ii) the interaction between surfactant and the additives, and (iii) the presence of additives at the air–solution interface. From the observed results it can be said that in general the surface excess becomes higher and higher when the solvent has higher surface energy.

From the surface excess quantity it is possible to calculate $A_{\min}$, the minimum area per molecule, from the relation[1]

$$A_{\min} = \frac{10^{14}}{N\Gamma_{\max}}\ \mathrm{nm}^2 \qquad (6)$$

where N is Avogadro's number. The magnitudes of $A_{\min}$

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Table 5. Thermodynamic Parameters of Adsorption for Poly(oxyethylene(10)) Lauryl Ether in the Presence of PEG 400 and Sucrose

	PEG 400			sucrose		
conc of additive (% (w/v))	$-\Delta G^\circ_{ad}$(35 °C) (kJ mol^{-1})	ΔH°_{ad} (kJ mol^{-1})	ΔS°_{ad} (kJ mol^{-1} K^{-1})	$-\Delta G^\circ_{ad}$(35 °C) (kJ mol^{-1})	ΔH°_{ad} (kJ mol^{-1})	ΔS°_{ad} (kJ mol^{-1} K^{-1})
0.0	52.1	−257	−0.67			
0.05	44.7	151	0.64			
0.1	45.1	22	0.22	45.6	295	1.10
0.3	44.6	57	0.33	46.8	315	1.18
0.5	45.7	−11	0.11	48.0	447	1.61
0.7	48.9	172	0.72	47.7	54	0.33
1.0	48.9	49	0.32	48.6	109	0.51

Table 6. Intrinsic Viscosity ([η]), Micellar Volume Including Hydration (V_h), and Volume of the Oxyethylene Chain (V_{OE}) of Poly(oxyethylene(10)) Lauryl Ether (5% w/v) in the Presence and Absence of Additives at Different Temperatures

	35 °C			40 °C			45 °C		
conc of additives (% PEG 400 (w/v))	[η] (cm^3/g)	V_h ($\times 10^4$ Å^3)	V_{OE} ($\times 10^4$ Å^3)	[η] (cm^3/g)	V_h ($\times 10^4$ Å^3)	V_{OE} ($\times 10^4$ Å^3)	[η] (cm^3/g)	V_h ($\times 10^4$ Å^3)	V_{OE} ($\times 10^4$ Å^3)
0.0	7.09	28.71	25.28	6.93	28.07	24.64	6.81	27.59	24.17
0.1	7.10	28.76	25.27	6.94	28.13	24.70	6.83	27.66	24.23
0.5	7.31	29.61	26.18	7.14	28.91	25.48	7.01	28.38	24.95
1.0	7.91	32.05	28.62	7.71	31.23	27.80	7.58	30.71	27.28

	35 °C			40 °C			45 °C		
% sucrose	[η] (cm^3/g)	V_h ($\times 10^4$ Å^3)	V_{OE} ($\times 10^4$ Å^3)	[η] (cm^3/g)	V_h ($\times 10^4$ Å^3)	V_{OE} ($\times 10^4$ Å^3)	[η] (cm^3/g)	V_h ($\times 10^4$ Å^3)	V_{OE} ($\times 10^4$ Å^3)
0.1	7.11	28.80	25.37	6.94	28.11	24.68	6.83	27.66	24.23
0.5	6.83	27.67	24.24	6.66	26.96	23.53	6.53	26.45	23.02
1.0	6.76	27.37	23.94	6.59	26.71	23.28	6.46	26.18	22.75

are of the order of 1.42 nm^2 or less, suggesting that the surface is a closed packed one and that the orientation of the surfactant molecules is almost perpendicular to the surface.[38]

The effectiveness of a surface active molecule is measured by surface pressure at the cmc; i.e., $\Pi_{cmc} = \gamma_0 - \gamma_{cmc}$, where γ_0 and γ_{cmc} are the surface tension of pure water and the surface tension at cmc, respectively. The Π_{cmc} is found to be high at higher temperature at a particular concentration, indicating more adsorption at the air/liquid interface at higher temperature. This higher adsorption at the interface indicates more hydrophobicity of the nonionic surfactant with the increase in temperature.

In Table 5 the thermodynamic parameters of the adsorption of poly(oxyethylene(10)) lauryl ether at the air/liquid interface, both in the absence and presence of PEG 400 or sucrose, are presented. The standard free energy of adsorption ΔG°_{ad} was calculated by the relation[39]

$$\Delta G^\circ_{ad} = RT \ln \text{cmc} - N\Pi_{cmc}A_{cmc} \qquad (7)$$

where Π_{cmc} and A_{cmc} are the surface pressure and area per molecule at the cmc. The standard state for the adsorbed surfactant here is a hypothetical monolayer at its minimum surface area/molecule but at zero surface pressure.[39] The second term in the equation represents the surface work involved in going from zero surface pressure to Π_{cmc} at constant minimum surface area/molecule, A_{min} ($=A_{cmc}$).[39] The standard entropy (ΔS°_{ad}) was obtained from the slope of the $\Delta G^\circ_{ad}-T$ plot, and the enthalpy (ΔH°_{ad}) of adsorption was evaluated by using the well-known thermodynamic relation. It is observed from Table 5 that the ΔG°_{ad} values are negative throughout, indicating that the adsorption of the surfactant at the air/water interface takes place spontaneously not only in pure aqueous solution but also in the presence of PEG 400 or sucrose.

Moreover ΔG°_{ad} values are more negative than their corresponding ΔG°_m values, indicating that when a micelle is formed, work has to be done to transfer the surfactant molecules in the monomeric form at the surface to the micellar stage through the aqueous medium.[1] In the absence of additives, ΔG°_{ad} values become less negative with an increase in temperature, suggesting that relatively more energy is required for the adsorption to occur. However, in the presence of both PEG 400 and sucrose ΔG°_{ad} decreases; i.e., the value becomes more negative with respect to the temperature increase, implying that dehydration of the hydrophilic group is required for the adsorption to take place and that since at higher temperature the surfactant is less hydrated, comparatively less energy is necessary for adsorption.

ΔH°_{ad} in pure aqueous solution is exothermic while ΔH°_m is endothermic. In the presence of sucrose and PEG 400, the results are somewhat different. This indicates that these additives interact with a surfactant hydrophilic group which is exothermic, but these interactions with the surfactant hydrophobic group are endothermic. The observed data are the final outcome of all these phenomena. The standard entropy change of adsorption (ΔS°_{ad}) in pure aqueous solution is negative, reflecting that well ordered structure at the air/water interface. But, in the presence of additives, ΔS°_{ad} values are highly positive, which may be ascribed to a large freedom of motion of the hydrocarbon chain at the interface and also due to the mixing of surfactant with additive molecules.

The intrinsic viscosity, which indicates solute–solvent interaction and also the size and shape of the particle, was calculated from the relative viscosities by the relation

$$[\eta] = \lim_{C\to 0} \frac{\eta_r - 1}{C} \qquad (8)$$

where the zero concentration limit indicates the absence of interparticle interactions. Some researchers have taken $[\eta]$ to be equal to $(\eta - 1)/C$ without the condition for limiting concentration.[40]

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Table 7. Thermodynamic Activation Parameters for Viscous Flow of Poly(oxyethylene(10)) Lauryl Ether (5% w/v) in the Presence and Absence of PEG 400 and Sucrose

conc of additive (% PEG 400 (w/v))	$\Delta G^{\ddagger}_{\text{vis}}$ (kJ mol^{-1})	$\Delta H^{\ddagger}_{\text{vis}}$ (kJ mol^{-1})	$\Delta S^{\ddagger}_{\text{vis}}$ (kJ mol^{-1} K^{-1})
0.0	63.9	0.52	−0.2
0.1	63.9	0.53	−0.2
0.5	63.9	0.61	−0.2
1.0	64.0	0.67	−0.2

% sucrose	$\Delta G^{\ddagger}_{\text{vis}}$ (kJ mol^{-1})	$\Delta H^{\ddagger}_{\text{vis}}$ (kJ mol^{-1})	$\Delta S^{\ddagger}_{\text{vis}}$ (kJ mol^{-1} K^{-1})
0.1	63.9	0.55	−0.2
0.5	63.9	0.61	−0.2
1.0	63.9	0.60	−0.2

The intrinsic viscosity, $[\eta]$,[40] decreases with an increase in temperature, indicating pronounced micellar dehydration. This is anticipated as micelles become compact with an increase in temperature due to dehydration of polyoxyethylene chains.[41] However the effects of PEG 400 and sucrose on $[\eta]$ are different at a given temperature. Decreased hydration of ethylene oxide chains of the micelle in the presence of sucrose probably leads to a lower $[\eta]$ value while cosolubilization and probable formation of mixed micelles with PEG 400 may be the reasons for an increasing $[\eta]$ value.

It was reported that $C_{12}E_n$ micelles are spherical, and the micellar molecular weight (M_m) of the oxyethylene chain of number n is given by the relation[42]

$$M_m = A_n M = (1025/n - 5.1)M \tag{9}$$

where A_n is the aggregation number and M is the molecular weight of $C_{12}E_n$. Therefore the micellar molecular weight evaluated for the title surfactant where $n = 10$ by eq 9 is

$$M_m = 6.1 \times 10^4$$

From the intrinsic viscosity the hydrated micellar volume (V_h) was computed by the relation

$$V_h = \frac{[\eta]M_m}{2.5N} \tag{10}$$

where N is Avogadro's number. The values are given in Table 6 .

The volume of the hydrocarbon core (V_c) and the volume of the palisade layer of ethylene oxide units (V_{OE}) were also calculated using the following equations

$$V_c = A_n V = 10^{24} A_n M_c/dN \tag{11}$$

$$V_{OE} = V_h - V_c \tag{12}$$

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 (0.802 g/cm^3) of the corresponding liquid n-alkane at 25 °C.

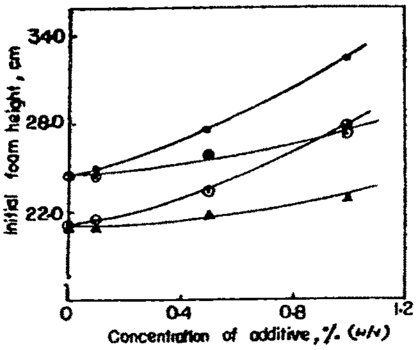

Figure 3. Initial foam height vs percent concentration of additives: ●, PEG 400 at 40 °C; ⊗, sucrose at 40 °C; ▲, PEG 400 at 50 °C; ⊙, sucrose at 50 °C.

Both the hydrated micellar volume (V_h) and the volume of the palisade layer of ethylene oxide (V_{OE}) units decrease as both temperature and concentration of sucrose increase. This was because water and the aquo-sucrose medium become poorer solvents at higher temperature. However, in the presence of PEG 400 both V_h and V_{OE} show an increase. We believe that PEG 400, having a OCH_2CH_2 group identical to the hydrophilic part of the nonionic surfactant, assumes itself as a part of it, leading to an increase in volume of the oxyethylene chain.[43] Such behavior is not seen with sucrose as additive. The thermodynamic activation parameters for the viscous flow were evaluated using the Frenkel–Eyring equation[44]

$$\ln(\eta V/Nh) = \frac{\Delta H^{\ddagger}_{\text{vis}}}{RT} - \frac{\Delta S^{\ddagger}_{\text{vis}}}{R} \tag{13}$$

where V, N, h, and R are the molar volumes, Avogadro's number, Planck's 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 $1/T$, activation enthalpy ($\Delta H^{\ddagger}_{\text{vis}}$) and activation entropy ($\Delta S^{\ddagger}_{\text{vis}}$) for the viscous flow were calculated.

All thermodynamic activation parameters for all systems are presented in Table 7. The $\Delta G^{\ddagger}_{\text{vis}}$ values are positive, indicating a nonspontaneous viscous flow. The constancy in the $\Delta G^{\ddagger}_{\text{vis}}$ value indicates no effect of the additives in the viscous flow. $\Delta H^{\ddagger}_{\text{vis}}$ values indicate that the viscous flow is endothermic. A negative $\Delta S^{\ddagger}_{\text{vis}}$ indicates a more ordered environment both in the presence and the absence of additives.

It is well-known that nonionic surfactants containing the polyoxyethylene groups produce less foam and also less stable foam than ionic surfactants, in aqueous media. However, the foaming efficiency of these nonionic surfactants can be altered by the addition of some organic additives. In Figure 3 the initial foam heights of 0.01% (w/v) of poly(oxyethylene(10)) lauryl ether at 40 and 50 °C in the presence and absence of PEG 400 and sucrose are presented. The increase in foam height, which is observed particularly in the case of PEG, can be attributed to enhanced viscosity, which retards the draining of liquid from the bubbles, leading to enhanced foam stability.

Both PEG 400 and sucrose decreased the cmc of the surfactant studied. It has been reported[16] that the additives which decrease the cmc of the surfactant solution lower the activity of the monomeric surfactant in solution and therefore decrease the rate of migration of the surfactant to the surface and the rate of attainment of surface tension equilibrium, leading to an increase in the foam height. Addition of PEG 400 and sucrose breaks the water matrix. Further the formation of structure occurs because of the hydrogen bond between free water molecules and these additives. The multiple hydrogen bonds with water prevent these polar additives from being forced

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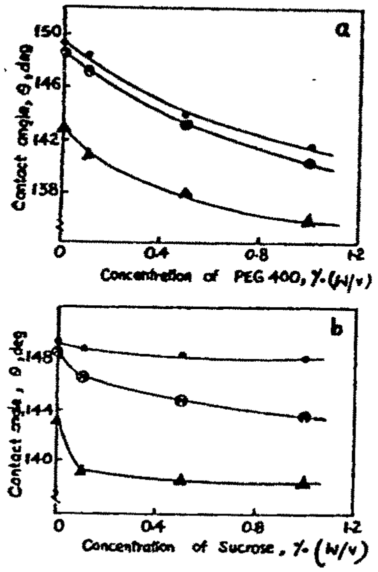

Figure 4. Plots of contact angle (*θ*) vs concentration of additives: (a) PEG 400; (b) sucrose; ●, 0.25%; ⊗, 0.5%; ▲, 1.0% surfactant.

out from between the surfactant molecules and into the interior of the micelles in the bulk phase, giving rise to greater stabilization of the foam.

The effects of different concentrations of PEG 400 and sucrose on the contact angle (*θ*) of a poly(oxyethylene(10)) lauryl ether solution of varying concentrations with a Teflon surface are shown in Figure 4. The contact angle (*θ*) is found to decrease with increasing additive concentrations. This reduction in the contact angle indicates the lowering of interfacial energy of the solid/liquid interface, suggesting interaction of the additives with the surfactant.

Conclusions

The surface and thermodynamic properties of adsorption and micellization of poly(oxyethylene(10)) lauryl ether in a series of aquo-PEG 400 and aquo-sucrose solutions at different temperatures were determined. The micellization process was exothermic in the presence of additives and endothermic in pure aqueous solution. The overall micellization process has been attributed to many features, antagonistic to each other. An enthalpy−entropy compensation effect was observed in these systems with an isostructural temperature of 312 K. Negative enthalpies of transfer ($\Delta\Delta H_m^{\circ,tr}$) indicate hydrophilic group−additive interactions. A decrease in the cloud point shows desolvation of the hydrophilic group of the surfactant in the presence of these additives. The free energy of adsorption was evaluated. The positive values for the 'work of transfer' suggest greater positive change upon adsorption than upon micellization. Large positive ΔS°_{ad} values in the presence of additives reflect greater freedom of motion of the hydrocarbon chain at the planar air/water interface. Variations in the micellar volume including hydration (V_h) and the volume of the oxyethylene chain (V_{OE}) evaluated from viscosity data indicate interactions of additives with the surfactant. The thermodynamic activation parameters for the viscous flow favor a more ordered environment. Both PEG 400 and sucrose increase the initial foam height of the surfactant as well as the stability. Contact angles of varying surfactant concentrations decrease as the concentration of additives is increased.

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