

Interfacial and Thermodynamic Properties of SDBS–C₁₂E₁₀ Mixed Micelles in Aqueous Media: Effect of Additives

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The interfacial and thermodynamic properties of SDBS/C₁₂E₁₀ mixed system in aqueous solution in the presence of additives, i.e., poly(ethylene glycol) 400, sucrose, and urea have been investigated. The critical micelle concentrations (cmc) were determined by both surface tension and conductivity measurements. The maximum surface excess (Γ_{\max}) and minimum area per molecule (A_{\min}) were determined from surface tension data. The thermodynamic parameters of micellization and adsorption were computed and discussed. The enthalpy–entropy compensation effect was observed in all the cosolvent systems. The partition coefficient of these hydrophilic additives between the micelle and the solvent was found to be zero. The transfer quantities, which are sensitive to the solvent structure, were also computed. The interaction parameters between the surfactant molecules both in the presence and absence of additives were evaluated by Rubingh's approach. Micellar aggregation number (N_{agg}) for the mixed system in the presence and absence of additives were determined by fluorescence measurements. ¹H NMR was also used to study the behavior of surfactants in mixed micelles.

Introduction

Surfactants are widely used in a variety of industrial and commercial applications.¹ They are largely exploited for their detergency, solubilization, and surface wetting capabilities in diverse areas such as mining, petroleum, chemical, pharmaceutical industries as well as in chemical, and biochemical research.² The commercial surfactants are invariably mixtures of different surfactants and are better in many ways than single surfactants.^{3,4} Studies involving the physicochemical properties of surfactant mixtures have proved powerful to optimize these properties by just changing the solution composition. This has led to both theoretical as well as practical interests^{5,6} because one can effectively tune the desired features to the range needed. Therefore, a thorough understanding of underlying physics and chemistry of such systems is highly desirable.

The various different physicochemical properties of micellar aggregates are very much sensitive to environmental conditions such as pH, temperature, additives, pressure, etc. In this respect, however, the interfacial and colloidal behaviors of single surfactant systems have been investigated widely over the past few decades, though those of surfactant mixtures have been investigated only to a limited extent.^{7–11} Also, it has been recognized that the partition coefficient of neutral solutes in micellar solutions can be computed with reasonable confidence from cmc determinations.¹² Moreover, cmc-based methods could be of great value in the evaluation of the effect of structure on the micellar solubilization of neutral additives. Because of increasingly widespread uses of such systems in modern applications, an effort was made to study the interfacial and aggregational behavior of the SDBS/C₁₂E₁₀ mixed surfactant system in the presence of neutral additives. The chosen neutral

additives were poly(ethylene glycol) 400 (PEG 400), sucrose, and urea. Since these additives are highly hydrophilic and neutral, their influence upon micellization is expected to be purely chemical and not electrochemical in nature.^{13–15}

This article deals with the physicochemical characterization which involves the cmc determination by both surface tension and conductivity measurements, determination of the degree of ionization of micelle (α), the standard thermodynamic parameters of micellization (ΔG°_m , ΔH°_m , and ΔS°_m), and the computation of partition coefficient of the solute between the micelle and the solvent. Interfacial parameters such as maximum surface excess (Γ_{\max}), minimum area per molecule (A_{\min}), and the standard thermodynamic parameters of adsorption ($\Delta G^\circ_{\text{ad}}$, $\Delta H^\circ_{\text{ad}}$, and $\Delta S^\circ_{\text{ad}}$) were also computed from surface tension data. The micellar aggregation numbers (N_{agg}) were determined by fluorescence measurements. ¹H NMR technique was used to study the behavior of the SDBS/C₁₂E₁₀ mixed system. However, this study is just confined to the changes in chemical shifts and spin lattice relaxation time (T_1) of C₁₂E₁₀ on addition of anionic SDBS. The effect of additives in the system mentioned is discussed.

Experimental Section

Materials. Polyoxyethylene (10) lauryl ether [C₁₂H₂₅(OCH₂CH₂)₁₀OH] (C₁₂E₁₀, Sigma), and sodium dodecyl benzene-sulfonate (SDBS, Sigma) were used without any further purification. PEG 400 (Merck, India), sucrose (AR, 99.9%, Qualigens, India), and urea (BDH, India) were used as received. Cetylpyridinium chloride (CPyCl) (Loba Chemie, Baroda, India) recrystallized twice from benzene and pyrene (Fluka, Germany) was used. All solutions were prepared in doubly distilled water.

Surface Tension Measurements. The surface tensions (γ) were measured by ring method using a du Nouy tensiometer (S. C. Dey and Co., Calcutta, India) at temperatures of 35, 40,

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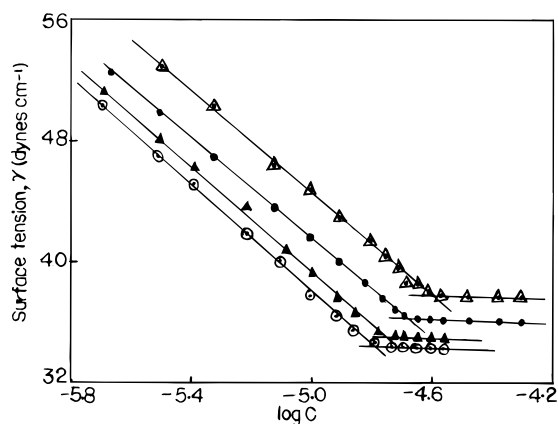


Figure 1. Representative plots of surface tension (γ) vs $\log C$ in various solvents (concentration is in molarity): (Δ) 0.3% sucrose at 35 °C and (\circ) 0.5% sucrose at 40 °C in 9:1 SDBS/ $C_{12}E_{10}$ solutions; (\bullet) 0.5% sucrose at 35 °C in 5:5 SDBS/ $C_{12}E_{10}$ solution; (\blacktriangle) 0.3% PEG 400 at 50 °C in 1:9 SDBS/ $C_{12}E_{10}$.

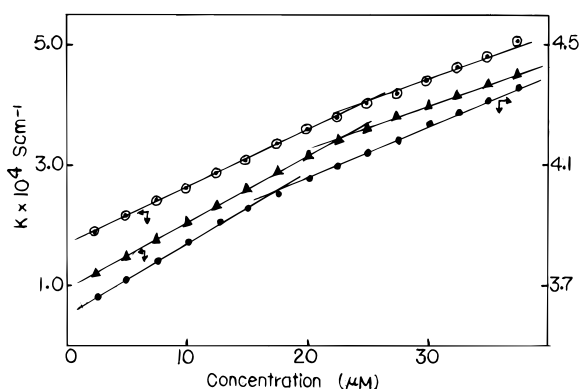


Figure 2. Representative plots of specific conductance (k) vs concentration in various solvents: (\circ) 0.1% urea at 40 °C in 5:5 SDBS/ $C_{12}E_{10}$; (\blacktriangle) 0.7% sucrose at 35 °C in 5:5 SDBS/ $C_{12}E_{10}$; (\bullet) 0.1% urea at 45 °C in 1:9 SDBS/ $C_{12}E_{10}$.

45, and 50 °C. The temperatures were maintained constant by circulating thermostated water through a jacketed vessel containing the solution. Representative plots of surface tension (γ) against \log surfactant concentration ($\log C$) are shown in Figure 1.

Conductivity Measurements. The conductance (k) measurements were done with a Mullard (UK) conductivity bridge. A dip type cell of cell constant 0.6645 cm^{-1} was used. The conductances of different solutions which were obtained on aliquot addition of a known concentrated (stock) surfactant solution to a given volume of the thermostated solvent were measured. Representative plots of k –concentration (μM) are shown in Figure 2.

Fluorescence Measurements. The micellar aggregation number of the surfactant solutions was determined by steady state fluorescence measurements. Pyrene was used as probe

and cetylpyridinium chloride (CPyCl) as quencher. The excitation and emission wavelengths were 335 and 385 nm, respectively. All measurements were carried out at room temperature (~ 25 °C) using a Shimadzu RF-5000 spectrophotofluorimeter.

An aliquot of a stock solution of pyrene in ethanol was transferred into a flask and the solvent was evaporated with nitrogen. The surfactant solution was added and the concentrations of pyrene and surfactant were kept constant at 10^{-6} M and 5 mM, respectively. The quencher concentration was varied from 0 to 2×10^{-5} M. The aggregation number (N_{agg}) was deduced from the equation¹⁶

$$\ln I = \ln I_0 - [Q]/[M] = \ln I_0 - N_{\text{agg}}[Q]/[S] - \text{cmc}$$

where $[Q]$, $[M]$, and $[S]$ are the concentrations of quencher, micelle, and total surfactant, respectively. The I_0 and I are the fluorescence intensities in absence and presence of quencher.

NMR Measurement. Proton NMR measurements were carried out in deuterium oxide (D_2O , 99.9 atom % D, Aldrich) solvent at room temperature (~ 25 °C). The mixed solutions of SDBS and $C_{12}E_{10}$ with total concentrations of 0.3 M were prepared for SDBS mole fractions of 0.0, 0.1, 0.3, 0.5, 0.7, 0.9, and 1.0, respectively. Proton NMR spectra were recorded with JEOL JNM FX-100 FTNMR spectrometer operating at 100 MHz and using deuterium field frequency lock on solvent D_2O . PNMR chemical shifts were referred to internal TMS. The proton longitudinal relaxation times (T_1) were measured using a $(180^\circ - \tau - 90^\circ, \text{FID})$ pulse sequence by the inversion recovery method. The relaxation time was calculated by the nonlinear least-squares fit using the instruments built-in software (provided by JEOL, Japan).

Results and Discussion

The micellization process is a function of temperature, additive, and solvent. The solvent property gets modified in the presence of an additive. In our present study, the cmcs of SDBS/ $C_{12}E_{10}$ mixed surfactant system of various mole ratios were determined at different temperatures and at different concentrations of additives (PEG 400, sucrose, and urea). Both surface tension and conductivity measurements were used. The cmc values obtained by both methods were in good agreement with each other. The cmc data are shown in Tables 1–3. The break points in the surface tension vs \log concentration or conductivity vs concentration plots were taken as cmc.

The temperature has very marked effect on the cmc of both ionic and nonionic surfactants.¹⁷ As temperature increases, the cmc of nonionic surfactant in the absence of any additive decreases. This is a typical characteristic of nonionic surfactant within the limited region of temperature studied. A minimum is sometimes observed at very high temperature. However, in the case of ionic surfactants the cmc decreases in the low-temperature region, shows a minimum, and then increase with increase in temperature.¹⁷ The formation of micelle is due to hydrophobic interaction. As temperature increases, the hydra-

TABLE 1: Effect of Sucrose on the Cmc of the SDBS/ $C_{12}E_{10}$ Mixed System at Different Temperatures and Mole Ratios

conc of sucrose, % (w/v)	cmc, mM											
	SDBS/ $C_{12}E_{10}$ = 9:1				SDBS/ $C_{12}E_{10}$ = 5:5				SDBS/ $C_{12}E_{10}$ = 1:9			
	35 °C	40 °C	45 °C	50 °C	35 °C	40 °C	45 °C	50 °C	35 °C	40 °C	45 °C	50 °C
0.0	0.0237	0.0248	0.0258	0.0268	0.0206	0.0214	0.0224	0.0234	0.0132	0.0144	0.0158	0.0168
0.1	0.0246	0.0252	0.0264	0.0276	0.0208	0.0212	0.0226	0.0238	0.0142	0.0156	0.0164	0.0170
0.3	0.0252	0.0264	0.0274	0.0286	0.0210	0.0218	0.0230	0.0242	0.0148	0.0153	0.0162	0.0174
0.5	0.0262	0.0276	0.0284	0.0292	0.0218	0.0226	0.0238	0.0248	0.0152	0.0164	0.0173	0.0186
0.7	0.0275	0.0284	0.0294	0.0302	0.0220	0.0231	0.0242	0.0250	0.0156	0.0168	0.0178	0.0191

TABLE 2: Effect of PEG 400 on the Cmc of the SDBS/C₁₂E₁₀ Mixed System at Different Temperatures and Mole Ratios

conc of PEG 400, % (w/v)	cmc, mM, at											
	SDBS/C ₁₂ E ₁₀ = 9:1				SDBS/C ₁₂ E ₁₀ = 5:5				SDBS/C ₁₂ E ₁₀ = 1:9			
	35 °C	40 °C	45 °C	50 °C	35 °C	40 °C	45 °C	50 °C	35 °C	40 °C	45 °C	50 °C
0.0	0.0237	0.0248	0.0258	0.0268	0.0206	0.0214	0.0224	0.0234	0.0132	0.0144	0.0158	0.0168
0.1	0.0250	0.0262	0.0272	0.0284	0.0210	0.0218	0.0228	0.0236	0.0150	0.0158	0.0166	0.0174
0.3	0.0256	0.0264	0.0274	0.0286	0.0212	0.0220	0.0232	0.0240	0.0154	0.0162	0.0170	0.0178
0.5	0.0260	0.0272	0.0282	0.0292	0.0218	0.0224	0.0234	0.0246	0.0158	0.0166	0.0174	0.0180
0.7	0.0268	0.0276	0.0288	0.0296	0.0220	0.0228	0.0238	0.0250	0.0162	0.0170	0.0176	0.0182

TABLE 3: Effect of Urea on the Cmc of the SDBS/C₁₂E₁₀ Mixed System at Different Temperatures and Mole Ratios

conc of urea, % (w/v)	cmc, mM, at											
	SDBS/C ₁₂ E ₁₀ = 9:1				SDBS/C ₁₂ E ₁₀ = 5:5				SDBS/C ₁₂ E ₁₀ = 1:9			
	35 °C	40 °C	45 °C	50 °C	35 °C	40 °C	45 °C	50 °C	35 °C	40 °C	45 °C	50 °C
0.0	0.0237	0.0248	0.0258	0.0268	0.0206	0.0214	0.0224	0.0234	0.0132	0.0144	0.0158	0.0168
0.1	0.0250	0.0262	0.0274	0.0282	0.0212	0.0218	0.0228	0.0240	0.0154	0.0162	0.0170	0.0182
0.3	0.0262	0.0274	0.0286	0.0298	0.0216	0.0224	0.0236	0.0245	0.0158	0.0168	0.0176	0.0188
0.5	0.0272	0.0284	0.0296	0.0308	0.0220	0.0226	0.0238	0.0248	0.0162	0.0172	0.0184	0.0196
0.7	0.0292	0.0301	0.0314	0.0325	0.0225	0.0238	0.0244	0.0252	0.0166	0.0176	0.0190	0.0202

tion of hydrophobic group decreases and hence the cmc is lower.¹⁷ The ionic repulsive forces are responsible for higher values of cmc in the ionic surfactants. In the case of nonionic surfactants, the breaking of water structure and the formation of icebergs surrounding the solute are also responsible for the lower cmc.^{7,8} However, for SDBS/C₁₂E₁₀ mixed system, a behavior similar to that of the ionic surfactants is observed with respect to temperature, implying that mixed micelles are ionic in nature. Also, in the presence of different concentrations of PEG 400, sucrose, and urea, a similar effect is observed. Additives break the three-dimensional water matrix. Both PEG 400, a water-soluble low molecular weight oligomer, and sucrose are highly hydrophilic and form hydrogen bonds with solvent water molecules.⁸ The micellar structure may be considered to be made up of two regions: an outer region composed of polar headgroups plus a portion of hydrocarbon chains in contact with water (i.e., ionic heads fully and hydrocarbon chains to various degrees), and an inner region, the hydrocarbon core, containing only all the remaining hydrocarbon chains not in contact with water.¹⁸ The strong hydrogen-bonding interactions of water with both PEG 400 and sucrose due to the presence of —OH groups have a major effect on the water at the micellar hydrocarbon—water interface which is otherwise structured by a hydrophobic effect; i.e., the structured water around the hydrophobic group is disrupted. In other words, the favorable hydrogen-bonding ability of these additives lead to poorer contribution to the hydrophobic interactions (and the van der Waals attraction) which is the driving force for micellization, and hence the higher cmc values. As the concentration of additives increase at the different mole fractions of SDBS/C₁₂E₁₀ studied, the cmc too increases. The antagonistic effects like (i) breaking of the water matrix by the additives, (ii) formation of structure in the solvent due to hydrogen bonding, (iii) and the electrostatic repulsion between the ionic species in the presence of these additives determine the overall effect observed. It is obvious from the tabulated data that urea too increases the cmc values of various SDBS/C₁₂E₁₀ mixed systems at all the mole ratios studied. It is well-known that urea and its derivatives are protein denaturants and have been found to be very efficient modifiers of aqueous solution properties.¹⁹ It has been suggested that urea acts on aqueous solution by two different mechanisms:²⁰ (i) an indirect mechanism in which urea acts as a “water structure breaker” facilitating the solvation of nonpolar solutes and (ii) a direct mechanism, whereby urea

participates in the solvation of hydrophobic solutes in water by replacing some water molecules in the hydration shell of the solutes. Several investigations^{21,22} on the action of urea in the micellar solutions have shown that urea increases the cmc and decreases the micelle size of ionic and nonionic surfactants. Our results too indicate an increase in the cmc values as the urea concentration increases. Also, it has been reported that the surfactant monomers are stabilized in aqueous urea solutions.²³ The disruption of water structure by urea may increase the hydration of polar headgroups of surfactants thereby enhancing the solubility of the unaggregated surfactant monomers i.e., increase in cmc. Therefore, an interplay of various properties like demicellization, monomer stability, water structure, and solvation of hydrophilic groups actually determine the overall experimentally obtained results obtained in the presence of PEG 400 and sucrose.

As the cmc can serve as a measure of micelle stability in a given state, the thermodynamic parameters of micellization can be determined from the temperature dependence of the cmc.²⁴ The standard free energy of micellization (ΔG°_m) was calculated using the relation¹⁷

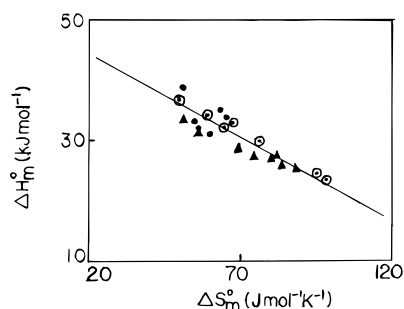
$$\Delta G^\circ_m = (2 - \alpha)RT \ln \text{cmc}$$

where cmc is in mole fraction scale. The degree of ionization of micelle (α) was computed from the ratio between the slopes of the postmicellar and premicellar regions.²⁵ The standard state is a hypothetical system with unit mole fraction of the surfactant solution at cmc. In Table 4, the ΔG°_m values are reported at 35 °C in the presence of various amounts of additives at 5:5 mole ratios of SDBS/C₁₂E₁₀. It can be noted from the given data that both in the absence and presence of additives, the ΔG°_m values become more negative with increase in temperature. This indicates that micelle formation is favored with rise in temperature. Moreover, the overall ΔG°_m values in the presence of PEG 400, sucrose, and urea at different SDBS/C₁₂E₁₀ mole ratios are negative, implying a spontaneous micelle formation. Also, it can be observed that the ΔG°_m values in the absence of these additives are lower than in the presence of the additives; i.e., the mixed micelle formation is relatively more favored in the absence than in the presence of the additives. As the micellization process is accompanied by an appreciable change in water structure (as mentioned earlier), the changes observed in ΔG°_m may be ascribed to the pronounced effect of these additives on

TABLE 4: Standard Thermodynamic Parameters of Micellization and Degree of Ionization of Micelle (α) for SDBS/C₁₂E₁₀ (5:5) Mixed System in Presence and Absence of Different Additives^a

conc. of additive % (w/v)	PEG 400				Sucrose				Urea			
	α (35 °C)	$-\Delta G_m^\circ$ (35 °C)	$-\Delta H_m^\circ$	ΔS_m°	α (35 °C)	$-\Delta G_m^\circ$ (35 °C)	$-\Delta H_m^\circ$	ΔS_m°	α (35 °C)	$-\Delta G_m^\circ$ (35 °C)	$-\Delta H_m^\circ$	ΔS_m°
0.0	0.50	57.0	15.2	136								
0.1	0.58	53.7	30.2	76	0.56	54.6	38.9	51	0.61	52.6	27.4	82
0.3	0.59	53.5	33.0	67	0.55	54.8	35.5	63	0.62	52.3	26.6	83
0.5	0.59	53.4	23.2	98	0.55	54.7	35.3	63	0.62	52.1	25.1	88
0.7	0.57	53.8	24.6	95	0.56	54.3	34.3	65	0.61	52.2	27.6	80

^a The maximum error in ΔG_m° is less than 1% and that of ΔH_m° is 7% and in ΔS_m° is 8%. The units for ΔG_m° , ΔH_m° , and ΔS_m° are kJ mol⁻¹, kJ mol⁻¹, and J mol⁻¹ K⁻¹ respectively.

**Figure 3.** Enthalpy-entropy compensation plot for all systems together: (●) sucrose; (○) PEG 400; (▲) urea.

water structure. The standard enthalpy (ΔH_m°) and entropy (ΔS_m°) of micellization were evaluated from $\Delta G_m^\circ - T$ plots. The slope and intercept gave ΔS_m° and ΔH_m° , respectively (correlation coefficient = 0.99). The overall micellization process, both in the presence and absence of these additives, is exothermic. The exothermic and endothermic characteristics of micellization are very specific to surfactants, additives, and temperature.^{26,27} Nusselder and Engberts²⁸ have stressed the importance of London dispersion forces as the main attractive force for the micellization process. It has been suggested that for the negative ΔH_m° , the dispersion forces play a major role in the micelle formation. Also, the exothermicity observed in our studies can be attributed to possible surfactant-additive interactions. It is to be noted that ΔH_m° is independent of temperature both in the presence and absence of PEG 400, sucrose, and urea for the SDBS/C₁₂E₁₀ mixed systems. This implies that no remarkable change in the environment surrounding the hydrocarbon chain of the surfactant molecule takes place as the temperature is changed. However, this independence may also be due to the error ($\pm 7\%$) associated with ΔH_m° . Increasing additive concentration does not change ΔH_m° to a large extent. This suggests that as the additive concentration increases, the environment surrounding the surfactant molecules does not vary much.

The entropy of micellization (ΔS_m°) is positive, indicating that the micellization process is entropy dominated in these systems, particularly when entropy change is high. The positive ΔS_m° is due to the melting of "icebergs" or "flickering clusters" around the hydrocarbon tails of the surfactant monomers and the increased randomness of the hydrocarbon chains in the micellar core.²⁹ As observed in Table 4, the magnitudes of ΔS_m° are lower in the presence of additives relative to that in their absence. This suggests that these additives still control the three-dimensional water matrix.

A linear correlation between ΔH_m° and ΔS_m° was observed in these systems with a slope of 285 K (Figure 3) as suggested by Lumry et al.³⁰ This was observed earlier also.^{7,8} The micellization process at this temperature of 285 K is totally

independent of any structural change and depends only on enthalpic factors.

Also, $\Delta\Delta H_m^{\circ, \text{tr}}$, the so-called transfer quantities, can be easily computed from the standard enthalpies of micellization. This is defined by²³

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

The $\Delta\Delta H_m^{\circ, \text{tr}}$ values for all the systems have been found to be negative. Such negative values were observed earlier for the transfer of amino acids and NaCl from water to aqueous urea. It was concluded that the hydrophilic group transfer from water to aqueous urea solutions was exothermic whereas for hydrophobic groups it was endothermic. Hence, the exothermicity of the transfer process in this case can be attributed to the polar hydrophilic group additive interaction. Moreover, the structure-breaking ability of the solutes may also be a reason for negative $\Delta\Delta H_m^{\circ, \text{tr}}$ values.

It was shown by Treiner et al.³¹ that for dilute solutions of polar additives in aqueous surfactant solution at the cmc, the following general form of classical Setchenow equation was well obeyed.

$$\log \text{cmc}_w / \text{cmc}_{w+A} = K_M m'$$

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 micellization constant, and m' is the molarity of the neutral additive. In dilute solutions with respect to the polar additive, the constant K_M takes the form³¹

$$K_M = 1/2[k_s^N + qM/2.303 \times 1000]$$

where k_s^N the familiar Setchenow constant or salting constant, q is the ideal partition coefficient of the solute between micelle and water, and M is the solvent molecular weight. The salting constant is calculated by the empirical relationship³¹

$$k_s^N = 0.637 - 0.014n(\text{CH}_2) - 0.1464R$$

where $n(\text{CH}_2)$ is the number of methylene groups in the linear hydrocarbon chain and R is the hard-sphere diameter of the additives calculated from van der Waals volumes. The R values for PEG 400, sucrose, and urea are 7.46, 8.04,³² and 4.70 Å,³² respectively.

The R value for PEG 400 was calculated by us from the van der Waals increments of atoms or groups as given by Bondi.³³ The k_s^N values thus calculated for all the three additives are negative indicating a salting-in effect in aqueous surfactant solutions. Also, the K_M values obtained at all three mole ratios of SDBS/C₁₂E₁₀ in the presence of PEG 400, sucrose, and urea are negative and the values are given in Table 5.

TABLE 5: Micellization Constant K_M (L mol⁻¹) for the SDBS/C₁₂E₁₀ Mixed System in the Presence of PEG 400, Sucrose, and Urea at Different Temperatures

SDBS/ C ₁₂ E ₁₀	PEG 400				sucrose				urea			
	35 °C	40 °C	45 °C	50 °C	35 °C	40 °C	45 °C	50 °C	35 °C	40 °C	45 °C	50 °C
9:1	-1.95	-1.62	-1.74	-1.26	-2.77	-2.99	-3.50	-2.16	-0.66	-0.59	-0.58	-0.60
5:5	-1.46	-1.33	-1.19	-1.71	-1.53	-2.15	-1.78	-1.53	-0.26	-0.38	-0.29	-0.21
1:9	-2.23	-2.12	-1.73	-1.27	-1.96	-1.84	-2.02	-3.09	-0.32	-0.35	-0.49	-0.46

TABLE 6: Maximum Surface Excess (Γ_{\max}) Values for the SDBS/C₁₂E₁₀ (5:5) Mixed System at Different Temperatures in the Presence and Absence of PEG 400, Sucrose and Urea

conc of additive, % (w/v)	$\Gamma_{\max} \times 10^{10} \text{ mol cm}^{-2}$											
	PEG 400				sucrose				urea			
	35 °C	40 °C	45 °C	50 °C	35 °C	40 °C	45 °C	50 °C	35 °C	40 °C	45 °C	50 °C
0.0	1.21	1.17	1.15	1.13								
0.1	1.02	1.17	1.26	1.32	1.61	1.68	1.71	1.77	1.13	1.19	1.28	1.33
0.3	1.02	1.10	1.17	1.21	1.49	1.57	1.64	1.69	1.07	1.12	1.17	1.34
0.5	0.97	1.02	1.07	1.20	1.42	1.53	1.59	1.59	1.02	1.08	1.15	1.29
0.7	0.98	1.00	1.05	1.16	1.42	1.50	1.61	1.61	0.97	1.07	1.12	1.26

TABLE 7: Standard Thermodynamic Parameters of Adsorption of the SDBS/C₁₂E₁₀ (5:5) Mixed System in the Presence and Absence of Different Concentrations of PEG 400, Sucrose, and Urea

conc of additive, % (w/v)	PEG 400			sucrose			urea		
	$-\Delta G^\circ_{\text{ad}}$	$-\Delta H^\circ_{\text{ad}}$	$\Delta S^\circ_{\text{ad}}$	$-\Delta G^\circ_{\text{ad}}$	$-\Delta H^\circ_{\text{ad}}$	$\Delta S^\circ_{\text{ad}}$	$-\Delta G^\circ_{\text{ad}}$	$-\Delta H^\circ_{\text{ad}}$	$\Delta S^\circ_{\text{ad}}$
0.0	79.9	-20.9	328						
0.1	74.5	24.9	161	70.6	28.2	137	79.1	41.3	123
0.3	77.6	29.3	157	72.4	24.2	157	78.2	42.6	115
0.5	76.2	36.4	129	71.1	25.0	150	77.5	38.2	127
0.7	78.0	30.4	154	70.3	18.1	169	77.3	34.9	138

^a The units for $\Delta G^\circ_{\text{ad}}$, $\Delta H^\circ_{\text{ad}}$, and $\Delta S^\circ_{\text{ad}}$ are kJ mol⁻¹, kJ mol⁻¹, and J mol K⁻¹, respectively.

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 these 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 increase.³⁴ The variation of the cmc with the addition of these solutes may be entirely ascribed to the effect of these additives on the bulk solvent properties. Therefore, the additives by interacting with both the surfactant monomers and the solvent molecules induce a shift of the equilibrium between the micelles and surfactant monomers in favor of the latter. 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 micelle.

The surface excess concentration under the conditions of surface saturation, Γ_{\max} , can conveniently be used as a measure of maximum extent of adsorption of surfactants using the well-known Gibbs adsorption equation.^{35,36} The values thus calculated for these systems are shown in Table 6 (at 5:5 SDBS/C₁₂E₁₀). It is observed that in the absence of additives maximum adsorption density (Γ_{\max}) showed a decrease with increasing temperature. This is due to the increased molecular motion of the surfactant as temperature rises, leading to thermal agitation at the air/water interface. However, as shown in Table 6, in the presence of additives Γ_{\max} increases with increase in temperature. The breaking of solvent structure and probably a decreased freedom of motion of hydrocarbon chains are the reasons for such behavior.

As the concentrations of additives i.e., PEG 400, sucrose, and urea, are increased at all mole ratios of SDBS/C₁₂E₁₀ studied, the Γ_{\max} values are found to decrease. The most

pronounced structural influence on Γ_{\max} comes from the nature of the headgroup. Such effect on Γ_{\max} can be attributed to the changed structure of the hydrophilic group of surfactant molecules caused by the interaction with the additives.

The limiting surface area per molecule of the surfactant, A_{\min} , at the surface was obtained at different SDBS/C₁₂E₁₀ mole ratios. As the concentration of additive is increased, the A_{\min} values increase showing a poorer packing at the air/water interface. As the temperature is increased, the A_{\min} values decrease in contrast to the effect observed in absence of additives. This can be ascribed to the fact that these additives lower the repulsion between the oriented heads, allowing a closer packing at the interface. Hence, the overall result observed can be attributed to various different factors such as (i) the changed structure around the headgroup due to surfactant hydrophilic group-additive interaction; (ii) the changed nature of water in the presence of additives; and (iii) presence of additives at the air/water interface.

In Table 7 the thermodynamic parameters of adsorption of SDBS/C₁₂E₁₀ (5:5) mixed system in the presence and absence of additives are shown. The standard free energy of adsorption was calculated by the reaction³⁷

$$\Delta G^\circ_{\text{ad}} = RT \ln \text{cmc} - n\Pi_{\text{cmc}}A_{\text{cmc}}$$

where Π_{cmc} and A_{cmc} are the surface pressure and area per molecule at cmc. The standard state of the adsorbed surfactant here is a hypothetical monolayer at its minimum surface area per molecule, but at zero surface pressure. 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 per molecule, A_{\min} ($=A_{\text{cmc}}$). The standard entropy of adsorption ($\Delta S^\circ_{\text{ad}}$) was obtained from the slope of $\Delta G^\circ_{\text{ad}}-T$ plot, and the enthalpy ($\Delta H^\circ_{\text{ad}}$) of adsorption was hence evaluated.

TABLE 8: Interaction Parameter (β^m) for the SDBS/C₁₂E₁₀ (5:5) Mixed System in the Presence of Different Concentrations of Additives at Different Temperatures

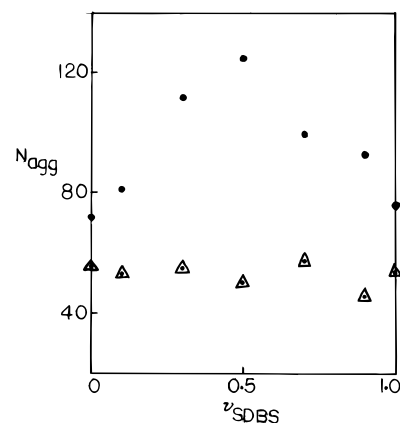
conc of additive, % (w/v)	β^m											
	PEG 400				sucrose				urea			
	35 °C	40 °C	45 °C	50 °C	35 °C	40 °C	45 °C	50 °C	35 °C	40 °C	45 °C	50 °C
0.0	-9.9	-8.8	-8.5	-8.4	-9.9	-8.8	-8.5	-8.4	-9.9	-8.8	-8.5	-8.4
0.1	-7.0	-3.4	-5.8	-9.2	-4.1	-7.9	-	-5.0	-4.0	-4.1	-3.9	-3.7
0.3	-6.9	-6.1	-4.4	-2.9	-3.0	-2.4	-9.1	-3.2	-4.3	-4.4	-4.4	-4.4
0.5	-8.5	-10.6	-7.9	-7.5	-8.8	-2.7	-4.3	-2.0	-4.5	-4.7	-4.7	-4.7
0.7	-4.3	-8.9	-3.6	-7.6	-2.7	-4.2	-8.7	-10.5	-4.5	-4.5	-4.6	-4.7

It is observed from Table 7 that the ΔG_{ad}° values are all 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 the additives. Moreover, the ΔS_{ad}° values are more negative compared to their corresponding ΔG_m° values, indicating that when the micelle is formed, work has to be done to transfer the surfactant molecule in its monomeric form at the surface to the micellar stage in aqueous medium. As the temperature is increased, the ΔG_{ad}° becomes more negative both in the presence and in the absence of additives. Dehydration of the hydrophilic group of surfactant is required for the adsorption to take place, and since at higher temperature the surfactant is less hydrated, lesser energy is necessary for the adsorption to occur. In other words, the adsorption at the air/water interface takes place relatively more spontaneously at higher temperature.

The ΔH_{ad}° values for all the systems are negative, suggesting an exothermic process of adsorption. Such exothermic and endothermic contributions toward the adsorption process can be ascribed to whether bond making or bond breaking predominates during adsorption. Also the exothermicity in adsorption can be attributed to hydrophilic group-additive interaction. The standard entropy of adsorption (ΔS_{ad}°) values are all positive, reflecting greater freedom of movement of hydrocarbon chains at the air/water interface. However, it should be mentioned that in the presence of additives the lowering of electrostatic repulsion between ionic species at the air/water interface reduces the freedom of motion of hydrocarbon chains leading to lower ΔS_{ad}° values.

The interaction between the surfactant molecules in the mixed micelle β^m was evaluated both in the presence and in the absence of additives using Rubingh's approach.³⁸ The values of β^m as shown in Table 8 are all negative, at all mole ratios of SDBS/C₁₂E₁₀ at different concentrations of additives. Such negative values of β^m have been reported earlier³⁸⁻⁴⁰ also for anionic-nonionic binary surfactant mixtures. This can be attributed to attractive interaction between SDBS and C₁₂E₁₀ headgroups leading to electrostatic stabilization. It is suggested that nonionic surfactants of poly(ethylene oxide) type have a weakly cationic character resulting either from oxonium ion formation with protons from the water⁴¹ or simply by sharing H of water by hydrogen bond formation. The attractive interaction may probably be due to this very weak cation with anionic surfactant.

The micellar aggregation number (N_{agg}) was determined by steady-state fluorescence measurements at different mole ratios of SDBS/C₁₂E₁₀. The data in Figure 4 indicate a synergistic effect in aggregation number. The values are larger than either of the two pure components (N_{agg} is 75 and 72 for SDBS and C₁₂E₁₀, respectively) and such a behavior can be ascribed to two competing factors.^{42,43} (1) Nonionic surfactants show a lower aggregation number due to increased steric forces. However, as the anionic SDBS incorporates into the micelle these steric interactions are decreased compared to pure C₁₂E₁₀

**Figure 4.** Micellar aggregation number (N_{agg}) vs mole fraction of SDBS (v_{SDBS}) at room temperature (see text): (●) without additive; (○) 0.3% PEG 400.

micelle. It is because the oxyethylene groups are highly hydrated and hence of large size and consequently high steric hindrance. The presence of SDBS decreases the size and hence the decrease in steric forces. (2) Due to the presence of interionic interactions, ionic surfactants have low aggregation number when the nonionic C₁₂E₁₀ gets incorporated into the micelle and the interionic interactions are decreased compared to pure SDBS micelle. Consequently, the repulsive headgroup interactions are much reduced, leading to larger mixed micelle compared to pure C₁₂E₁₀ or SDBS.

However, in the presence of additives like PEG 400, sucrose, and urea, the N_{agg} values are considerably lowered. Both PEG 400 and sucrose due to the presence of -OH groups have major effect on the water at the micellar hydrocarbon-water interface. Also, it has been reported²² that urea replaces some water molecules in the solvation layer of the micelle headgroups, leading to direct participation of urea in the solvation of the micelle. Since the urea molecule is 2.5 times larger than a water molecule²² and the substitution of water molecules by urea molecules will cause an increase in the surface area per headgroup, there is lowering of the micellar aggregation number. It is to be noted that the extent of decrease in N_{agg} values is the same in the presence of PEG 400, sucrose, and urea. The overall effect is indicative of the hindrance in the micelle formation in the presence of these additives, and all three additives seem to provide the same amount of hindrance. However, with a definite increase in the concentration of additives, a small increase in the aggregation number was observed. The N_{agg} values were 51 ± 3 , 55 ± 3 , 59 ± 3 , and 63 ± 3 for 0.1%, 0.3%, 0.5%, and 0.7% (w/v) additive (i.e., PEG 400, urea, and sucrose) concentrations, respectively, at all SDBS/C₁₂E₁₀ mole ratios. This shows that all systems show almost the same aggregation number in the presence of additives though in the absence of additives a maximum is observed at 0.5 SDBS (Figure 4).

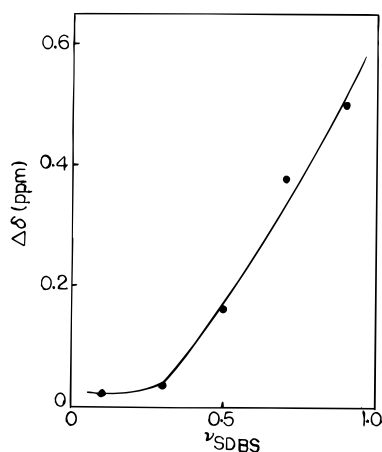


Figure 5. Change in upfield shift of oxyethylene proton signal ($\Delta\delta$) vs mole fraction of SDBS (ν_{SDBS}).

Proton NMR spectroscopy was also used for the studies of SDBS/ $C_{12}E_{10}$ mixed surfactant behavior. The peak assignments were done for $C_{12}E_{10}$ with the 3.60 ppm peak corresponding to the oxyethylene moiety, 0.87 ppm (CH_3), 1.29 ppm [$(\text{CH}_2)_9$], and 1.58 ppm for methylene protons adjacent to the oxyethylene group.⁴⁴

The peak assignments for SDBS were done as reported.⁴⁵ The changes in the chemical shifts on the gradual addition of SDBS were monitored and the chemical shift due to oxyethylene group showed significant changes compared to other peaks. Figure 5 shows the changes in the chemical shift of oxyethylene proton on addition of SDBS. It is observed that the POE signal shifts to higher magnetic field in the presence of SDBS; i.e., the extent of upfield shift depends on the mole fraction of SDBS in the mixed system. Such upfield shift was observed earlier⁴⁶ also for anionic–nonionic surfactant mixture which has been ascribed to the interaction of POE chain with the benzene ring of anionic surfactant, i.e., sodium *p*-octylbenzenesulfonate. However, in our studies no appreciable changes in the peak due to phenyl protons near the alkyl chains was observed. UV spectroscopy also did not show any change in the position of λ_{max} (220 nm for phenyl ring) in the mixed system.

Evidence for the interaction can be provided by the changes in the chemical shift of poly(ethylene glycol) in SDBS. The poly(ethylene glycol) in D_2O shows a peak at $\delta = 3.67$ ppm corresponding to the resonance of ethylene oxide proton.⁴⁷ This moves upfield to $\delta = 3.54$ ppm on addition of SDBS. Moreover, the phenyl proton shows a downfield shift from $\delta = 7.50$ ppm to $\delta = 7.57$ ppm. This is indicative of interaction between SDBS/ $C_{12}E_{10}$. However, it is difficult to pinpoint a single “ OCH_2CH_2 ” group which interacts with SDBS from the present NMR data.

The ^1H longitudinal relaxation time was measured for this mixed system. Since the oxyethylene signal was sufficiently intense and well resolved and showed appreciable changes with SDBS, the T_1 measurements were done only for poly(oxyethylene) protons that resonate at $\delta = 3.60$ ppm. As the resolution of aromatic proton signal was poor at higher mole fractions of $C_{12}E_{10}$ the T_1 measurements were not done.

As shown in Figure 6 the T_1 values initially decrease on the very first addition of SDBS and remains almost constant up to SDBS = 0.5 and then increase considerably on further addition of SDBS. This can be rationalized to the restricted motion of oxyethylene chains at lower mole fractions of SDBS in comparison to pure $C_{12}E_{10}$. On further addition of SDBS, the

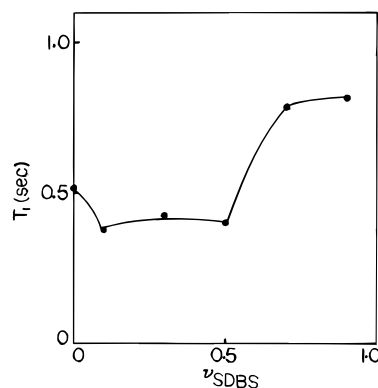


Figure 6. Spin–lattice relaxation time (T_1) vs mole fraction of SDBS (ν_{SDBS}).

micellar structure loosens up due to mutual Coulombic repulsions of the ionic heads in the mixed micelle.

Conclusions

The interfacial and thermodynamic properties of micellization and adsorption of SDBS/ $C_{12}E_{10}$ binary surfactant system in aquo–PEG 400, aquo–sucrose, and aquo–urea solutions at different mole ratios of SDBS, temperature, and concentrations of additives were determined. The mixed micellization of SDBS– $C_{12}E_{10}$ is more favored in the absence than in the presence of additives. The overall micellization process was exothermic and entropy of micellization was positive. The overall micellization process has been attributed to various antagonistic features. An enthalpy–entropy compensation effect was observed for all solvent systems with an isostructural temperature of 285 K. The $\Delta\Delta H_{\text{mtr}}^{\circ}$ values were all negative attributed to the surfactant hydrophilic groups additive interaction. The Γ_{max} and A_{min} values indicate marked effect of these additives on the mixed system. The standard free energy of adsorption is negative throughout. The positive values for the “work of transfer” suggest positive changes upon adsorption than upon micellization. The N_{agg} values decrease for the SDBS/ $C_{12}E_{10}$ mixed system in the presence of additives. The ^1H NMR studies indicate an interaction between the oxyethylene–benzene ring of nonionic–anionic surfactants, respectively.

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