Bull. Chem. Soc. Jpn., 73, 281—287 (2000)

Solution Properties of Sodium Dodecylbenzenesulfonate (SDBS): Effect of Additives

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(Received April 8, 1999)

The solution properties of sodium dodecylbenzenesulfonate (SDBS) in an aqueous medium in the presence of additives, like polyethylene glycol 400 (PEG 400), sucrose, and urea, have been investigated. The critical micelle concentration (cmc) was determined by both surface-tension and conductivity methods. The cmc values were found to increase along with an increase in the temperature in both the presence and absence of additives at all of the concentrations studied. The interfacial parameters, such as the maximum surface excess (Γ_{max}) and minimum area per molecule (A_{min}), were computed from surface-tension data. The thermodynamic parameters of micellization and adsorption at air/water interfaces were also evaluated. Other properties, such as the micellar aggregation number (N_{agg}), viscosity, foaming, wetting, and detergency by dye solubilization, were also studied.

During the last few decades, due to growing interest in surfactant systems, additive–surfactant–water ternary systems have gained wide importance.[1—3] They provide vital information about the solute–solute and solute–solvent interactions in surfactant solutions, and, hence, have lead to extensive structural, kinetic, and thermodynamic studies. It is well known that the aggregation and surface properties of surfactants in solution are dependent on various external factors, such as the temperature, pressure, and presence of additives. Hence, the properties of surfactant solutions can be effectively tuned to a desired range and application by altering (i) the tendency to form micelles, as reflected by the cmc, and (ii) the structure and shape of micelles etc. by changing the solution conditions. Such studies on the physicochemical properties of surfactant systems are of both theoretical and practical interest. In pursuance of our own interest[4—9] to investigate the solution properties of pure and mixed surfactants, we studied the effect of nonionic additives, like polyethylene glycol 400 (PEG 400), sucrose, and urea, on sodium dodecylbenzenesulfonate (SDBS), the "working horse" of the detergent industry.

In this paper we report on the effects of an additive on the critical micelle concentrations (cmc), the degrees of ionisation of the micelle (α), interfacial adsorption parameters (Γ_{max} and A_{min}) at air/water interfaces, aggregation numbers (N_{agg}), thermodynamic parameters of micellization and adsorption, foaming, viscosity, wetting, and detergency by dye solubilization method.

Experimental

Materials: Sodium dodecylbenzenesulfonate (SDBS, Sigma), PEG 400 (Merck, India), sucrose (AR, 99.9%, Qualigens, India), pyrene (Fluka, Germany), and urea (BDH, India) were used as received. Hexadecyl pyridinium chloride (CPyCl) (Loba Chemie, Baroda, India) recrystallized twice from benzene was used. All solutions were prepared in doubly distilled water.

(i) Surface Tension Measurements: The surface tension (γ) was measured by a ring method using a du Noüy tensiometer (S. C. Dey and Co., Calcutta, India) at different temperatures of 35, 40, 45, and 50 °C. All measurements were carried out at a constant temperature maintained by circulating thermostated water through a jacketed vessel containing the solution. Representative plots of the surface tension vs. logarithm of the surfactant concentration (M) are shown in Fig. 1. The reproducibility (standard deviation of the mean) in the cmc was found to be ±0.5%, calculated from the

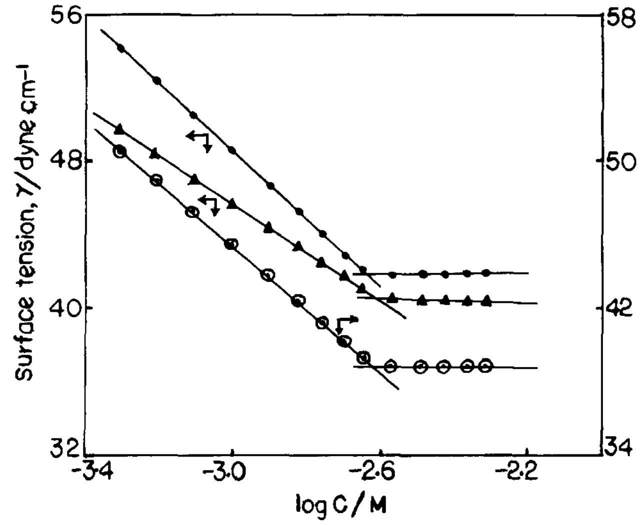

Fig. 1. Representative plots of surface tension (γ) vs. log C for SDBS–additive–water systems.
● 0.5% Sucrose at 35 °C; ▲ 0.5% PEG 400 at 40 °C; ○ 0.1% Urea at 40°C.

experimental cmc data from at least two runs.

(ii) Conductivity Measurements: The conductance measurements were carried out with a Mullard (UK) conductivity bridge. A dip-type cell having a cell constant of 0.6645 cm^{-1} was used. The conductances of the solutions, by the aliquot addition of a known concentrated surfactant solution (stock) to a known volume of the thermostated solvent, were measured. Representative plots of the specific conductance (k)–concentration (M) are shown in Fig. 2. The reproducibility in the cmc (the standard deviation of the mean) was found to be ±0.5%.

(iii) Fluorescence Measurements: The aggregation number (N_{agg}) was determined by a steady state fluorescence method. Pyrene and 1-hexadecyl pyridinium chloride (CPyCl) were used as the probe and quencher, respectively. The excitation wavelength was 335 nm and the emission wavelength was 385 nm. All measurements were carried out at room temperature (ca. 25 °C) using a Shimadzu RF5000 spectrophotofluorimeter. The concentration of pyrene and the surfactant were constant at 10^{-6} M and 5 mM (1 M = 1 mol dm^{-3}), respectively. The quencher concentration was varied from 0—2×10^{-5} M. The detail procedure is described elsewhere.[6]

(iv) Contact Angle Measurements: The wetting characteristics of the surfactant solution was determined by a contact-angle measurement. A contact 'θ' meter, obtained as a gift from Department of Color Chemistry, University of Leeds, Leeds, UK was used to measure the contact angle. The surfactant solution was placed as a drop on a PTFE [poly(tetrafluoroethylene)] surface using a microsyringe. The contact angles were determined, and the averages of at least four determinations are reported. All measurements were carried out at room temperature (ca. 30 °C). The error in the contact angle is ±1°.

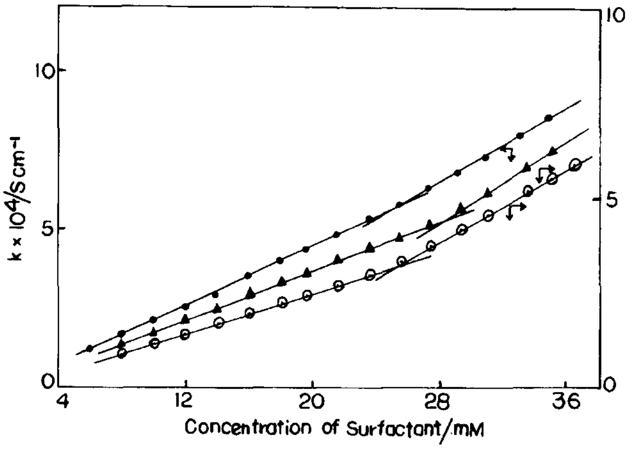

Fig. 2. Representative plots of specific conductance (k) vs. concentration for SDBS–additive–water systems.
● 0.3% Urea at 45 °C; ▲ 0.3% PEG 400 at 40 °C; ⊙ 0.5% Sucrose at 45°C.

(v) Viscosity Measurements: The viscosities of the surfactant solution (5% w/v) were measured with the help of an Ubbelohde viscometer at different temperatures (35, 40, 45, and 50 °C) in both the absence and presence of additives (different amounts). The densities of the solutions were measured using a pyknometer.

(vi) Foaming Measurements: The foaming efficiency of the surfactant was determined by measuring the initial foam height using Ross–Miles method.[7] The concentration of the surfactant was 0.15 mM and the reproducibility of the initial foam heights was within ±2%.

(vii) Detergency Studies: A 0.5% (w/v) benzene solution of water-insoluble dye Blue 2089 [dioxo-9,10-dihydro anthracene 1,4-bis(methylamine)] was used. About one drop, i.e. 0.05 ml, of this dye solution was placed on cotton fabric (3.5″×3.5″) and thoroughly dried. The fabric was then placed in 100 ml of a surfactant solution of known concentration and kept under constant stirring. Then 3 ml of this solution was withdrawn at regular time intervals. The total concentration of the surfactant was kept constant at 10 mM. The absorbance of the solutions was determined at a λ_{max} of 645 nm using a UV-visible (Shimadzu 240) spectrophotometer.

Results and Discussion

The critical micelle concentrations (cmc) of sodium dodecylbenzenesulfonate (SDBS) was determined at 35, 40, 45, and 50 °C by both surface-tension and conductivity methods. The values obtained by both methods agree well with each other. The cmc values of SDBS, both in the presence and absence of PEG 400, sucrose, and urea at different temperatures, are given in Table 1. The CMC was found to increase with increasing temperature within the limited range of the temperatures studied, both in the presence and absence of additives. In general, for ionic surfactants a minimum in cmc at lower temperature is always observed along with a subsequent increase as the temperature increases. At higher temperature the dielectric constant of the solution decreases, resulting in a greater repulsion between the ionic heads of the surfactant molecules, resulting in a higher cmc.[10] The increase in the cmc at higher temperatures is also due to the disruption of the water structure around the hydrophobic portion of the surfactant molecules that opposes micellization, hence a higher cmc.[11]

It can be observed from Table 1 that both PEG 400 and sucrose increase the critical micelle concentration of SDBS at all concentration levels studied. It is well known[12] that the

Table 1. cmc Values for Sodium Dodecylbenzenesulfonate (SDBS) in Aqueous Solution in Presence of PEG 400, Sucrose, and Urea at Different Temperatures (cmc in mM)

Concn of additive	PEG 400				Sucrose				Urea			
% (w/v)	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	1.99	2.32	2.64	3.02	—	—	—	—	—	—	—	—
0.1	2.06	2.42	2.82	3.08	2.12	2.46	2.76	3.08	2.17	2.46	2.72	3.10
0.3	2.18	2.46	2.94	3.12	2.14	2.46	2.83	3.12	2.20	2.48	2.82	3.14
0.5	2.26	2.44	2.96	3.18	2.20	2.52	2.88	3.14	2.24	2.52	2.94	3.16
0.7	2.28	2.52	3.02	3.24	2.55	3.00	3.18	3.34	2.54	2.98	3.19	3.19

micellar structure may be considered to be made up of two regions, an outer region comprising polar head groups 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 the remaining hydrocarbon chains not in contact with water. The stronger hydrogen bonding interactions of water with both PEG 400 and sucrose are due to the presence of –OH groups that have a major effect on water at the monomer hydrocarbon–water interface, which is otherwise structured by a hydrophobic effect i.e. the structured water around the hydrophobic group is disrupted, which leads to a poorer contribution to the hydrophobic interactions, which are the driving force for micellization, and hence a higher cmc.

The effect of urea on the cmc of SDBS can be explained by its water structure-breaking property. Because urea is a strong protein denaturant, its demicellization property (i.e. higher cmc) is probably a manifestation of that. It has been suggested[13] that the surfactant monomers become stabilized in aqueous urea solutions, therefore, micellization occurs at higher concentrations. Wang et al.[14] have investigated the effect of urea on the microenvironmental properties of SDBS micellar solutions by ESR spectroscopy and surface-tension measurements at the air/water interface. They, too, have reported an increase in the cmc upon the addition of urea, as observed in our results, and attributed that to a mechanism wherein the urea replaces some water molecules that solvate the hydrophobic chain and the polar head group of the surfactant.

This was further corroborated from micellar aggregation number. The micellar aggregation number (N_{agg}) was determined by steady state fluorescence quenching for SDBS in both the presence and absence of PEG 400, sucrose, and urea. The N_{agg} values for SDBS (N_{agg} = 75) are lowered in the presence of all of these additives, although not much effect was observed with respect to increasing the additive concentration. The N_{agg} value was 61±2 and did not show any effect of either the nature of the additive (i.e. PEG 400, sucrose, and urea) or the additive concentrations. As mentioned earlier, PEG 400 and sucrose, due to the presence of –OH groups, i.e. the hydrogen-bonding ability with the solvent, have major effects on the water at the monomer hydrocarbon–water–interface. Also, it has been reported[15] that urea replaces some water molecules in the solvation layer of micelle head groups, leading to the direct participation of urea in the solvation of the micelle. Because the urea molecule is 2.5-times lager than the water molecule and the substitution of water molecules by urea leads to an increase in the surface area per head group, the aggregation number of SDBS decreases.[15] The overall effect is indicative of same amount of hindrance in the micelle formation in presence of all these additives.

The dependence of cmc upon the temperature was used to evaluate the standard thermodynamic parameters of micellization for SDBS-additive systems. The standard free energy of micellization was evaluated using the relation[11]

$$\Delta G^{\circ}_{\mathrm{m}} = (2 - \alpha)RT \ln \mathrm{cmc}.$$

cmc is in the mole-fraction scale and α is the degree of ionisation of the micelle computed from the ratio between the slopes of the post micellar and premicellar regions of conductance vs. the concentration plots.[16] The 'α' values (Table 2) did not show any significant difference as the additives or the additive concentrations were changed. This indicates that the nature of the micelles in the absence and in presence of the additives is similar. The standard state is a hypothetical system with a unit mole fraction of the surfactant at cmc. From Table 2 it can be observed that the $\Delta G^{\circ}_{\mathrm{m}}$ values were all found to be negative in both the presence and absence of additives for SDBS, indicating a spontaneous micellization process The standard enthalpy ($\Delta H^{\circ}_{\mathrm{m}}$) and entropy ($\Delta S^{\circ}_{\mathrm{m}}$) of micellization were computed from the well known relation

$$\Delta G^{\circ}_{\mathrm{m}} = \Delta H^{\circ}_{\mathrm{m}} - T\Delta S^{\circ}_{\mathrm{m}}.$$

The overall micellization process was found to be exothermic. $\Delta H^{\circ}_{\mathrm{m}}$ was independent of the temperature because a remarkable change did not occur in the environment surrounding the hydrocarbon chain of the surfactant molecules in the presence of additives when the temperature was varied. Also, this temperature independence of $\Delta H^{\circ}_{\mathrm{m}}$ can be due to the high error (±7%) associated with $\Delta H^{\circ}_{\mathrm{m}}$. The standard entropy of micellization ($\Delta S^{\circ}_{\mathrm{m}}$) for the SDBS-additive system was all positive, indicating that the micellization process is entropy dominated, particularly when the entropy change is high. However, it can be observed from Table 2 that the

Table 2. Thermodynamic Parameters of Micellization of Sodium Dodecylbenzenesulfonate (SDBS) in Aqueous Solution in Presence of PEG 400, Sucrose, and Urea

Concn of additive	PEG 400					Sucrose					Urea				
% (w/v)	α (35 °C)	$-\Delta G^{\circ}_{\mathrm{m}}$ (35 °C)	$-\Delta H^{\circ}_{\mathrm{m}}$	$\Delta S^{\circ}_{\mathrm{m}}$	$\Delta\Delta H^{\circ\,\mathrm{tr}}_{\mathrm{m}}$	α (35 °C)	$-\Delta G^{\circ}_{\mathrm{m}}$ (35 °C)	$-\Delta H^{\circ}_{\mathrm{m}}$	$\Delta S^{\circ}_{\mathrm{m}}$	$\Delta\Delta H^{\circ\,\mathrm{tr}}_{\mathrm{m}}$	α (35 °C)	$-\Delta G^{\circ}_{\mathrm{m}}$ (35 °C)	$-\Delta H^{\circ}_{\mathrm{m}}$	$\Delta S^{\circ}_{\mathrm{m}}$	$\Delta\Delta H^{\circ\,\mathrm{tr}}_{\mathrm{m}}$
0.0	0.69	34.2	46.8	−40	—	—	—	—	—	—	—	—	—	—	—
0.1	0.66	34.5	23.7	35	23.1	0.68	34.4	22.0	40	24.8	0.68	34.3	23.3	36	23.5
0.3	0.67	34.5	24.2	33	22.6	0.68	34.3	16.2	59	30.6	0.68	34.4	22.4	39	24.4
0.5	0.66	34.7	20.2	47	26.5	0.67	34.5	20.6	45	26.2	0.67	34.5	19.6	48	27.2
0.7	0.66	34.6	20.8	45	26.0	0.66	34.7	22.9	38	23.9	0.67	34.3	17.6	54	29.2

$\Delta G^{\circ}_{\mathrm{m}}$, $\Delta H^{\circ}_{\mathrm{m}}$, and $\Delta\Delta H^{\circ\,\mathrm{tr}}_{\mathrm{m}}$ are in kJ mol^{-1} and $\Delta S^{\circ}_{\mathrm{m}}$ in J mol^{-1} K^{-1}.

absolute value of $\Delta H^{\circ}_{\mathrm{m}}$ is larger than that of $T\Delta S^{\circ}_{\mathrm{m}}$, which indicates that both enthalpic as well as the entropic forces contribute to the overall micellization process in these cases. It should also be noted that $\Delta S^{\circ}_{\mathrm{m}}$ is negative in the absence of additives (Table 2). This indicates that micelle formation brings about overall order to the system. However, in the presence of additives, micelle formation will include the breaking of the water–additive bondings as well as surfactant monomer–additive bondings (the reason for stabilization of surfactant). This causes relatively more randomness to the system concerning micelle formation in the presence of additives, and hence $\Delta S^{\circ}_{\mathrm{m}}$ is positive when micelle formation occurs in additive solutions.

A linear correlation[17] between $\Delta H^{\circ}_{\mathrm{m}}$ and $\Delta S^{\circ}_{\mathrm{m}}$ was seen in this SDBS–additive system. The slope of the line was 290 K (Fig. 3), which lies well within the suggested value for water[17] i.e. 270—294 K. Such enthalpy–entropy compensation was observed for many physicochemical processes, including micellization and monolayer formation. At this isostructural temperature the micellization process is entirely dependent upon the enthalpic forces and is independent of any structural change.

The transfer enthalpy of micellization ($\Delta\Delta H^{\circ\,\mathrm{tr}}_{\mathrm{m}}$) was also calculated from the relation[18]

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

The standard state here is a hypothetical system in which the mole fraction of the surfactant at cmc is unity. The $\Delta\Delta H^{\circ\,\mathrm{tr}}_{\mathrm{m}}$ values were all positive. The heat change due to the corresponding monomer transfer is important to the overall $\Delta\Delta H^{\circ\,\mathrm{tr}}_{\mathrm{m}}$ values. This is because of the presence of the monomer–additive interactions, as mentioned in an earlier paragraph.

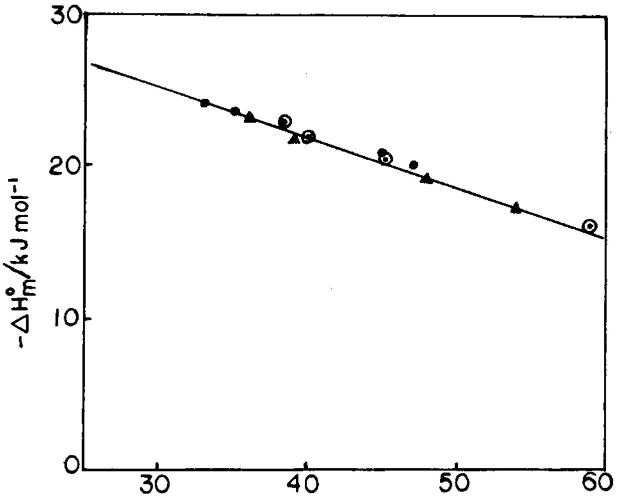

Fig. 3. Enthalpy–entropy compensation plot for SDBS with all systems put together.
● PEG 400; ○ Sucrose; ▲ Urea.

The interfacial adsorption parameters, such as the maximum surface excess (Γ_{max}) and the minimum area per molecule (A_{min}) at air/water interface (Table 3), were computed using the Gibbs relations,[19]

$$\Gamma_{\mathrm{max}} = -\frac{1}{2\times 2.303RT}\left(\frac{\mathrm{d}\gamma}{\mathrm{d}\,\log C}\right)\ \mathrm{mol\,cm^{-2}},$$

$$A_{\mathrm{min}} = \frac{10^{14}}{N\Gamma_{\mathrm{max}}}\ \mathrm{nm^{2}\,molecule^{-1}},$$

where R, T, γ, N, and C are the gas constant, absolute temperature, surface tension, Avogadro number, and molar concentration of the surfactant, respectively. The minimum area per molecule, (A_{min}) increases (Γ_{max} decreases) as the temperature increases in the absence of any additive. However, in the presence of additives, a reverse trend is observed in A_{min} with respect to the temperature. An increase in the temperature leads to an increase in the molecular motion of the surfactant molecules due to thermal agitation, causing a poorer packing at the air/water interface. Hence, the presence of these additives allows a closer packing of the surfactant molecules at the air/water interface as the repulsive force decreases. The overall observed effect can be ascribed to various different factors, such as (i) a changed structure around the head group due to the surfactant hydrophilic group–additive interaction, (ii) the changed nature of water in the presence of additives, and (iii) the presence of additives at the air/water interface. It can be seen from the Gibbs adsorption equation that A_{min} is proportional to T and inversely proportional to $\mathrm{d}\gamma/\mathrm{d}\,\log C$. There is no parity between the rate of variation of T and the rate of variation of $\mathrm{d}\gamma/\mathrm{d}\,\log C$. We believe that the overall result is the culmination of all factors mentioned above.

The standard thermodynamic parameters of adsorption at the air/water interface for the SDBS–additive–water ternary system were evaluated and are given in Table 4. The standard free energy of adsorption ($\Delta G^{\circ}_{\mathrm{ad}}$) was calculated using the relations[20]

Table 3. The Minimum Area per Molecule (A_{min}) of SDBS in Aqueous PEG 400, Sucrose, and Urea Solutions at Different Temperatures

Concn of additive	$A_{\mathrm{min}}/\mathrm{nm}^2$											
% (w/v)	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	1.48	1.75	1.80	1.83	—	—	—	—	—	—	—	—
0.1	1.43	1.42	1.39	1.36	1.08	1.05	1.04	1.01	1.41	1.38	1.35	1.30
0.3	1.49	1.45	1.44	1.38	1.10	1.09	1.06	1.04	1.42	1.39	1.37	1.33
0.5	1.54	1.52	1.48	1.43	1.11	1.10	1.07	1.05	1.45	1.44	1.42	1.35
0.7	1.55	1.57	1.59	1.54	1.12	1.11	1.10	1.08	1.48	1.46	1.38	1.37

Table 4. Thermodynamic Parameter of Adsorption of Sodium Dodecylbenzenesulfonate (SDBS) in Presence of Aqueous PEG 400, Sucrose, and Urea

Concn of additive	PEG 400			Sucrose			Urea		
% (w/v)	$-\Delta G^\circ_{ad}$ at 35 °C kJ mol^{-1}	$-\Delta H^\circ_{ad}$ kJ mol^{-1}	ΔS°_{ad} J mol^{-1} K^{-1}	$-\Delta G^\circ_{ad}$ at 35 °C kJ mol^{-1}	$-\Delta H^\circ_{ad}$ kJ mol^{-1}	ΔS°_{ad} J mol^{-1} K^{-1}	$-\Delta G^\circ_{ad}$ at 35 °C kJ mol^{-1}	$-\Delta H^\circ_{ad}$ kJ mol^{-1}	ΔS°_{ad} J mol^{-1} K^{-1}
0.0	59.7	−3.2	205	—	—	—	—	—	—
0.1	50.5	21.5	94	52.0	22.3	96	52.3	26.2	85
0.3	51.8	23.7	91	53.8	33.2	66	52.7	24.2	92
0.5	53.7	24.3	96	52.7	19.8	106	52.5	24.8	90
0.7	54.1	24.7	95	53.1	23.8	66	53.7	28.3	82

$$\Delta G^\circ_{ad} = \Delta G^\circ_m - N\Pi_{cmc}A_{cmc},$$

$$\Delta G^\circ_{ad} = \Delta H^\circ_{ad} - T\Delta S^\circ_{ad},$$

where Π_{cmc} and A_{cmc} are the surface pressure (the surface pressure was calculated from the relation $\Pi_{cmc} = \gamma_o - \gamma_{cmc}$, where γ_o and γ_{cmc} are the surface tension of pure solvent and that of the surfactant solution at cmc, which were measured) and the minimum area per molecule at cmc. The standard state 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 area per molecule, A_{min} ($= A_{cmc}$). The ΔG°_{ad} values for SDBS both in presence and absence of additives were negative indicating a spontaneous adsorption process. However, the ΔG°_{ad} values were more negative compared to their corresponding ΔG°_m, suggesting that when a micelle is formed work has to be done to transfer the surfactant molecule in the monomeric form from the surface to the micellar stage through an aqueous medium.

The standard enthalpy of adsorption (ΔH°_{ad}) was found to be positive in absence of additives, whereas it was negative in the presence of additives. Such an overall exothermic/endothermic behavior in the adsorption process can be ascribed to whether the bond making or the bond breaking predominates during adsorption. The bonds broken here may free the water molecules from around the hydrocarbon chains of the surfactant, from additive–water bonding, and from surfactant head group–water bonding. The standard entropy of the adsorption (ΔS°_{ad}) values are all positive and are due to the greater freedom of motion of the hydrocarbon chains at the interface, and are also due to the mixing of the surfactant molecules with additives. It can be observed from Table 4 that ΔS°_{ad} is larger in the absence of additives than in their presence. The free water molecules around the hydrocarbon chains form structures with these additives, which lower the freedom of motion of the hydrocarbon chains at the air/water interface. This leads to a more structured system, thereby lowering the ΔS°_{ad}. The ΔS°_{ad} values in the presence of all three additives are similar, which indicates that the structure of the air/water interface is somewhat similar in presence of these additives. It is interesting to note that although urea is a structure breaker, it does form a hydrogen bond[21,22] with water, and thereby forms a structured system, just like by PEG and sucrose. That is why all three additives behave in a somewhat similar manner. However, we believe that the additive and the surfactant are both important for the overall final behavior, because for a nonionic surfactant, Myrj 45, the effects of additives, PEG 400 and sucrose, were different.[4] There is also possibility of interaction between urea and hydrocarbon part of SDBS. Ahluwalia et al.[18] mentions that it is not clear which type of interaction is responsible for the behavior and surfactants in aqueous urea solutions.

Other performance properties of surfactants, like wetting, viscosity, foaming, and detergency by dye solubilization method, were studied. The wetting efficiency of SDBS was studied by determining the contact angle (θ) in the presence of PEG 400, sucrose, and urea. As shown in Fig. 4, the contact angle (θ) decreases in the presence of these additives, which can be ascribed to a variation of the surface activity of the surfactant due to a surfactant-additive interaction.

The viscosity of 5% (w/v) SDBS was also determined at different concentrations of PEG 400, sucrose, and urea. The intrinsic viscosity, which indicates the solute–solvent interaction and also the size and shape of the particle, was calculated from the relative viscosities by the relation

$$[\eta] = \lim_{C \to 0} \frac{\eta_r - 1}{C},$$

where the zero-concentration limit indicates the absence of interparticle interactions. Some researchers have taken $[\eta]$ to be equal to $(\eta_r - 1)/C$ without the condition for limiting concentration. It has been defined to be the "shape factor,"[23] and is expected to have a value of 2.5—4 cm^3 g^{-1} for globular particles. If the limit of concentration is taken to be zero, the effect of the concentration on the geometry of the particle is lost; we therefore computed the shape factor without taking the limit to zero, as was done by other researchers.[24,25] The relative viscosity of a surfactant solution in both the absence and presence of additives was computed with respect to a water and aqueous additive solution, respectively. The thus-calculated intrinsic viscosity $[\eta]$ was found to be 5 cm^3 g^{-1} for SDBS in the absence of any additive, which indicates that the SDBS micelles at this concentration are not exactly spherical in nature. Also, in the presence of different additive concentrations, the $[\eta]$ values were around 5—7 cm^3 g^{-1},

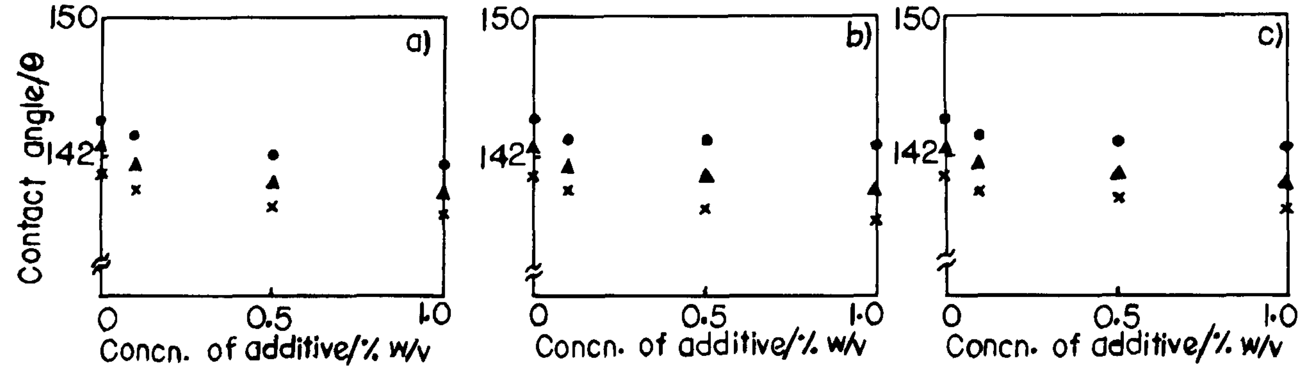

Fig. 4. Plot of contact angle (θ)–additive concentration for SDBS in presence of (a) PEG 400; (b) sucrose; (c) urea at total surfactant concentration.
● 5 mM; ▲ 10 mM; × 20 mM.

implying that additives do not change the micelle shape to a large extent. This was also concluded, as mentioned earlier, from the calculated 'α' values (Table 2).

The thermodynamic activation parameters for viscous flow were evaluated using the Frenkel–Eyring equation,[26]

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

where V, N, h, and R are the molar volume, Avogadro's number, Planck's constant, and the gas constant, respectively; $\Delta H^{\neq}_{\mathrm{vis}}$ and $\Delta S^{\neq}_{\mathrm{vis}}$ are the viscosity activation enthalpy and entropy obtained from the slope and intercept of $\ln(\eta V/Nh)$ vs. $1/T$ plot. The $\Delta H^{\neq}_{\mathrm{vis}}$ (2.22±0.01) kJ mol^{-1}, $\Delta S^{\neq}_{\mathrm{vis}}$ (5.4±0.02) J mol^{-1} K^{-1}, and $\Delta G^{\neq}_{\mathrm{vis}}$ at 35 °C (0.55±0.02) kJ mol^{-1} values were found to be independent of the additives.

The $\Delta G^{\neq}_{\mathrm{vis}}$ values are all positive, indicating a non-spontaneous flow. The constant values of $\Delta G^{\neq}_{\mathrm{vis}}$ indicate that no effect of these additives takes place in viscous flow at the concentration range studied. The $\Delta H^{\neq}_{\mathrm{vis}}$ and $\Delta S^{\neq}_{\mathrm{vis}}$ values suggest that the viscous flow is endothermic, and that there is no effect of the additives on the viscous flow. The viscosity activation parameters did not show any significant change in the presence of additives; hence, only the average values are reported.

Foaming is an inherent property of a surfactant. It is known that the foaming efficiency of surfactants can be altered by the addition of additives. In Fig. 5 the initial foam height of SDBS in both the presence and absence of different additives and at different concentrations are shown. Although the foam height slightly decreased in the presence of additives, a very stable foam was obtained. These additives form multiple hydrogen bonds with water, and thereby prevent these polar additives from being forced out between the surfactant molecules and into the interior of the micelles in bulk phase; i.e. these additives are held together through hydrogen bonds in the palisade layer of the micelles, giving rise to a greater stabilization of the foam.[27] This is similar to the phenomena which occurr in the surface layers at the solution/air interface of foams. Additives that are solubilized in the micelle interior are not available for surface films, while those that are solubilized in the palisade layer of micelles are present in the surface films of the foam lamellae. Hence, in this case closer packing, lower surface tension and higher surface viscosity serve to enhance the foam stability.[28] As shown earlier in viscosity studies as well as in the 'α' values, the micelles seem to behave similarly in the presence of these additives. The same seems to be true concerning its shape. Closer packing at the air/water interface was also suggested earlier (Table 3).

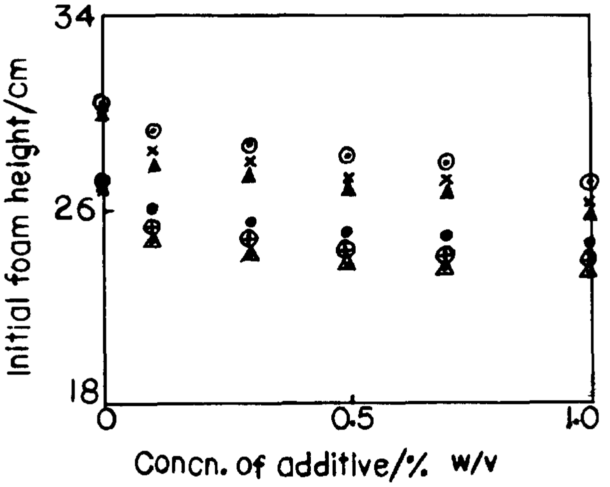

Fig. 5. Initial foam height vs. concentration of additive for SDBS (total concn = 0.15 mM).
● PEG 400 at 40 °C; ⊕ Sucrose at 40 °C; △ Urea at 40 °C; ⊙ PEG 400 at 50 °C; × Sucrose at 50 °C; ▲ Urea at 50 °C.

In detergency, the solubilization of soil from fabric into the detergent solution is one of the most important events, that involves the removal of oily soil. The location of the solubilizate in the micelle varies with the nature of the solubilized material, and, more importantly, it reflects the type of interaction that occurs between the surfactant and solubilizate.[29] The solubilization capacity of a micellar solution depends on such conditions as the structure of the surfactant, the nature of the solubilizate, the temperature, and the presence of additives. The solubilization of oil soluble Blue 2089 dye in an SDBS solution in both the presence and absence of PEG 400, sucrose, and urea at room temperature from cotton fabric was studied. As a general trend, the dye-removal efficiency of SDBS was found to be relatively lower than that of a nonionic surfactant. The lower solubilization by SDBS

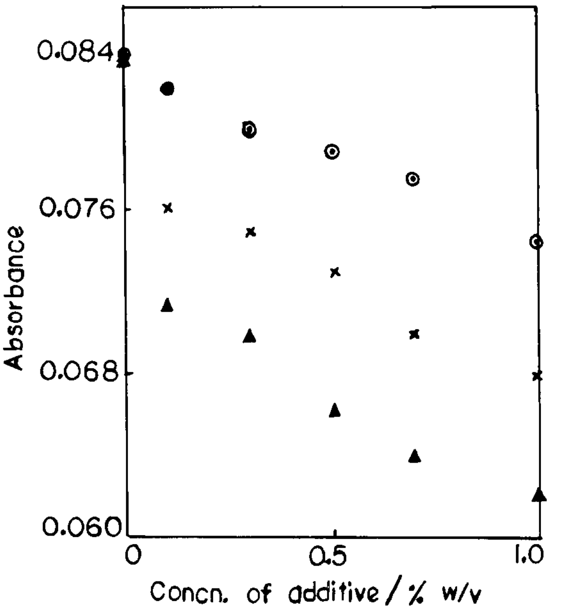

Fig. 6. Absorbance vs. additive concentration for SDBS (total concn = 10 mM) after 10 min.
○ PEG 400; ⊗ Sucrose; ▲ Urea.

can be ascribed to looser packing of the micelles due to coloumbic repulsions between them. As shown in Fig. 6, the additives decrease the solubilization capacity of SDBS, although not to a great extent. This is because the additives are non-penetrating, and are expected to locate themselves at the micelle–solvent interface. This prevents the micelles from getting close to one another, thereby increasing the intermicellar distance. In other words, the micelles are no longer packed closer to one another. It also should be understood that the surfactant monomers are stabilized by additives, and, hence, the detergency of the surfactant should decrease in the presence of additives, which was what we observed.

Conclusions

The various solution properties of sodium dodecylbenzenesulfonate (SDBS) in aquo-PEG 400, aquo-sucrose, and aquo-urea solutions at different temperatures and additive concentrations were studied. The critical micelle concentration of SDBS was found to increase with the temperature both in presence and absence of additives. The overall micellization process was spontaneous and exothermic. The entropy of micellization was positive. An enthalpy-entropy compensation was observed for SDBS–additive–water ternary systems. The $\Delta\Delta H^\circ{}_{\mathrm{m}}{}^{\mathrm{tr}}$ was found to be positive. The additives effect the interfacial parameters, $\Gamma_{\max}$ and $A_{\min}$. The adsorption process was more spontaneous than the process of micellization. The micellar aggregation number (N_{agg}) decreased in the presence of additives. Other performance properties, such as wetting, viscosity, foaming, and detergency, were also effected in the presence of these nonionic additives. The overall effects of all three additives i.e. PEG 400, sucrose and urea are somewhat similar. This is probably because of the hydrogen-bonding characteristic of urea[21,22] as well as two other molecules. However, the effect of urea is slightly difficult to explain,[18] as it is known that it has a water structure-breaking property.

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