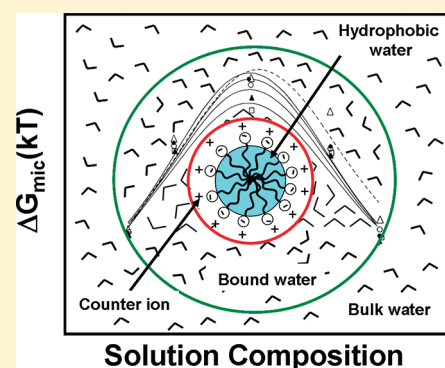


Interfacial and Self-Aggregation of Binary Mixtures of Anionic and Nonionic Amphiphiles in Aqueous Medium

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ABSTRACT: Interfacial and bulk properties of sodium dodecyl sulfate (SDS), polyoxyethylene (20) sorbitan monooleate (Tween-80), and their binary mixtures in aqueous medium have been investigated using surface tension, conductance, and fluorescence measurements at different temperatures. The critical micelle concentration (CMC), counterion binding, polarity index, aggregation number, thermodynamics of interfacial adsorption, and micellization are evaluated. The entropic contribution is found to be the predominant factor in micelle formation. The aggregation number and the polarity index of the micelle interior estimated by the pyrene fluorescence technique show interesting temperature dependence. The size and composition of the mixed micelles vary with the total concentration. The micellar compositions, activities of the individual components in the mixed species, and intersurfactant interactions are also estimated following regular solution theory, excess thermodynamic functions, and a molecular thermodynamic model. The surfactant mixtures are found to be nonideal with a lower degree of counterion binding compared to the individual members. Mixed micelles are nonspherical in nature at all temperatures when the mole fraction (α) of the ionic part in mixtures is high but transform to spherical when α_{SDS} is ≤ 0.50 .



■ INTRODUCTION

Surfactant systems find extensive applications in various commercial and industrial fields. Because of better performance and cost effectiveness, mixtures of surfactants are preferred over the individual members in industrial, pharmaceutical, and technological formulations for the purpose of solubilization, dispersion, suspension, etc. The amphiphiles aggregate in solution to form micelles at and above a critical concentration called the critical micelle concentration or “CMC”. Micelle formation and interfacial adsorption behavior of the surfactants depend on various environmental factors, e.g., temperature, pressure, pH, presence of additives, etc. A thorough understanding of the physicochemical properties of the micellar and interfacial adsorption behavior such as thermodynamics of micelle formation, adsorption, counterion binding, surface excess, microenvironment, solubilization properties, catalyzing functions, etc. is a prerequisite for detailed exploration of the properties and functions of the surfactant systems. Investigations on the physicochemical characterization of the mixed micellar solutions usually yield necessary information to optimize and design surfactant mixtures with the desired properties. Thus, such investigations are considered very important from practical considerations as well as intrinsic theoretical interest.^{1–17}

In spite of widespread applications, mixed surfactant solutions are not well understood at a fundamental molecular level. Usually,

the detergent mixtures for particular applications are formulated on empirical or trial and error basis. Several theoretical treatments have been developed to understand the molecular basis of mixed surfactant solutions.^{11–15} A recent molecular thermodynamic approach^{15–19} offers a significant advancement in this direction. However, the theoretical model needs comprehensive and systematic testing on carefully collected data obtained by different methods.

In recent years, considerable investigations on the interfacial and bulk properties of mixed surfactants have been reported;^{12–30} however, systematic studies are limited. This presentation deals with the detailed investigations on the physicochemical characterization of sodium dodecyl sulfate (SDS) and polyoxyethylene (20) sorbitan monooleate (Tween-80 or Tw-80), and their binary mixtures in aqueous solution. SDS is the most widely used in chemical, biochemical, and industrial fields (formulations). Tween-80 is often utilized as a stabilizing and solubilizing agent in pharmaceutical and technological purposes.

The values of CMC, counterion binding, and adsorption properties of the individual and mixed surfactant systems have been determined at five different temperatures (283–313 K). The thermodynamics of micellization and adsorption behavior

Received: May 6, 2011

Revised: August 5, 2011

Published: September 02, 2011

are evaluated. The effect of temperature on the aggregation number and polarity index of the micellar species is obtained from fluorescence measurements. The composition of the mixed micellar species and intramicellar interaction has also been estimated following the recent theoretical treatments.^{12–19}

■ EXPERIMENTAL SECTION

Materials. SDS was obtained from Sigma. It was purified by crystallization from ethanol and impurity is less than 1%. Tween-80 (Aldrich) was used as received. The fluorescence probe, pyrene (Aldrich), was purified by gel chromatography with cyclohexane and then by subliming the resultant product. Cetylpyridinium chloride (CpCl) (Aldrich), the quencher, was purified several times by recrystallization from mixed solvents of acetone and isopropyl alcohol after decolorization with activated carbon in the mixed solvents. All solutions were prepared in doubly distilled water.

Surface Tension Measurements. Surface tensions (γ) of the surfactant solutions were measured with a du Noüy tensiometer Model Krüss 8 by the principle of detachment of a platinum ring. A Hamilton microsyringe was used to add surfactant solution gradually to water in the measuring vessel maintained at the required temperature (± 0.05 K) by circulating water from a Haake GH thermostat. The accuracy of measurement was 0.05 mN/m and tensions were measured at 283, 293, 298, 303, and 313 K. The measurements were duplicated, and the mean value was recorded.

Conductance Measurements. Conductance measurements of the solutions were taken in a Denver conductometer, model 50, using a cell of cell constant 1.01 cm^{-1} . The measured conductance values were accurate within $\pm 0.5\%$. The surfactant solution was progressively added using a Hamilton microsyringe to water taken in a small-jacketed beaker type container, and the conductance was measured after thorough mixing and attaining temperature equilibrium. The measurements were recorded at the five different temperatures.

Fluorescence Measurements. Steady state pyrene fluorescence emission spectra were recorded in a Perkin-Elmer (model MP F44B) and a Kontron (SFM 25) spectrofluorometer. Fluorescence measurements have been done at different temperatures circulating thermostated water around the fluorescence cell chamber. The excitation wavelength was 335 nm, and the pyrene concentration, around $10^{-5}\text{ mol dm}^{-3}$. The ratio of the intensity of pyrene emission at 373 and 383 nm, respectively, given I_1/I_3 provides an estimate of the polarity index sensed by pyrene in the micellar solubilization site. The aggregation numbers (\bar{N}) were determined from quenching experiments using pyrene as a probe and cetylpyridinium chloride as a quencher (concentration ≈ 0 to $6 \times 10^{-4}\text{ M}$) following the procedure in the literature.²⁴ The probe and the quencher are considered to be located in the same micellar environment and distributed between the aqueous and micellar pseudophases in accordance with Poisson statistics.

The relationship of the average aggregation number to the pyrene fluorescence intensity in the absence and presence of a quencher is given by the equation¹⁰

$$\ln(I_0/I) = \frac{[Q] \times \bar{N}}{[S] - \text{CMC}}$$

where $[Q]$ and $[S]$ are the concentrations of quencher and surfactant respectively. I_0 and I stand for pyrene emission

intensity in the absence and presence of the quencher respectively. \bar{N} is determined from the plot of $\ln(I_0/I)$ vs $[Q]$. \bar{N} and I_1/I_3 values were checked by time-resolved fluorescence quenching experiments. The solutions were degassed to remove oxygen before measurements were recorded. The detailed procedure has been described elsewhere.^{23,24}

Cloud Point Determination. The cloud point (CP) was determined by controlled heating in a melting point apparatus. The pure surfactants or their combinations was taken in a specially designed sealed tube to maintain the vapor pressure developed inside. By setting the tube properly in the melting point apparatus, we continued the heating until clouding or turbidity appeared. The sample was then allowed to cool and the temperature for the disappearance of turbidity was also noted. The mean value of the appearance and disappearance of turbidity was considered as the cloud point.^{31–34} The reproducibility of the measurement was found to be within ± 0.2 K; because the CP values are high, the determined values have been rounded off to the nearest degree and presented in the table.

■ RESULTS AND DISCUSSION

Critical Micelle Concentration (CMC). The CMC values of the single and mixed surfactants obtained by different methods at 283, 293, 298, 303, and 313 K are presented in Table 1. Careful mixing of Tw-80 with SDS with the allowance of long time (if required, more than 10 h) has helped to obtain the intermediate CMC values of binary mixtures from those of pure surfactants. The break points in the plot of surface tension (or surface pressure), specific conductivity, and the ratio of the first and third vibronic peaks in monomeric pyrene emission spectrum (I_1/I_3) against concentration of the surfactants were taken as CMC values and some representative illustrations are shown in Figure 1a–c. The CMCs of the binary mixtures lay in between the CMC values of the individual detergents and the values obtained show comparable trend with other combinations recently studied.^{4,6,20–30,35–38}

The effect of temperature on the CMC values of surfactants (Figure 2) in aqueous solution is found to be quite complex. Hydrophobic interaction is considered to be responsible for micelle formation. Increase of temperature disrupts hydration of hydrophilic groups of the surfactant favoring micellization and also breaks down the structured water around the hydrophobic moieties and thereby opposing micelle formation. The interplay of the relative magnitude of the antagonistic effects becomes the deciding factor in the increase or decrease of CMC values over a specified range of temperature. Usually, the CMC of nonionic detergents decreases with increasing temperature. A minimum has been reported at very high temperatures.¹⁷ In the case of ionic surfactants, the CMC decreases with increasing temperature, reaches a minimum in the lower temperature range and then increases at higher temperatures. The results obtained by other workers^{15,28,35–42} on pure SDS and Tw-80 by different methods are comparable with the data presented in Table 1. The CMCs of the mixed SDS/Tw-80 of 9:1 composition show gradual increase with increase in temperature from 283 to 313 K, indicating the ionic character of the mixed species (Figure 2). However, in the case of mixed solutions having different compositions, the CMC shows a gradual decrease similar to that of Tw-80 (in the mixed systems, repulsive forces diminish due to the decreasing ionic and increasing nonionic component).

Table 1. Critical Micellar Concentration (CMC, 10^{-5} mol dm $^{-3}$) of Binary Combination of SDS and Tween-80 at Different Temperatures

α_{SDS} (SDS:Tw-80)	temp (K)	surface tension	conductance	fluorescence	av CMC	ln CMC
1.0 (1:0)	283	891 (840 ^a)	855 (840 ^a)	907	884	−4.73
	293	831 (820 ^a)	822 (820 ^a)	863	839	−4.78
	298	798 (793 ^b)	806 (810, ^a 820)	815	806	−4.82
	303	813 (810 ^c)	815 (818 ^a)	825	820	−4.80
	313	841	849 (847, ^a 860)	861	851	−4.77
0.9 (9:1)	283	7.58	7.74	7.78	7.74	−9.47
	293	8.51	8.61	8.79	8.73	−9.35
	298	8.71	8.94	9.06	8.90	−9.33
	303	8.91	9.11	9.20	9.07	−9.31
	313	9.12	9.13	9.47	9.24	−9.29
0.75 (3:1)	283	4.36	4.42	4.59	4.46	−10.02
	293	4.17	4.38	4.48	4.34	−10.05
	298	3.80	3.92	4.22	3.86	−10.16
	303	3.63	3.74	4.06	3.78	−10.18
	313	3.31	3.60	3.78	3.54	−10.25
0.50 (1:1)	283	2.34	2.60	2.66	2.53	−10.39
	293	1.99	2.20	2.47	2.22	−10.72
	298	1.66	1.98	2.21	1.95	−10.85
	303	1.72	1.92	2.11	1.91	−10.87
	313	1.51	1.81	1.95	1.75	−10.95
0.25 (1:3)	283	1.69		1.78	1.74	−10.96
	293	1.55		1.58	1.58	−11.04
	298	1.27		1.38	1.38	−11.19
	303	1.22	1.23	1.28	1.28	−11.27
	313	1.12	1.26	1.23	1.23	−11.31
0.10 (1:9)	283	1.45		1.65	1.55	−11.08
	293	1.23		1.49	1.36	−11.03
	298	1.08		1.24	1.16	−11.36
	303	1.03		1.15	1.09	−11.43
	313	0.96		1.08	1.03	−11.48
0.00 (0:1)	283	1.41		1.55	1.48	−11.12
	293	1.20		1.31	1.26	−11.28
	298	1.00 (1.00 ^c)		1.12	1.06	−11.46
	303	0.95 (1.10 ^d)		1.02 (1.00 ^d)	0.99	−11.53
	313	0.90		1.01	0.95	−11.56

^a Reference 29. ^b Reference 35. ^c Reference 36. ^d Reference 22. ^e Reference 37.

Counter Ion Binding. Ionic as well as ionic-nonionic mixed micelles are associated with a considerable amount of counterions. The counterion dissociation properties of the pure and mixed micellar aggregates were evaluated from the ratio of the post micellar and premicellar slopes (the fraction of micellar dissociation) corresponding to the linear plots of specific conductance of the surfactant solution at different concentrations in accordance with the method of Evans.⁴³ The fraction of counterion bound to the micelle is calculated by subtracting counterion dissociation from unity, and the results are presented in Table 2. The counterion binding (g) gradually decreases with the rise of temperature for SDS and its mixture with Tw-80. In the SDS/Tw-80 mixtures, the values go down with increasing concentration of nonionic Tw-80. The lower values of g found in the mixture compared to pure SDS micelles signify lowering of effective surface charge density in the mixed micelles. In the subsequent section, it is observed that the aggregation number

decreases with the decrease of surface charge density in the SDS/Tw-80 mixtures at the compositions of 9:1 and 3:1. On the other hand, an opposite trend of increasing aggregation number is found in the equimolar mixture of SDS and Tw-80 (1:1). Scamehorn et al.³⁸ also observed similar trends in the micelle of ionic/nonionic systems.

Interfacial Behavior. Surfactants orient at the air–water interface resulting in decrease of surface tension. The amount of surfactant adsorption per unit area of surface at different concentrations can be calculated with the help of Gibbs adsorption equation. For surfactant mixtures in water, the Gibbs surface excess of surfactants relative to zero excess of water per unit area of surface is related to the surface pressure, Π [where Π = surface tension of water (γ_0) – surface tension of surfactant solution (γ)] by the equation^{22,40}

$$d\Pi = \sum \nu_i \Gamma_i RT \, d \ln a_i$$

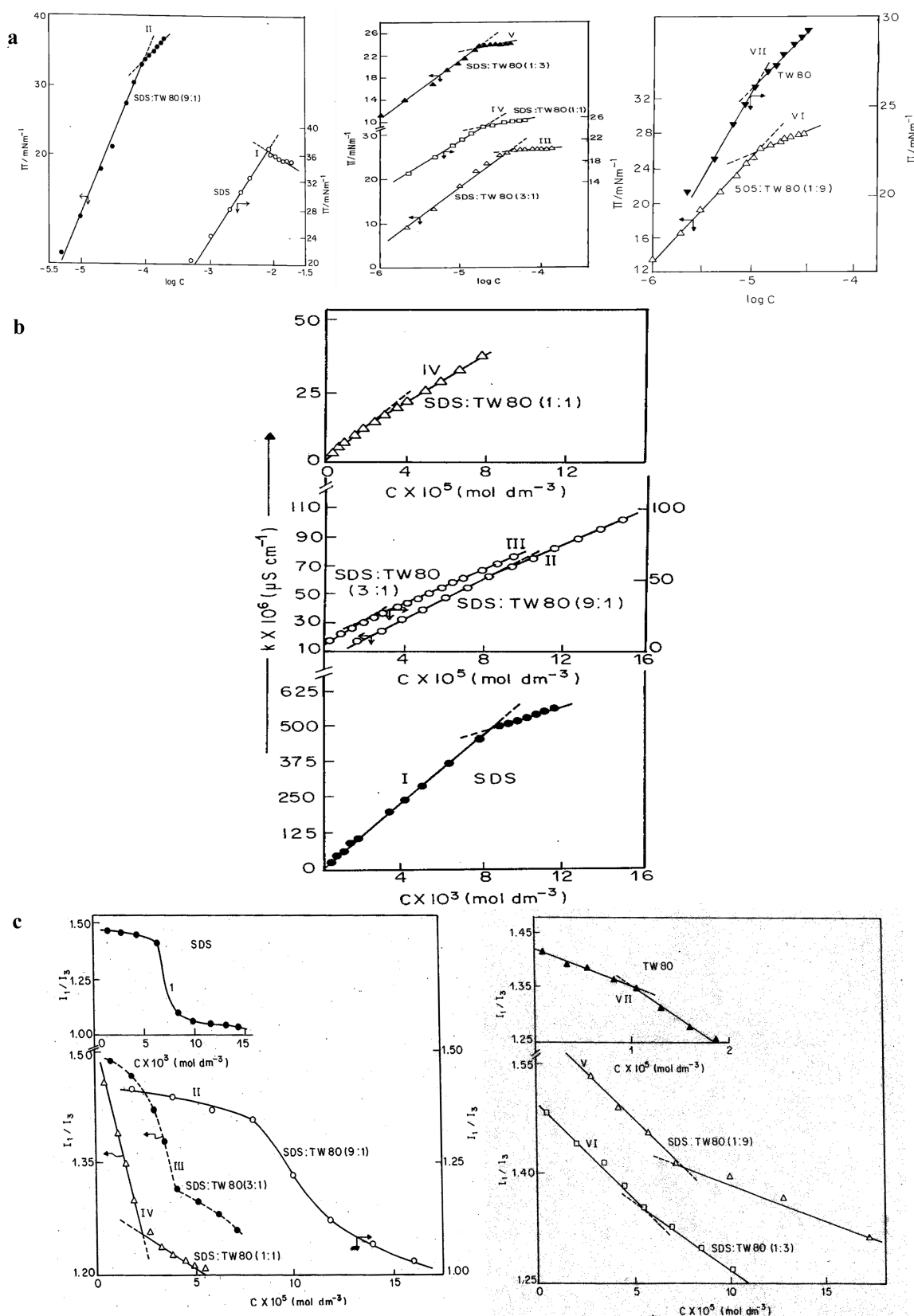


Figure 1. (a) Surface pressure (Π) as a function of $\log C$ (mol dm^{-3}) for pure and mixed systems of SDS and Tw-80 at 298 K. The type of system and the ordinate scale are indicated in each plot. (b) Specific conductance (κ) vs concentration (C) plots for pure and mixed surfactants at 298 K. (c) Determination of CMC using micropolarity (I_1/I_3) vs concentration (C) plots for pure and mixed surfactants at 298 K. The components in inset are SDS and Tw-80. The surfactant system and the ordinate scale are indicated in each plot.

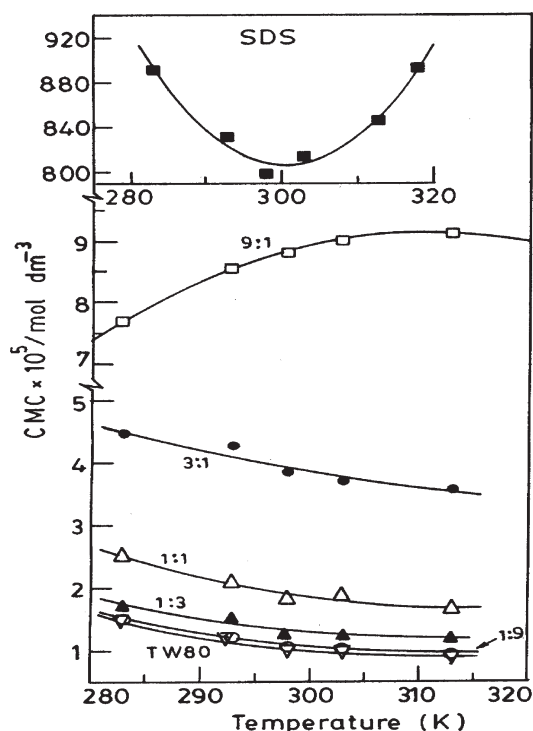


Figure 2. Critical micelle concentration (CMC) vs temperature plots for pure and mixed surfactant systems.

where ν indicates the number of ions per surfactant molecule, Γ_i represents the surface excess or adsorption density, a_i is the activity of the i th component in the mixed adsorbed film, and T and R are the absolute temperature and universal gas constant, respectively. When the composition of the components of the surfactants in the aqueous solution is constant and C is the total surfactant concentration in solution,

$$\Gamma_{\max} = \frac{\nu}{2.303RT} [d\Pi / (d \log C + d \log f_{\pm})]_{T,P}$$

where f_{\pm} is the mean activity coefficient of the surfactant in solution. The maximum surface excess ($\Gamma_{\max}^{\text{tot}}$ in mol m^{-2}) and the minimum area per molecule of a surface active compound (A_{\min}^{tot} in $\text{nm}^2/\text{molecule}$) can be estimated from the relationships

$$\Gamma_{\max}^{\text{tot}} = (1/2.303RT) \lim_{C \rightarrow \text{CMC}} (d\Pi / d \log c) \quad (1)$$

and

$$A_{\min}^{\text{tot}} = 10^{18} / N \Gamma_{\max}^{\text{tot}} \quad (2)$$

where N is the Avogadro number. Here, $d \log f_{\pm}$ was neglected because the surfactant solutions were always dilute.

$\Gamma_{\max}^{\text{tot}}$ and A_{\min}^{tot} and Π_{CMC} have been evaluated for the present systems from the least-squares slopes of Π against $\log C$ (Figure 1) and are presented in Table 2. $\Gamma_{\max}^{\text{tot}}$ values are of the same order as reported for other systems.^{23–27} Composition dependence of $\Gamma_{\max}^{\text{tot}}$ for pure and mixed surfactant systems of SDS and Tw-80 at different temperatures (Supporting Information: Figure A) represent that Γ_{\max} for the individual surfactants at higher mole fractions are found to be higher than those of the mixtures ($\Gamma_{\max}^{\text{tot}}$) and A_{\min} values of the pure surfactants are obviously lower than their corresponding one (A_{\min}^{tot}) below 30 °C. At and above 303 K, an opposite trend is observed. The

pure components occupied a greater area per molecule compared to mixtures as a result of mutual repulsion at and above ambient temperature. The presence of the nonionic Tw-80 molecules at the interface decreased repulsion and, consequently, the area. Assuming ideal mixing of the interacting surfactants, the minimum area per molecule of the mixed aggregates can be expressed as

$$[A_{\min}^{\text{tot}}]_{\text{mix}} = \alpha A_{\min}^{\text{SDS}} + (1 - \alpha) A_{\min}^{\text{Tw}} \quad (3)$$

where α is the mole fraction of SDS in the binary surfactant mixture. The values of $[A_{\min}^{\text{tot}}]_{\text{mix}}$ obtained from the above equation are given in parentheses of Table 2. The experimental A_{\min}^{tot} values of the mixed micelles are found to be lower than the calculated ones above 298 K and reflected the degree of interaction of the amphiphiles involved; the results also indicate nonideal mixing with different surface compositions. On the other hand, the opposite trend is found in the range of 283–298 K.

Energetics of Micellization and Interfacial Adsorption.

Because the micellar phase is in its standard state, assuming the concentration of free surfactants in the presence of micelle to be constant and equal to CMC, the standard free energy of micelle formation per mole of monomer unit for the binary combination of ionic and nonionic surfactants is given by the equation²³

$$\Delta G_m^0 = (1 + g)RT \ln X_{\text{CMC}} \quad (4)$$

where X_{CMC} is the CMC expressed in mole fraction unit. The standard enthalpy change and entropy change of micellization, respectively, can be expressed as

$$\Delta H_m^0 = -RT^2 \left[(1 + g) \frac{d \ln X_{\text{CMC}}}{dT} + \ln X_{\text{CMC}} \frac{dg}{dT} \right] \quad (5)$$

and

$$\Delta S_m^0 = (\Delta H_m^0 - \Delta G_m^0) / T \quad (6)$$

In the evaluation of the thermodynamic parameters for micelle formation mentioned above, $d \ln X_{\text{CMC}} / dT$ and dg/dT values are obtained from the nonlinear plots of the $\ln X_{\text{CMC}}$ vs T as well as g vs T . Therefore, to evaluate the ΔH_m^0 and ΔC_{pm}^0 , polynomial forms of variation of both $\ln X_{\text{CMC}}$ and g with temperature have been used for handling the practical situation.⁷ Regarding that, the equations used are

$$\Delta H_m^0 = a + bT + cT^2 \quad (7)$$

and

$$\Delta C_{pm}^0 = d\Delta H_m^0 / dT = b + 2cT \quad (8)$$

where a , b , and c are respective polynomial constants. Using the CMC_{av} (Table 1) and g values (Table 2) (in eqs 4–7), the values of (ΔG_m^0) , (ΔH_m^0) , (ΔS_m^0) , and (ΔC_{pm}^0) for the pure and mixed surfactants have been evaluated and presented in Table 3.

It is found that the values of ΔG_m^0 and ΔC_{pm}^0 become more negative with rise in temperature, suggesting that higher temperature favors micelle formation. The thermodynamic parameters presented in Table 3 do not show a wide difference, on the whole, a slight variation is observed. The formation of different micellar systems is thus comparable from an energetic point of view. The positive ΔS_m^0 values are attributed to disorder or randomness resulting from the flickering of clusters surrounding the nonpolar tail of the surfactant monomers and the

Table 2. Interfacial Behaviors of the Binary Mixtures of SDS and Tween-80 at Different Temperatures

α_{SDS}	temp (K)	Π_{CMC} (erg cm ⁻²)	$10^6 \Gamma_{\text{max}}^{\text{total}}$ (mol m ⁻²) ^a	$A_{\text{min}}^{\text{total}}$ (nm ² /molecule)	counterion binding (g)
1.00	283	38.17	3.70	0.46	0.590
	293	37.02	3.12	0.53	0.575
	298	37.43	2.78	0.60	0.570
	303	36.56	2.66	0.62	0.560
	313	34.04	2.29	0.73	0.540
0.90	283	28.76	2.98	0.53 (0.49)	0.298
	293	28.53	2.84	0.58 (0.54)	0.261
	298	31.20	2.95	0.56 (0.62)	0.237
	303	33.51	3.02	0.55 (0.64)	0.207
	313	34.39	2.90	0.57 (0.77)	0.159
0.75	283	26.08	3.09	0.54 (0.54)	0.257
	293	25.02	2.62	0.64 (0.58)	0.225
	298	27.88	2.43	0.68 (0.65)	0.198
	303	29.50	2.61	0.64 (0.69)	0.176
	313	32.24	2.67	0.62 (0.79)	0.145
0.50	283	25.54	2.38	0.70 (0.59)	0.244
	293	24.52	2.23	0.73 (0.63)	0.185
	298	25.43	2.24	0.74 (0.70)	0.152
	303	29.65	2.53	0.66 (0.68)	0.142
	313	32.32	2.60	0.64 (0.70)	0.112
0.25	283	24.39	1.90	0.87 (0.65)	
	293	26.98	2.16	0.77 (0.69)	
	298	26.22	2.06	0.80 (0.75)	
	303	29.86	2.37	0.70 (0.73)	0.082
	313	30.51	2.56	0.65 (0.69)	0.041
0.10	283	25.28	1.78	0.93 (0.70)	
	293	28.02	2.10	0.78 (0.72)	
	298	26.90	2.08	0.82 (0.77)	
	303	31.30	2.44	0.65 (0.75)	
	313	31.88	2.65	0.63 (0.68)	
0.00	283	24.78	2.18	0.76	
	293	26.20	2.21	0.75	
	303	27.67	2.26	0.73	
	313	29.01	2.34	0.71	

^a The average errors in $\Gamma_{\text{max}}^{\text{total}}$ are $\pm 3\%$.

assembling of the hydrophobic ends in similar environments in the micellar interior. The positive change in entropy values signify that the pure and mixed combinations of SDS and Tw-80 are entropy controlled except 9:1 and 1:1 combinations, where the negative change in entropy suggests that the entropy as well as enthalpy are involved in the micellization of these (9:1 and 1:1) mixed compositions.

The standard free energy of adsorption (ΔG_{ad}^0) of the surfactants at the air–saturated monolayer interface has been evaluated from the relationship^{15,22,23,40}

$$\Delta G_{\text{ad}}^0 = \Delta G_{\text{m}}^0 - \left(\frac{\Pi_{\text{CMC}}}{\Gamma_{\text{max}}} \right) \quad (9)$$

where Π_{CMC} is the surface pressure at CMC. The standard entropy of adsorption (ΔS_{ad}^0) was obtained from the slope of the ΔG_{ad}^0 – T plot (Figure 3), and hence the enthalpy of adsorption (ΔH_{ad}^0) was obtained. The ΔG_{ad}^0 values (Supporting Information: Table A) show negative values. The values become more negative with increasing temperature. All the systems, as a whole

have shown comparable spontaneity of adsorption. These values indicate that the adsorption process is more favorable for the surfactant mixtures compared to the individual detergents; i.e., the adsorption of the mixed amphiphiles is more favorable than that of the pure amphiphiles. The ΔG_{ad}^0 values obtained in the present study are comparable to the recent results reported for mixed systems.^{21–30} These values of equimolar combination of SDS and Tw-80 (1:1) show that the adsorption process is the most favorable in this combination. These are more negative compared to the corresponding ΔG_{m}^0 values; i.e., the adsorption process is more spontaneous than micelle formation. Micelle formation in the bulk is a secondary process and less spontaneous than interfacial adsorption. Similar to adsorption, the higher negative values of ΔG_{m}^0 for equimolar combination also indicate more favorable micellization compared to the all other combinations. ΔH_{ad}^0 and ΔH_{m}^0 are both exothermic and endothermic respectively, suggesting that the process of bond making (association) and bond breaking (dissociation) prevail during the total process of adsorption and micellization. The higher positive entropy of adsorption than the entropy of micellization

Table 3. Thermodynamic Behaviors of Micellization of Binary Mixtures of SDS and Tween-80 at Different Temperatures^a

temp (K)	$-\Delta G_m^0$ (kJ mol ⁻¹)						
	α_{SDS}						
	1.0	0.9	0.75	0.5	0.25	0.1	0
283	32.7	41.2	41.5	42.7	35.2	35.5	35.6
293	33.8	41.1	42.0	42.5	36.8	37.1	37.3
298	34.4	40.9	42.1	42.4	37.7	38.1	38.3
303	34.7	40.5	42.1	42.8	40.1	38.9	39.2
313	35.2	40.1	42.5	43.3	42.7	40.3	40.6

temp (K)	$-\Delta H_m^0$ (kJ mol ⁻¹)						
	α_{SDS}						
	1.0	0.9	0.75	0.5	0.25	0.1	0
283	1.7	45.3	32.7	35.2	-12.2	-15.1	-18.4
293	6.4	46.7	33.5	41.0	-10.4	-12.3	-14.1
298	8.8	46.8	34.4	44.5	-9.4	-10.7	-11.8
303	11.4	48.2	34.7	47.5	-9.0	-9.0	-9.2
313	17.2	49.6	35.6	54.2	-6.7	-5.2	-3.4

temp (K)	$\Delta S_m^0/\Delta C_{pm}^0$ (J K ⁻¹ mol ⁻¹)						
	α_{SDS}						
	1.00	0.9	0.75	0.5	0.25	0.1	0
283	109.7/-434	-14.7/-104	31.2/-112	26.5/-582	81.4/-161	72.0/-258	60.8/-380
293	93.5/-489	-19.3/-130	29.0/-103	5.1/-617	90.1/-172	84.5/-304	79.0/-458
298	85.9/-516	-19.7/-144	25.7/-98	-7.0/-635	94.9/-178	91.1/-328	88.9/-496
303	76.7/-543	-25.4/-157	24.4/-94	-15.5/-652	102.6/-184	98.7/-351	98.7/-535
313	57.6/-598	-30.3/-184	22.2/-85	-34.9/-688	115.1/-195	112.1/-397	118.6/-612

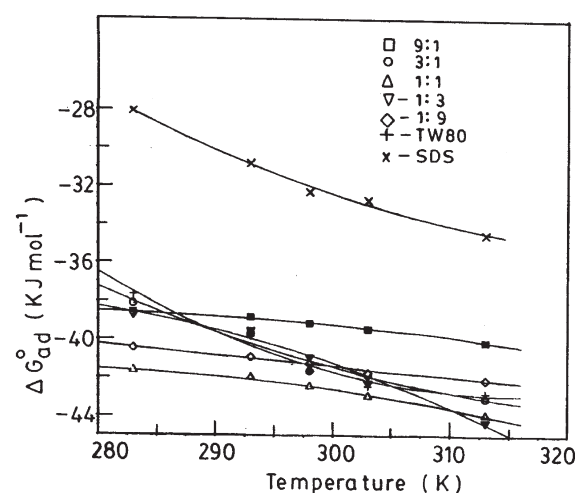
^a The average errors in all cases are $\pm 3\%$.

supports the freedom of movement of hydrocarbon chain toward the air–water interface. As suggested by Lumry et al.,⁴⁴ we observed a fairly linear compensation between ΔS_m^0 and ΔH_m^0 in SDS, Tw-80 and their combinations with slope of $1/299$ K (Figure 4). The empirical expression for micellization stands as

$$\Delta S_m^0 = \frac{1}{299} \Delta H_m^0 + \sigma \quad (10)$$

Then, the micellization compensation takes place at 299 K (T_c) and the intercept corresponds to the entropy change at a specific temperature giving $\Delta H_m^0 = 0$, and here the driving force of micelle formation arises due to the entropy term. The value of σ is $R \ln \text{CMC}$ for nonionic surfactants or their combinations and $(1 + g)R \ln \text{CMC}$ for ionic or their combinations (pseudophase model).

Micropolarity. The ratio of the first and third vibronic peaks, I_1/I_3 , in a monomeric pyrene fluorescence emission spectrum is known to be sensitive to the local polarity index of the probe microenvironment and solubilization site.^{43–45} The low and high values of I_1/I_3 indicate nonpolar and polar environment, respectively. The I_1/I_3 values of pure and mixed micellar combinations of SDS and Tw-80 at different concentrations (Supporting Information: Table B) and at different temperatures (Table 4) denote that the values of the mixed combinations are more or less similar and lower than the pure

Figure 3. Standard free energy of adsorption (ΔG_{ad}^0) vs temperature plots for pure and mixed surfactants.

components (closer to that of Tw-80), suggesting that the solubilization site of pyrene and the micropolarity of the micellar aggregates are less polar than water, but more polar than typical hydrocarbons. The micropolarity (I_1/I_3) of individual and their combinations has a tendency to decrease with the rise of

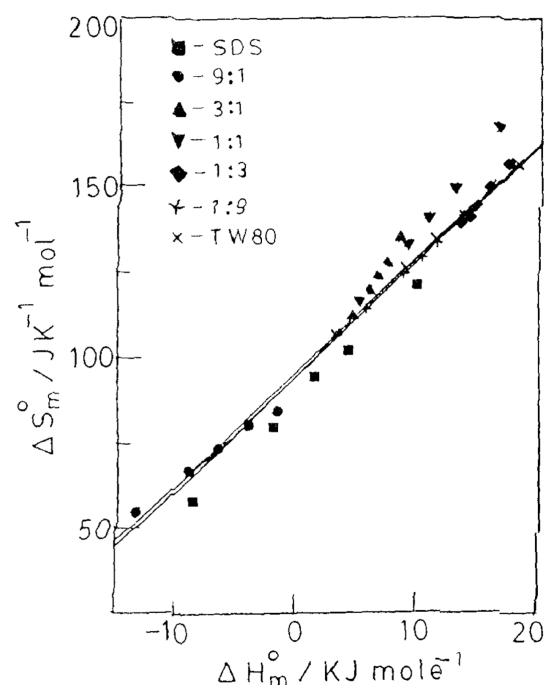


Figure 4. Entropy changes vs enthalpy changes in the micellization of SDS and Tw-80 and their binary mixtures.

temperature ((Supporting Information: Figure B) and increases with the decreasing concentration (Figure 5), showing more or less a close behavior in polar environment. Komaromy-Hiller et al.⁴⁶ found an appreciable decrease in I_1/I_3 by adding SDS and CTAB in TX-114 with the rise of temperature.

Aggregation Number. Aggregation numbers (\bar{N}) of the pure and mixed surfactant systems determined from $\ln(I_0/I)$ vs $[Q]$ plot (Supporting Information: Figure C) are given in Table 4 and \bar{N} vs T plots are depicted in Figure 6. The effect of temperature on \bar{N} depicts an opposing trend. \bar{N} of SDS decreases with increasing temperature, and \bar{N} values of Tw-80 show a significant increase with the rise of temperature.^{42,47} It is significant to mark the micellization of ionic surfactant SDS, the entropy decreases with the decreasing aggregation number following the rise of temperature, but the trend is opposite in nature for nonionic surfactant Tw-80, where entropy increases with the increasing number of aggregation. The \bar{N} values of the mixed aggregates are generally observed to be higher and lower compared to the pure ionic and nonionic surfactants, respectively. These values of the mixtures do not exhibit any regular trend corresponding to the mole fractions of SDS. This may be due to considerable difference in cohesions and shapes of the molecules for the mixed aggregate.⁴⁸ The gradual rise of \bar{N} values of the mixed micelles with the rise of temperature (particularly maximum in equimolar combination) finds support from the observed lowest cloud point (112 °C/385 K) and trend in lowering of entropy as well as change in heat capacity values (Table 3).⁴⁷ The reduction of repulsive headgroup interaction and dehydration of the micelles with rise of temperature are responsible for the most favorable growth of mixed entity.

Intermicellar Interaction and Mixed Micellar Composition. The mixed surfactant solutions may be ideal or nonideal. If the micelle formation is ideal, the CMC values of the mixture can be evaluated from those of the individual surfactants. Thus, the CMC of the surfactant mixture may be obtained

Table 4. Microenvironment (I_1/I_3), Aggregation Number (\bar{N}), and Cloud Point of Pure and Binary Mixtures of SDS and Tween-80 (100 mM) at Different Temperatures

α_{SDS}	temp (K)	microenvironment I_1/I_3	aggregation no. (\bar{N})	cloud point (°C)
1.00	283	1.094	98	146
	303	1.057	75	
	318	1.065	60	
0.90	283	1.055	102	151
	303	1.031	90	
	318	1.023	79	
0.75	283	1.107	91	112
	303	1.082	76	
	318	1.056	68	
0.50	283	1.096	70	127
	303	1.067	88	
	318	1.043	136	
0.25	283	1.094	65	130
	303	1.068	75	
	318	1.045	82	
0.10	283	1.093	68	89
	303	1.056	79	
	318	1.029	93	
0.00	283	1.091	110	143
	303	1.048	126	
	318	1.018	143	

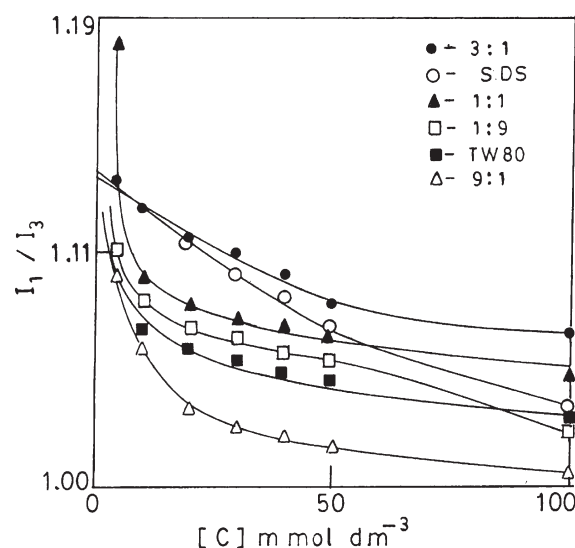


Figure 5. Micropolarity (I_1/I_3) vs concentration (C) plots for pure and mixed surfactant systems.

from the relation^{15–17,22,40}

$$\frac{1}{\text{CMC}_{\text{mix}}} = \sum_{i=1}^n \frac{\alpha_i}{f_i \text{CMC}_i} \quad (11)$$

where CMC_i and CMC_{mix} are the critical micelle concentrations of the i th component and the mixtures respectively; α_i and f_i are

the mole fraction and activity coefficient of the component i , respectively, in the mixed micelle. In an ideal case, $f_i = 1$ and eq 11

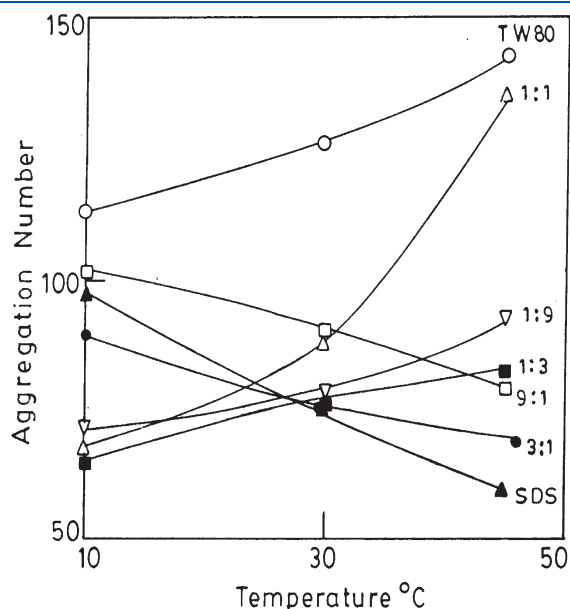


Figure 6. Aggregation number vs temperature plots for pure and mixed surfactant systems of SDS and Tw-80.

assumes the following form, known as the Clint equation (ideal)¹² for the binary mixtures of SDS and Tw-80.

$$\frac{1}{\text{CMC}_{\text{mix}}} = \frac{\alpha}{\text{CMC}_{\text{SDS}}} + \frac{1-\alpha}{\text{CMC}_{\text{Tw}}} \quad (12)$$

The experimentally measured CMC_{mix} are found to be lower than those calculated by the ideal equation. Similar deviations were observed for other binary mixtures.^{23–30,40,49}

Nonideal micellar solutions are usually modeled on the basis of different theoretical treatments of Rubingh,¹⁴ Rosen at interface,¹¹ Motomura,¹³ Blankschtein et al. (SPB),^{15–19} and Maeda.^{50,51} These treatments have been used to explain molecular interaction in the mixed micelles of binary combinations as well as for predicting CMC and f_i .

In the case of regular solution theory modeled by Rubingh,¹⁴ the micellar mole fraction of a surfactant in the total mixed system (X_R) can be evaluated following iterative method by the equation

$$\frac{(X_R)^2 \ln(\alpha_{\text{SDS}} \text{CMC}_{\text{mix}} / X_R \text{CMC}_{\text{SDS}})}{(1-X_R)^2 \ln[(1-\alpha_{\text{SDS}}) \text{CMC}_{\text{mix}} / (1-X_R) \text{CMC}_{\text{Tw}}]} = 1 \quad (13)$$

From the X_R values, it is convenient to calculate the molecular interaction parameter, β_R , and the activity coefficients of SDS and Tw-80, f_R^{SDS} and f_R^{Tw} , respectively (Table 5), following the

Table 5. Micellar Composition (X_R , X_M , X_{SPB}), Mole Fraction at the Monolayer (X_{ROS}), Interaction Parameter (β_R , $\beta_{\text{SPB}}^{\text{calc}}$, $\beta_{\text{SPB}}^{\text{pred}}$, β_{ROS}), Activity Coefficients (f_R , f_{SPB}) of Binary Mixtures of SDS and Tween-80 at Different Temperatures by Rubingh (R), Motomura (M), Rosen (ROS), and Sarmoria, Puvvada, Blankschtein (SPB)

α_{SDS}	temp (K)	X_R	X_M	X_{SPB}	β_R	$\beta_{\text{SPB}}^{\text{pred}}$ (kT)	$\beta_{\text{SPB}}^{\text{calc}}$ (kT)	f_R^{SDS}	f_R^{Tw}	$f_{\text{SPB}}^{\text{SDS}}$	$f_{\text{SPB}}^{\text{Tw}}$	air–water interface	
												X_{ROS}	β_{ROS}
0.90	283	0.247	0.261	0.175	−6.08	−4.60	−4.05	0.032	0.690	0.063	0.883	0.254	−6.30
	293	0.181	0.171	0.163	−4.44	−4.10	−4.08	0.051	0.864	0.060	0.897	0.183	−4.50
	298	0.116	0.104	0.154	−3.14	−3.81	−3.83	0.086	0.959	0.055	0.908	0.107	−3.00
	303	0.072	0.066	0.146	−2.32	−3.66	−3.68	0.136	0.988	0.034	0.909	0.063	−2.12
	313	0.026	0.022	0.142	−1.06	−3.60	−3.64	0.366	0.399	0.055	0.924	0.017	−0.61
0.75	283	0.152	0.184	0.109	−5.15	−4.86	−4.33	0.025	0.888	0.042	0.953	0.168	−5.52
	293	0.102	0.060	0.097	−4.05	−3.92	−3.95	0.040	0.959	0.038	0.962	0.103	−4.11
	298	0.081	0.080	0.093	−3.36	−4.04	−3.85	0.055	0.983	0.036	0.965	0.084	−3.82
	303	0.042	0.051	0.087	−2.69	−3.91	−3.94	0.085	0.995	0.035	0.974	0.051	−3.40
	313	0.058	0.052	0.081	−3.30	−3.82	−3.80	0.053	0.989	0.035	0.974	0.083	−3.98
0.50	283	0.105	0.132	0.058	−5.30	−4.25	−4.18	0.015	0.944	0.027	0.986	0.138	−6.27
	293	0.090	0.101	0.051	−5.00	−4.16	−4.10	0.016	0.960	0.026	0.989	0.115	−5.82
	298	0.070	0.101	0.050	−4.63	−4.26	−4.21	0.018	0.977	0.025	0.991	0.119	−6.12
	303	0.024	0.020	0.042	−3.16	−3.93	−3.94	0.049	0.999	0.026	0.991	0.116	−6.22
	313	0.062	0.036	0.037	−4.71	−3.69	−3.90	0.016	0.982	0.026	0.995	0.116	−6.21
0.25	283	0.088	0.105	0.026	−6.18	−4.21	−4.19	0.007	0.954	0.021	0.997	0.106	−6.77
	293	0.050	0.030	0.022	−5.14	−4.04	−4.02	0.010	0.989	0.021	0.998	0.036	−4.70
	298	0.022	0.035	0.020	−4.12	−4.11	−4.11	0.019	0.997	0.020	0.998	0.064	−5.83
	303	0.015	0.036	0.018	−3.74	−3.97	−3.96	0.026	0.999	0.021	0.998	0.068	−6.14
	313	0.030	0.038	0.020	−4.50	−4.00	−4.02	0.015	0.996	0.022	0.998	0.068	−6.14
0.10	283	0.050	0.078	0.010	−6.02	−4.12	−4.18	0.004	0.985	0.018	0.999	0.094	−7.74
	293	0.030	0.056	0.011	−5.35	−4.02	−4.05	0.007	0.995	0.019	0.995	0.063	−6.90
	298	0.015	0.012	0.009	−4.79	−4.06	−4.06	0.010	0.999	0.018	0.999	0.022	−5.28
	303	0.009	0.005	0.006	−4.29	−3.98	−3.88	0.015	0.999	0.019	0.999	0.052	−6.81
	313	0.029	0.004	0.006	−5.82	−3.95	−3.99	0.004	0.995	0.020	0.999	0.052	−6.81

equations

$$\beta_R = \frac{\ln(\alpha_{\text{SDS}} \text{CMC}_{\text{mix}} / X_R \text{CMC}_{\text{SDS}})}{(1 - X_R)^2} \quad (14)$$

$$f_R^{\text{SDS}} = \exp[\beta_R(1 - X_R)^2] \quad (15)$$

$$f_R^{\text{Tw}} = \exp \beta_R X_R^2 \quad (16)$$

Here, β_R is a measure of the interaction between the components in the micelle obtained from the experimental CMC data. The formation of a mixed micelle is ideal when $\beta_R = 0$, whereas a positive β_R indicates antagonism and a negative one suggests synergism toward mixed micelle formation. The magnitude of β_R indicates the degree of nonideality.

Rosen¹¹ used this regular solution model to interpret the behavior of binary surfactant mixtures (ROS) at air–liquid interface on the basis of the following assumptions:

- (i) the ratio of the partial molar areas of the two surfactants in the mixed monolayer, A_1 and A_2 , equals the ratio of the molar areas of the two individual surfactants at the same interfacial tension and
- (ii) molar areas of the surfactants at the interfaces remain unchanged if they are mixed with a second surfactant component and using modified Gibbs adsorption equation

$$\text{interfacial area, } A = 2.303RT / \left(\frac{d\gamma}{d \log C} \right) \quad (17)$$

For this purpose, two equations involved in the iteration procedure are

$$\beta_{\text{ROS}} = \frac{\ln \frac{\alpha_{\text{SDS}} \text{CMC}_{\text{mix}}}{\text{CMC}_{\text{SDS}} X_{\text{ROS}}} - \frac{\gamma A_{\text{SDS}}}{RT} \left[1 - \frac{A_{\text{mix or } A_{\text{av}}}}{X_{\text{ROS}} A_{\text{SDS}} + (1 - X_{\text{ROS}}) A_{\text{Tw}}} \right]}{(1 - X_{\text{ROS}})^2} \quad (18)$$

and

$$\frac{X_{\text{ROS}}^2}{(1 - X_{\text{ROS}})^2} = \frac{\ln \frac{\alpha_{\text{SDS}} \text{CMC}_{\text{mix}}}{\text{CMC}_{\text{SDS}} X_{\text{ROS}}} - \frac{\gamma A_{\text{SDS}}}{RT} \left[1 - \frac{A_{\text{mix or } A_{\text{av}}}}{X_{\text{ROS}} A_{\text{SDS}} + (1 - X_{\text{ROS}}) A_{\text{Tw}}} \right]}{\ln \frac{(1 - \alpha_{\text{SDS}}) \text{CMC}_{\text{mix}}}{\text{CMC}_{\text{Tw}} (1 - X_{\text{ROS}})} - \frac{\gamma A_{\text{Tw}}}{RT} \left[1 - \frac{A_{\text{mix or } A_{\text{av}}}}{X_{\text{ROS}} A_{\text{SDS}} + (1 - X_{\text{ROS}}) A_{\text{Tw}}} \right]} = 1 \quad (19)$$

where A_{SDS} , A_{Tw} , A_{mix} , γ , and α_{SDS} represent the experimental results obtained for the area minimum per SDS molecule, the area minimum per Tw-80 molecule, area minimum in mixed monolayer, surface tension at the air–water interface, and mole fraction of SDS in mixed monolayer, respectively. The interaction parameter at monolayer (β_{ROS}) and computed mole fraction at the monolayer (X_{ROS}) are presented in Table 5.

Motomura et al.¹³ proposed a method to evaluate mixed micellar composition (X_M) in terms of excess thermodynamic function. For a binary mixture of surfactants, they considered that surfactant 1 dissociates giving ν_{1a} anions and ν_{1c} cations, whereas surfactant 2 dissociates giving ν_{2b} cations and ν_{2d} anions and the following relations hold.

$$\hat{X}_2 = \frac{\nu_2 \alpha_2}{\nu_1 \alpha_1 + \nu_2 \alpha_2} \quad (20)$$

$$\hat{\text{CMC}}_{\text{mix}} = (\nu_1 \alpha_1 + \nu_2 \alpha_2) \text{CMC}_{\text{mix}} \quad (21)$$

where subscripts 1 and 2 refer to surfactants 1 and 2, respectively, α stands for the stoichiometric mole fraction, and ν represents the number of ions contributed by a surfactant. The fundamental equation for the micellar mole fraction of a surfactant in the total surfactant mixture is

$$X_M = \hat{X}_2 - (\hat{X}_1 \hat{X}_2 / \hat{\text{CMC}}_{\text{mix}}) (\partial \hat{\text{CMC}}_{\text{mix}} / \partial \hat{X}_2)_{T,P} \quad (22)$$

The determination of $(\partial \hat{\text{CMC}}_{\text{mix}} / \partial \hat{X}_2)$, i.e., the slope of $\hat{\text{CMC}}$ vs \hat{X}_2 plot, then leads to the evaluation of X_M presented in Table 5.

A significant advancement in modeling surfactant mixtures is the molecular thermodynamic theory proposed by Sarmoria, Puvvada, and Blankshtein (SPB) in recent years.^{15–17} The theory takes into account the electrostatic interactions between

the charged head groups and the packing of the nonpolar tail groups in the core of the micelle and enables us to predict quantitatively the solution behavior of the surfactant mixtures. Thus, the CMC of the mixture (Table 6), the interaction parameter β , micellar compositions (X_{SPB}) and monomer compositions (Table 5) are predicted. In Figure 7a,b, $\ln \text{CMC}$ vs α_{SDS} and $\ln \text{CMC}$ vs X_{av} have been plotted for comparison (showing different nature) where X_{av} is the average micellar composition of X_M , X_R , and X_{SPB} . Blankshtein et al.^{15–17} have proposed the following equations to calculate the physicochemical properties of the micellar aggregates. Thus, the eq 12 has been modified and the following relations have been proposed.

$$\frac{1}{\text{CMC}_{\text{mix}}} = \frac{\alpha_{\text{SDS}}}{f_{\text{SPB}}^{\text{SDS}} \text{CMC}_{\text{SDS}}} + \frac{1 - \alpha_{\text{SDS}}}{f_{\text{SPB}}^{\text{Tw}} \text{CMC}_{\text{Tw}}} \quad (23)$$

$$f_{\text{SPB}}^{\text{SDS}} = \exp \left[\frac{\beta_{12} (1 - \alpha^*)^2}{kT} \right] \quad (24)$$

$$f_{\text{SPB}}^{\text{Tw}} = \exp \left[\frac{\beta_{12} \alpha^{*2}}{kT} \right] \quad (25)$$

where $f_{\text{SPB}}^{\text{SDS}}$ and $f_{\text{SPB}}^{\text{Tw}}$ are the activity coefficients of SDS and Tw-80 in the mixed micelle. β_{12} is the predicted interaction parameter between the surfactants 1 and 2, α^* is the optimal micellar composition (where the free energy of micellization attains its minimum value), K is the Boltzmann constant, and T is the absolute temperature. The values of β_{12} are used to estimate

Table 6. Free Energy and Interaction Parameter of Ionic (SDS) and Non-Ionic (Tween-80) Surfactant Mixtures Obtained from Maeda Models in Aqueous Medium at Different Temperatures

temp (K)	Maeda model ⁵⁰					Maeda model ⁵¹					
	α_{SDS}	B_0	B_1	B_2	$-\Delta G_{\text{Ma}}$	X_{Ma}	f_1	f_N	G^{ex}	$-\beta_{\text{Ma}}$	
283	0.90	15.18	0.39	6.08	23.30	0.667	0.012	1.58	2.81	12.60	
	0.75		1.30	5.15	24.33	0.321	0.011	1.14	1.35	6.20	
	0.50		1.15	5.30	28.13	0.005	0.003	0.83	0.19	47.60	
	0.25		0.27	6.18	31.92	-0.120					
293	0.90	15.34	2.10	4.44	24.01	0.672	0.014	2.15	2.61	11.84	
	0.75		2.49	4.05	27.27	0.278	0.013	1.20	1.06	5.28	
	0.50		1.54	5.00	32.45	-0.060					
	0.25		1.40	5.14	35.73	-0.150					
303	0.90	15.58	4.43	2.32	24.47	0.600	0.016	2.54	2.26	9.69	
	0.75		4.06	2.69	27.76	0.240	0.014	1.26	0.85	4.60	
	0.50		3.59	3.16	32.74	-0.120					
	0.25		3.01	3.74	36.76	-0.220					
313	0.90	15.63	5.78	1.06	24.90	0.630	0.016	2.74	2.23	9.58	
	0.75		3.54	3.30	28.93	0.240	0.014	1.19	0.86	4.86	
	0.50		2.13	4.71	34.84	-0.140					
	0.25		2.34	4.50	38.42	-0.220					
298	0.75	15.52	3.54	3.14	24.26	0.650	0.015	2.41	2.42	10.63	
	0.50		3.32	3.36	27.60	0.25	0.140	1.26	0.90	4.80	

α^* , $f_{\text{SPB}}^{\text{SDS}}$, and $f_{\text{SPB}}^{\text{Tw}}$ (Table 5) by using the relation

$$\frac{\beta_{12}(1-2\alpha^*)}{kT} + \ln\left(\frac{\alpha^*}{1-\alpha^*}\right) = \ln\left[\frac{\alpha_{\text{SDS}}\text{CMC}_{\text{Tw}}}{(1-\alpha_{\text{SDS}})\text{CMC}_{\text{SDS}}}\right] \quad (26)$$

Blankschtein et al.^{18,19} have extended the simplified working model and combined a molecular model of mixed micellization with thermodynamic framework to predict a broad spectrum of solution properties of the mixed surfactant systems. The molecular model accounts for micellar mixing of nonidealities resulting from electrostatic and steric interaction between the surfactant hydrophilic heads and from the packing of surfactant hydrophobic tails of unequal length in the micellar core to predict properties for binary mixtures containing nonionic, anionic, cationic, and zwitterionic surfactants. To correlate practical performance with fundamental measurement of synergism for the mixture, they introduced the quantity $\Delta G_{\text{mic}} = G_{\text{mic}}^{\text{ideal}} - G_{\text{mic}}$ where ΔG_{mic} measures the difference between the ideal and actual free energies of mixed micelle formation. $G_{\text{mic}}^{\text{ideal}}$ and G_{mic} generally stand as

$$G_{\text{mic}}^{\text{ideal}} = \alpha G_{\text{mic}}^{\text{A}} + (1-\alpha) G_{\text{mic}}^{\text{B}} + kT[\alpha \ln \alpha + (1-\alpha) \ln(1-\alpha)] \quad (27)$$

and

$$G_{\text{mic}} = \alpha G_{\text{mic}}^{\text{A}} + (1-\alpha) G_{\text{mic}}^{\text{B}} + kT[\alpha \ln \alpha + (1-\alpha) \ln(1-\alpha)] + \beta \alpha(1-\alpha) \quad (28)$$

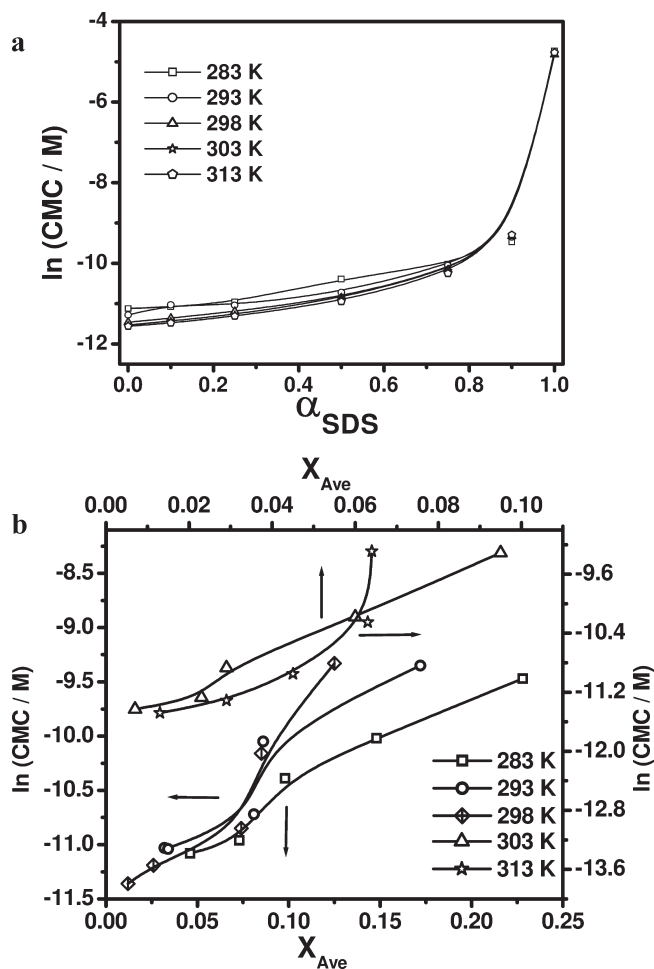


Figure 7. (a) $\ln \text{CMC}$ vs α_{SDS} for mixed surfactant systems of SDS and Tw-80 at different temperatures. (b) $\ln \text{CMC}$ vs X_{Ave} for mixed surfactant systems of SDS and Tw-80 at different temperatures.

where α is the mole fraction of the solution composition and β is the interaction parameter. $G_{\text{mic}}^{\text{A}}$ and $G_{\text{mic}}^{\text{B}}$ of the surfactants A and B are associated with the free energy change per monomer for the transfer of free energy (G_{tr}), the interfacial free energy (G_{int}), the packing free energy (G_{pack}), the steric free energy (G_{st}), and the electrostatic free energy (G_{elec}). The free energy term for $G_{\text{mic}}^{\text{A}}$ and $G_{\text{mic}}^{\text{B}}$ are calculated by considering an approximate value for the anionic/nonionic mixture¹⁹ as $G_{\text{mic}}^{\text{A}} = -10kT$, $G_{\text{mic}}^{\text{B}} = -12kT$, and $G_{\text{mic}}^{\text{AB}} = -2kT$. Substituting these values in eqs 27 and 28, the results obtained are used in the plot of $(G_{\text{mic}}^{\text{ideal}} - G_{\text{mic}})$ against solution composition (Figure 8). The peak in the plot corresponds to the solution composition, revealing that the micelle formation is the most favorable for practical application in equimolar composition (1:1) over other compositions. It is worthy to mention that the ΔG_{mic} measures the difference between the ideal and actual free energies of mixed micelle formation at a given solution composition and also stipulates a measure of synergism in the formation of mixed micelle over the total composition range. The molecular thermodynamic theory provides useful information on the optimal composition required to maximize synergism in several diverse applications.

Maeda⁵⁰ has developed a convincing model for solutions with moderately high ionic strength, where the electrostatic interaction in the ionic/nonionic mixed micellar system is short-ranged,

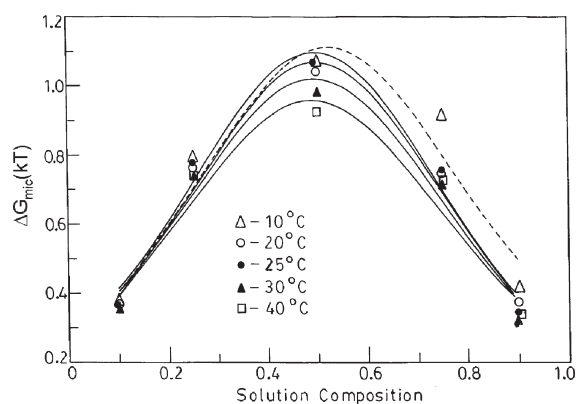


Figure 8. Difference between G_{mic}^{ideal} and the predicted G_{mic} [ΔG_{mic} (kJ/mol)] vs solution composition of SDS in aqueous solution of SDS and Tw-80 at different temperatures.

but not negligible. The standard free energy change due to micellization process is given by a polynomial function of the ionic mole fraction (α_{SDS}) in the micellar phase as

$$\Delta G_{Ma}^0 = RT(B_0 + B_1\alpha_{SDS} + B_2\alpha_{SDS}^2) \quad (29)$$

where

$$B_0 = \ln X_{C_2} \quad (30)$$

X_{C_2} is the CMC of nonionic surfactant (Tw-80) in the mole fraction unit. If component 2 self-assembles, the micellar free energy change is expressed as a dimensionless quantity, B_0 ($=\ln X_{C_2} = \Delta G_m^0/RT$). The standard free energy change accompanied with the change in the CMC values of the nonionic micelles when an ionic species enters the micelle is associated with parameter B_1 .⁵⁰ B_2 is the interaction parameter in the micellar phase. R and T are the universal gas constant and absolute temperature, respectively. Again,

$$B_1 + B_2 = \ln\left(\frac{X_{C_1}}{X_{C_2}}\right) \quad (31)$$

and

$$B_2 = -\beta_R \quad (32)$$

X_{C_1} is the CMC of the ionic surfactants in the mole fraction unit and β_R is the interaction parameter in the micellar phase obtained from eq 14.

The B_0 , B_1 , B_2 , and ΔG_{Ma}^0 values are presented in Table 6. B_0 values are always constant for binary mixtures. In this system, the B_1 values decrease and B_2 values increase with the decreasing fraction of α_{SDS} excepting $\alpha_{SDS} = 0.9$ at 283 and 293 K. But with the rise of temperature, in reverse trend, B_1 values increase and B_2 values decrease, except at 313 K. The increase of B_1 is due to the increase in intermolecular association within the micelles and the positive values of B_1 for this system are due to less tail–tail interactions. The ΔG_{Ma}^0 values obtained at different temperatures decrease regularly with increasing α_{SDS} in this binary system, and they deviate more than the free energy (ΔG_m^0) values obtained from eq 4, revealing the binding of counterion to the ionic/nonionic mixed micelles.

On the basis of the Gibbs–Duhem equation considered by Hall,⁵² Maeda proposed another theoretical model⁵¹ of excess free energy (G^{ex}) of the ionic/nonionic mixed micelle, which is

even applicable to the system of low ionic strength. The essential relation is

$$G^{ex} = X_{Ma} \ln f_I + (1 - X_{Ma}) \ln f_N \quad (33)$$

where f_I and f_N are the activity coefficients of the ionic (SDS) and the nonionic (Tw-80) surfactants, respectively, and X_{Ma} is the micellar mole fraction of the ionic species according to this model. X_{Ma} can be calculated by plotting $\ln CMC_{mix}$ vs stoichiometric mole fraction of the ionic species (α_{SDS}) using the relation

$$X_{Ma} = \frac{\alpha_{SDS} \left[1 - (1 - \alpha_{SDS}) \frac{d \ln CMC_{mix}}{d \alpha_{SDS}} \right]}{\left[1 + \nu(1 - \alpha_{SDS}) \left\{ \alpha_{SDS} \left(\frac{d \ln CMC_{mix}}{d \alpha_{SDS}} \right) + 1 \right\} \right]} \quad (34)$$

ν is the counterion binding (g) presented in Table 2 in aqueous medium. The activities of the ionic (a_I) and the nonionic (a_N) components are given by

$$a_I = X_{Ma} f_I = \alpha_{SDS} \frac{CMC_{mix}}{C_{SDS}}$$

and

$$a_N = (1 - \alpha_{SDS}) f_N = (1 - \alpha_{SDS}) \frac{CMC_{mix}}{C_{Tw}}$$

where C_{SDS} , C_{Tw} , and CMC_{mix} are the CMC of pure SDS, Tw-80, and the mixtures, respectively.

The interaction parameter (β_{Ma}) in the micellar phase can be calculated from

$$\beta_{Ma} = \frac{G^{ex}}{X_{Ma}(1 - X_{Ma})} \quad (35)$$

Table 6 shows the X_{Ma} , f_I , f_N , G^{ex} , and β_{Ma} values related to this theory. In all cases, X_{Ma} is lower than the α_{SDS} and X_{Ma} decreases with decreasing concentration of the ionic species (α_{SDS}). In the low mole fraction of ionic species (below $\alpha_{SDS} \leq 0.50$), a discrepancy is observed in this system. The values of the activity coefficient of ionic (f_I) and nonionic species (f_N) decrease with the decreasing mole fraction of α_{SDS} . This is due to considerable difference in CMC values of SDS and Tw-80. In this system, G^{ex} and β_{Ma} values decrease with the decreasing stoichiometric mole fraction of SDS and negative values of β_{Ma} indicate synergism of this ionic/nonionic mixture.

The CMC values calculated by following equations of Rubingh's treatment (RS theory) and molecular thermodynamic theory (SPB) have been compared with the observed and ideal values (Table 7).

$$\frac{1}{CMC_R} = \frac{\alpha}{f_R^{SDS} CMC_{SDS}} + \frac{1 - \alpha}{f_R^{Tw} CMC_{Tw}}$$

and

$$\frac{1}{CMC_{SPB}} = \frac{\alpha}{f_{SPB}^{SDS} CMC_{SDS}} + \frac{1 - \alpha}{f_{SPB}^{Tw} CMC_{Tw}}$$

The calculated CMCs (CMC_R) are found to be lower than the experimental values. Both the values of CMC_R and CMC_{SPB} approach the observed CMCs (CMC_{obs}) with increasing mole fraction of Tw-80 as well as with increasing temperature. It is observed that the X_R , X_M , X_{SPB} , and X_{Ma} values are low compared

Table 7. Critical Micelle Concentration (CMC) of Binary Mixtures of SDS and Tween-80 at Different Temperatures by Rubingh (R), Sarmoria, Puvvada, and Blankschtein (SPB), Clint (Ideal), and Experimental Observation (Obs)

α_{SDS}	temp (K)	10 ⁵ CMC			
		Rubingh (R)	SPB	Clint	obs
0.90	283	7.44	11.01	14.55	7.74
	293	8.49	9.03	12.43	8.73
	298	8.53	7.66	10.48	8.90
	303	8.72	7.44	9.79	9.07
	313	8.76	7.31	9.41	9.24
0.75	283	4.28	5.14	5.89	4.46
	293	4.17	4.16	5.02	4.34
	298	3.68	3.50	4.22	3.96
	303	3.63	3.71	3.95	3.78
	313	3.36	3.30	3.79	3.54
0.50	283	2.42	2.81	2.96	2.53
	293	2.12	2.38	2.52	2.22
	298	1.83	1.83	2.12	1.95
	303	1.85	1.85	1.98	1.91
	313	1.66	1.76	1.90	1.75
0.25	283	1.67	1.95	1.97	1.74
	293	1.51	1.56	1.68	1.58
	298	1.28	1.30	1.42	1.38
	303	1.25	1.25	1.33	1.28
	313	1.17	1.21	1.27	1.23
0.10	283	1.48	1.66	1.69	1.55
	293	1.30	1.32	1.41	1.36
	298	1.10	1.10	1.17	1.16
	303	1.04	1.05	1.10	1.09
	313	0.97	1.02	1.05	1.02

to the corresponding stoichiometric mole fractions, and the values of X_{SPB} are higher than X_{R} and X_{M} at and above 25 °C. The values of different CMCs (obtained by different methods) at different temperatures (Table 7) are compared and are found to be lower than the ideal values. But with increasing temperature (>298 K), the CMCs gradually converge to almost same values. The results suggest that the binary mixtures of SDS/Tw-80 tend to behave ideally at the above-mentioned situations.

The values of the interaction parameter β_{R} by Rubingh's method are higher than the predicted values of Sarmoria, Puvvada, and Blankschtein (SPB). The β_{ROS} values at the air–water interface (monolayer film) are closely comparable with β_{R} values. Similar results for CMC_{obs} , X_{R} , X_{M} , X_{SPB} , and the activity coefficients have been reported in the case of other surfactant systems.^{21–23,27,29,30,40,47,49} The negative β values (β_{R} , β_{SPB} , β_{ROS} , and β_{Ma}) obtained by four different methods for binary combinations of SDS and Tw-80 at different temperatures (Table 6) indicate the synergistic behavior of the system. The activity coefficient values (Table 6) obtained from different theoretical treatments closely follow the rule $f_{\text{R}}^{\text{SDS}} + f_{\text{R}}^{\text{Tw}}$ or $f_{\text{SPB}}^{\text{SDS}} + f_{\text{SPB}}^{\text{Tw}} = 1$. The values of the activity coefficient and the negative β values of the system indicate a tendency of perfect mixing.

The structural features of the micellar aggregates can be assessed by the geometry or “packing” properties, which generally depend on three parameters: (i) the surface area (A) of the micelle, (ii) the volume (ν) of the micelle, which can be

Table 8. Values of Critical Chain Length (l_{C}), Volume of Hydrophobic Chain (ν), Surface Area of Polar Head Group (A), Packing Parameter (P), and Radius (R) of Pure SDS and Tween-80 Micelles

surfactant	l_{C} (nm)	ν (nm ³)	A (nm ²)	P	R (nm)
SDS	1.672	0.350	0.46–0.73	0.46–0.29	2.283 1.438
Tw-80	2.431	0.512	0.76–0.71	0.28–0.30	2.021–2.163

Table 9. Values of Packing Parameter (P) in Binary Mixed Micelles of SDS and Tween-80 at Different Temperatures and at Different Stoichiometric Compositions (α)

α_{SDS}	P_{effect}			
	283 K	293 K	303 K	313 K
0.90	0.424	0.362	0.382	0.370
0.75	0.389	0.311	0.330	0.340
0.50	0.300	0.290	0.320	0.330
0.25	0.242	0.266	0.300	0.323

considered to be fluid and incompressible, and (iii) the maximum effective length (l_{C}), a semiempirical parameter, applicable only for a smaller extension of the hydrophobic chain. Israelachvili⁵³ used these parameters to estimate the geometry of the micellar aggregate by the value of the packing parameter (P) which can be expressed as

$$P = \frac{\nu}{l_{\text{C}}A} \quad (36)$$

Tanford⁵⁴ mentioned that for a saturated hydrocarbon chain with n_{C} number of carbon atoms,

$$l_{\text{C}} \leq l_{\text{max}} \approx (0.154 + 0.1265n_{\text{C}}) \text{ nm and } \nu \approx (0.0274 + 0.0269n_{\text{C}}) \text{ nm}^3$$

The surface area (A) of the pure amphiphile can be obtained from Table 2.

The micellar aggregates will be mentioned as spherical ($P < 1/3$), nonspherical ($1/3 < P < 1/2$), bilayers ($1/2 < P < 1$), or inverted structures ($P > 1$), depending on the value of the packing parameter. The radius of the aggregate, R , was evaluated from $R = 3\nu/A$ nm.

With the values of l_{C} , ν , and A , the values of P and R have been calculated and presented in Table 8. In the case of a spherical micelle, R is less than l_{C} . For SDS, at low temperature, as R exceeds l_{C} , it should be nonspherical arising due to repulsion among the ionic headgroup in an ionic/nonionic mixed micelles. But at higher temperature, the SDS aggregates are spherical ($R < l_{\text{C}}$). In Tw-80, the micellar pack remains spherical with their micellar radius not exceeding l_{C} . In a similar way, the aggregation of binary mixed micelles can be evaluated in terms of the effective packing parameter (P_{effect}) as

$$P_{\text{effect}} = (\nu/Al_{\text{C}})_{\text{effect}} = \sum \nu_i X_i^{\text{mic}} / \sum (A_i X_i^{\text{mic}}) l_{\text{C}} \quad (37)$$

where X_i^{mic} is the mole fraction of the i th component (X_{R}) in the micelle of the binary mixtures taken from Table 6. The surface area (A) of the mixed micelles at different stoichiometric mole fractions is used from Table 2. From Table 9, it is marked that the mixed micelles are nonspherical at all temperatures when the mole fractions of the ionic part in mixtures are high but transform to spherical shape with the higher mole fraction of the nonionic part ($\alpha_{\text{SDS}} \leq 0.50$).

CONCLUSION

The CMC values of mixed micelles obtained by Rubingh and SPB show reasonable agreement with the observed values but are rather lower than that of Clint, which clarifies the presence of nonideality of the mixed micelles. The experimental results and the theoretical estimates of CMC come closer at high temperatures.

The mole fraction of a particular component obtained from a different theoretical model in the mixed micelles is generally lower than the stoichiometric mole fraction of the ionic component, indicating the low extent of transfer of that surfactant (SDS) from the solution into the micelle. The counterion association capacity of the micelles is observed to be low in the mixed species compared to the individual components.

The negative values of excess free energy (G^{ex}) and interaction parameter, β (β_{R} , β_{SPB} , β_{ROS} , and β_{Ma}), obtained from different methods for the binary combination of SDS and Tw-80 at different temperatures indicate the synergistic behavior, which generally decreases with the increasing temperature, and the negative β values signify the evidence of fair degree of interaction in mixing.

The ΔG_{m}^0 values are more negative compared to the ΔG_{ad}^0 in high concentrations of ionic surfactant, whereas the reverse trend is observed in the case of high concentrations of nonionic surfactant; i.e., the micelle formation in the bulk is predominant up to equimolar concentration, and then the adsorption process is more spontaneous than micelle formation in the high concentration of nonionic surfactant. The higher positive entropy of adsorption (ΔS_{ad}^0) than the entropy of micellization (ΔS_{m}^0) supports the freedom of movement of the hydrocarbon chain toward the air–water interface. A fair linear compensation between ΔS_{m}^0 and ΔH_{m}^0 with a slope of 1/299 K suggests that the micellization compensation takes place at 299 K (T_{C}) and, as $\Delta H_{\text{m}}^0 = 0$, the driving force of micelle formation is entropy controlled at and above this 299 K.

The free energy of micellization (ΔG_{Ma}^0) obtained from Maeda's model is comparable, but they deviate from ΔG_{m}^0 , revealing the consequence of counterion binding to the ionic/nonionic mixed micelles.

The aggregates of amphiphile SDS are nonspherical at low temperature as the micellar radius exceeds the critical chain length but change to spherical at and above 303 K. Tw-80 forms spherical micelles from 283 to 313 K. The P_{effect} suggests that the mixed micelles are nonspherical at the temperatures investigated, when the mole fraction of ionic component are $\alpha_{\text{SDS}} \geq 0.50$ and changes to spherical when the mole fraction of the nonionic increases ($\alpha_{\text{SDS}} \leq 0.50$) in micelle mixtures.

The low cloud point (CP) of Tw-80, which is the usual nature of the nonionic surfactant, increases on adding ionic SDS to justify the increasing trend in aggregation number with increasing temperature, where the mole fraction of the nonionic surfactant is high ($\alpha_{\text{SDS}} < 0.50$). The aggregation number decreases with the rise of temperature where the ionic mole fractions are high ($\alpha_{\text{SDS}} > 0.50$), in agreement with the high CP of mixtures. The lowest CP value of 1:1 composition of SDS and Tw-80 among others is very significant ($\alpha_{\text{SDS}} = 0.50$), as pure Tw-80 generates a phase toward the hydrophobic/hydrophilic character of the mixture, which indicates the usefulness of this mixture from water solubilization to oil solubilization for the preparation of emulsion, dispersion, etc. This result corresponds to Figure 8, where the solution reveals that the micelle formation is the most favorable for the practical application in equimolar composition over the other composition.

ASSOCIATED CONTENT

S Supporting Information. Plots of composition dependence of maximum surface excess, micropolarity (I_1/I_3) vs temperature, and $\ln(I_0/I)$ vs $[Q]$ and I_0/I vs $[Q]$ for determination of aggregation number for pure and mixed surfactant systems of SDS and Tw-80 at different temperatures. Tables of thermodynamic behaviors of adsorption at different temperatures and microenvironment (I_1/I_3) of different molar concentrations at 303 K for binary mixtures of SDS and Tween-80. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ACKNOWLEDGMENT

A.D.B. thanks the Polymer Science unit, IACS to pursue the work.

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