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ORIGINAL CONTRIBUTION

Mixed micellization of anionic–nonionic surfactants in aqueous media: a physicochemical study with theoretical consideration

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Abstract Mixed micellization of binary and ternary mixtures of anionic and nonionic surfactants, such as lithium dodecyl sulfate, polyoxyethylene(23)laurylether, and polyoxyethylene-*tert*-octylphenylether, is studied in aqueous solution using tensiometric, conductometric, and spectrophotometric methods. Although tensiometry and conductometry complement each other closely, the spectroscopic critical micellar concentration (cmc) is far from agreement with tensiometric study. Several parameters, e.g., cmc, degree of counterion binding, free energies of micellization, and interfacial adsorption, have been evaluated. Established theories of Clint, Rosen, Rubingh, Motomura, Georgiev, Maeda, and Blankschtein were applied to evaluate the mole fraction of different components in the self-aggregated phase, the interaction parameter, free energy contributions, and expected cmc.

Keywords Mixed micelle · Critical micellar concentration · Theoretical model

Introduction

A significant amount of research work has been devoted for searching the physicochemical properties of a mixed micelle containing two or more surfactants of variable structures in solution. Their extensive use has currently been promoted owing to their much favorable practical applications than single-component systems. In this respect, industrial, pharmaceutical, technological, and biochemical fields are of great importance. Thus, in the pharmaceutical field, a mixed micelle has been found to enhance the absorption of various drugs in the human body [1–3]. A number of cationic and anionic surfactant mixtures have been used in cleaning products to facilitate the dissolution and improved tolerance of water hardness [4]. Due to their synergistic behavior at the critical micellar concentration (cmc), cosmetic industries use the mixed micelles in low concentrations to avoid potential skin irritation [5–7]. This synergistic phenomenon can also be highly beneficial for the environment as it allows the amount of surfactant released and hence their impact to be substantially reduced [8].

In view of the tremendous application potentials and economical consideration of a mixed micelle, it is necessary to search for the most suited surfactant combinations with desired requirements (such as surface activity, solubility, and catalytic property). In mixed micellar systems of ionic, nonionic, and zwitterionic surfactants, three types of interactions may operate, viz., favorable (ionic–nonionic, ionic–zwitterionic, and cationic–anionic), unfavorable, and ideal mixing (nonionic mixtures). In an aqueous medium, pure and mixed surfactants can form micelles after a threshold concentration, called cmc, which can be assessed by various methods to understand the self-organizing behavior of surfactants.

From a theoretical point of view, mixed surfactant systems have been the object of great investigations and attracted much interest in recent years to provide appropriate thermodynamic models capable not only of describing the behavior of mixed systems but also for predicting their properties [9–16].

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In this work, we have used lithium dodecyl sulfate (LDS), polyoxyethylene(23)laurylether (Brij-35), and polyoxyethylene-*tert*-octylphenylether (TX-100) in binary and ternary mixtures in an aqueous medium. These surfactants differ in size and structure; LDS and Brij-35 have 12 carbon atoms in the linear chain, whereas TX-100 consists of eight carbon atoms attached with phenyl ring. There are 23 ethylene oxide residues in Brij-35 and nine to ten ethylene oxide residues in TX-100. In this paper, micellization and other physicochemical properties (e.g., extent of counterion binding, interfacial adsorption, thermodynamics of micellization, mutual interaction parameter and micellar compositions, etc.) of the pure and mixtures have been studied. Theories of Clint [17, 18], Rosen [9, 19], Rubingh [20], Motomura [21, 22], Georgiev [23], Maeda [24, 25], and Blankschtein [26, 27] have been used to find the path of interaction among the micellar components.

Experimental

Materials

The anionic surfactant LDS was a product of Merck (Germany), and the nonionic amphiphiles Brij-35 (or Bj-35) and TX-100 (or Triton X-100) were purchased from Sigma (USA). All the products were used without further purification. All solutions were prepared in doubly distilled water, and the experiments were performed at 298.15±0.1 K.

Methods

Tensiometry

The tensiometric experiments are performed using a platinum ring by the ring detachment method in a calibrated K9 Tensiometer (Krüss, Germany). A detailed procedure has been reported earlier [10–16]. Each experiment was repeated several times to achieve good reproducibility. The measured surface tension (γ) values were corrected according to the procedure of Harkins and Jordon. The γ values were accurate within ±0.1 mN m^{-1}.

Conductometry

The conductance measurements were taken with a Pye-Unicam PW-9509 conductivity meter at a frequency of 2,000 Hz using a conductivity cell of cell constant 1.0 cm^{-1}. The same procedure of the addition of the surfactant as in tensiometry was followed. The accuracy of the measurements was within ±1%. The measurement details can be found elsewhere [10–16].

Absorption spectrophotometry

A UV-visible (240) Shimadzu (Japan) spectrophotometer operating in dual-beam mode was employed for spectral measurements using a matched pair of quartz cuvettes of path length 1 cm under a thermostated condition (298.15 K). Spectral measurements were taken on the basis that TX-100 absorbs a maximum at 276.5 nm, and the absorbance (A) gets perturbed at the micellar point [14]. In this case, 3 mL of water are taken in a pair of cuvettes. Surfactant solution is then progressively added in the sample cell as required. Optical density at each stage of surfactant addition is measured after thoroughly at the absorption maximum (276.5 nm) of TX-100. Then, the absorbance was plotted against the logarithm of surfactant concentration, and the breakpoint of the profile was considered as the cmc.

Results and discussion

Critical micellar concentration

The cmcs of pure and mixed micellar systems of binaries (LDS/TX-100, LDS/Bj-35, and TX-100/Bj-35) and ternaries (LDS/TX-100/Bj-35) were determined from the point of intersection between two continuous lines obtained by tensiometry ($\gamma-\log[\mathrm{surf}]$), conductometry ($\kappa-[\mathrm{surf}]$), and spectrophotometry ($A-\log[\mathrm{surf}]$), and these representative figures of the above three methods are illustrated in Fig. 1a, b, and c, respectively, and the values are presented in Tables 1 and 2. In mixed systems with LDS as one component, tensiometric and conductometric methods were used to determine cmc, whereas for the nonionic pair, the spectrophotometric method replaced conductometry. It is shown from Table 1 that the cmc values of different mixed surfactant combinations fall within the cmc ranges of pure ones, and for ionic/nonionic mixtures, cmc values shift toward the nonionic side. It is observed that the cmc values of various binary compositions increase with increasing mole fraction of LDS (α_{LDS}) for the mixtures of LDS/TX-100 and LDS/Bj-35 and mole fraction of TX-100 ($\alpha_{\mathrm{TX\text{-}100}}$) for TX-100/Bj-35 mixtures. The tensiometric cmc values are higher than the corresponding conductometric method in ionic/nonionic mixtures, but in most of the nonionic/nonionic combinations, spectrophotometric cmc values are larger than that of the tensiometric method. From Table 1, it is shown that the theoretical cmcs for TX-100/Bj-35 are lower than the experimental values, whereas the reverse is true for other two combinations. In all binaries, the experimental cmc values deviate from Clint cmc (discussed in the "Theoretical section") indicating a nonideal behavior of solution mixture. The variation in cmc (experimental cmc, Clint cmc, and SPB

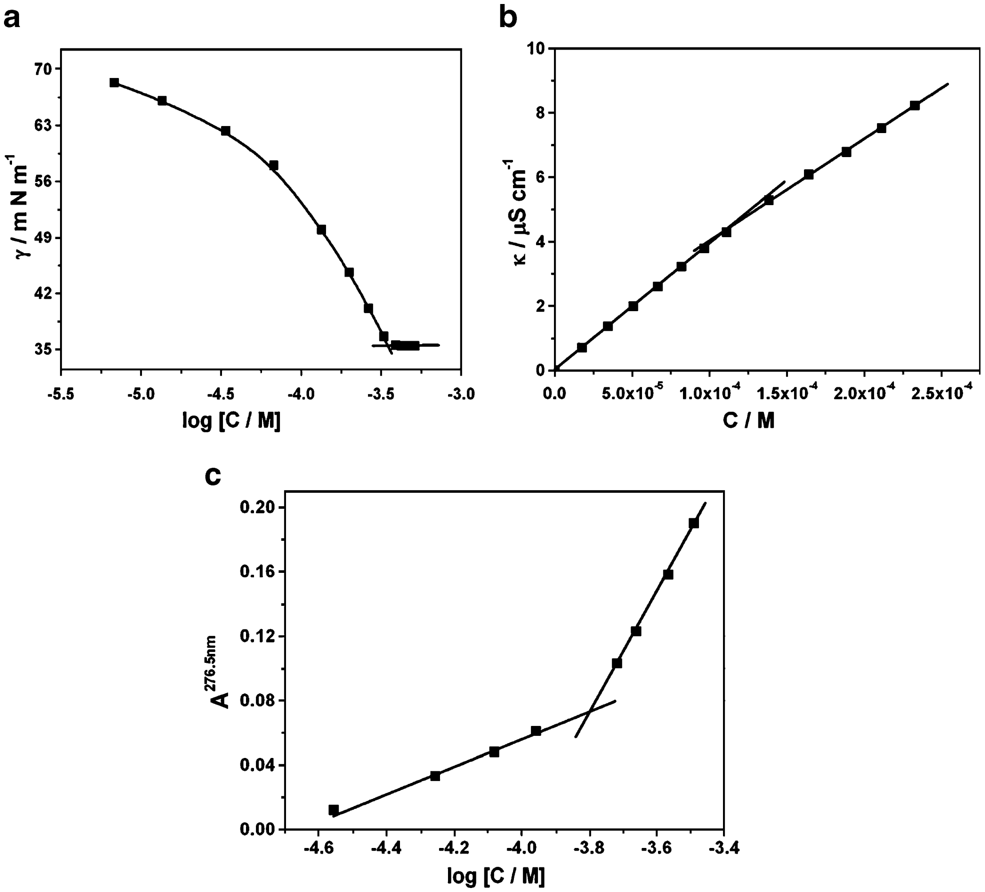

Fig. 1 Representative tensiometric (**a**), conductometric (**b**), and spectrophotometric (**c**) profiles for the dilution of concentrated surfactant mixtures in water

cmc [discussed in the "Theoretical section"]) with a composition in case of three binary mixtures are pictorially represented in Fig. 2. In this work, we obtain the same trend in cmc values of binary mixtures (anionic/nonionic and nonionic/nonionic) comparable to our earlier works [10–16]. In Table 2, the cmc values of the ternaries increase systematically with an increasing proportion of LDS in the mixture. This observation is comparable with our previous work [10, 14–16].

Adsorption at the air/water interface

Surfactants, due to their amphiphilic nature in the aqueous medium, adsorbs at the air/solution interface. This results in the lowering of cohesive force among water molecules at the interface, and thus the surface tension of water decreases on the progressive addition of the surfactant solution. This process continues up to complete saturation of the interface by the amphiphiles. Beyond this limit, surfactants get aggregated in bulk solution to form micelles without hampering the interface, showing no change in surface tension values on surfactant addition. The point of discontinuity in a γ vs. log C indicates the tensiometric cmc. The Gibbs surface excess ($\Gamma_{\max}$) [10–16] has been calculated from the least-square slope of the Π vs. log C plot (figure not shown to save space) using Eq. 1,

$$\Gamma_{\max} = \frac{1}{2.303nRT} \underset{C\to\mathrm{cmc}}{Lt} \frac{d\Pi}{d\log C} \qquad (1)$$

where Π is the surface pressure ($\gamma_{\mathrm{H_2O}} - \gamma_{\mathrm{surfactant}}$), R is the universal gas constant, T is the absolute temperature, and n is unity. Here, the contribution arising out of the counterion of the anionic surfactant, LDS, has been neglected. Its estimation from the knowledge of extent of counterion condensation at the micellar interface seems to be a crude approximation due to the large discrepancy in the radius of curvature, which significantly affects the counterion condensation between micellar and air/solution interfaces. C is the total molar amphiphile concentration in molarity scale. In this case, for a dilute solution, activity is replaced by concentration.

The area of exclusion ($A_{\min}$) per surfactant head group at complete air/solution interfacial saturation near the cmc region can be calculated using the relation [10–16],

$$A_{\min} = \frac{10^{18}}{N_A \Gamma_{\max}} \qquad (2)$$

where N_{A} is the Avogadro's number.

Table 1 Critical micellar concentration[a] (cmc) of pure, binary, and ternary mixtures of surfactants at 298.15 K

$\alpha_{\text{TX-100}}$ (I) or α_{LDS} (II)	Tensiometry	Conductometry	Spectrophotometry	Average cmc	cmc_c
TX-100/Bj-35 (10^4 cmc/mol dm^{-3}) (I)					
0.0	0.49	–	0.49		–
0.1	0.63	–	1.45		0.53
0.2	0.81	–	1.57		0.58
0.3	0.99	–	1.62		0.64
0.4	1.05	–	1.67		0.71
0.5	1.12	–	1.73		0.79
0.6	1.32	–	1.77		0.90
0. 7	1.51	–	1.82		1.05
0.8	1.62	–	1.86		1.26
0.9	1.79	–	1.96		1.57
1.0	2.07	–	2.07		–
LDS/TX-100 (10^4 cmc) (II)					
0.0	2.07	–	–	2.07	–
0.1	1.86	1.70	–	1.78	2.29
0.2	1.95	1.78	–	1.86	2.57
0.3	2.20	2.22	–	2.21	2.92
0.4	2.35	2.48	–	2.41	3.38
0.5	2.57	2.59	–	2.58	4.02
0.6	3.21	3.08	–	3.15	4.96
0.7	3.82	3.27	–	3.55	6.46
0.8	4.96	4.89	–	4.93	9.28
0.9	8.40	7.58	–	7.99	16.4
1.0	71.61	71.61	–	71.61	–
LDS/Bj-35 (10^4 cmc) (II)					
0.0	0.49	–	–	0.49	–
0.1	0.51	0.51	–	0.51	0.54
0.2	0.52	0.55	–	0.54	0.61
0.3	0.66	0.63	–	0.64	0.70
0.4	0.70	0.65	–	0.68	0.81
0.5	0.72	0.69	–	0.71	0.97
0.6	0.86	0.73	–	0.80	1.21
0.7	1.03	0.80	–	0.92	1.61
0.8	1.18	1.15	–	1.16	2.38
0.9	2.43	2.40	–	2.42	4.62
1.0	71.61	71.61	–	71.61	–

[a] The average error in cmc is ±3%.

Table 2 Critical micellar concentration[a] (cmc) of ternary mixtures of surfactants at 298.15 K

$\alpha_{\text{LDS}}/\alpha_{\text{TX-100}}\alpha_{\text{Bj-35}}$	Tensiometry	Conductometry	Spectrophotometry	Average cmc (Clint cmc)
	10^4 cmc/mol dm^{-3}			
0.125/0.250/0.625	0.99	1.00	1.11	1.00 (0.72)
0.125/0.625/0.250	1.16	0.96	1.46	1.06 (1.23)
0.250/0.125/0.625	0.98	0.98	1.20	0.98 (0.75)
0.250/0.625/0.125	1.59	1.34	1.52	1.46 (1.79)
0.333/0.333/0.333	1.24	0.97	1.60	1.10 1.19)
0.625/0.125/0.250	1.60	1.58	1.79	1.59 (1.73)
0.625/0.250/0.125	2.05	1.98	1.94	2.02 (2.61)

[a] The average error in cmc is ±3%.

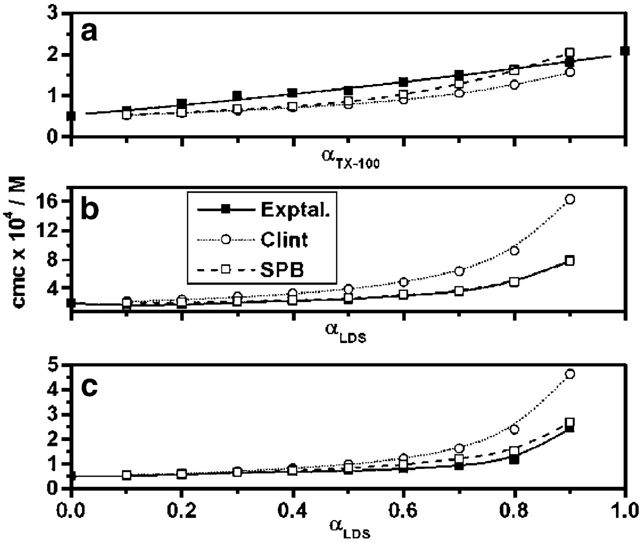

Fig. 2 Variation of cmc as a function of composition in mixed systems; **a** TX-100/Bj-35, **b** LDS/TX-100, and **c** LDS/Bj-35

$\Gamma_{\max}$ and $A_{\min}$ are expressed in mol m^{-2} and nm^2 molecule^{-1} units, respectively. The values of Π_{cmc} (surface pressure at cmc of the solution), $\Gamma_{\max}$, and $A_{\min}$ of binary and ternary mixtures are reported in Tables 3 and 4, respectively. It is observed from Table 3 that Π_{cmc} and $\Gamma_{\max}$ values decrease with an increasing mole fraction of LDS in ionic/nonionic mixed systems, indicating gradual lowering of surface activity of those binaries, whereas in case of nonionic/nonionic binary combinations, the surface activity increases with increasing stoichiometric mole fraction of TX-100. The same trend is also followed in case of ternary mixtures (Table 4); that is, in mixtures, the greater the mole fraction of TX-100, the greater is the surface activity of the mixtures. Due to the repulsion between the same charges in LDS molecules, they have larger $A_{\min}$ values (Table 3). In Table 3, the trend in $A_{\min}$ values of binaries is just the reverse to that of $\Gamma_{\max}$ as expected from the reciprocal interdependence.

The more surface active an amphiphile is, it is more efficient in lowering the surface tension of water and smaller is the amount of surfactant required to lower the surface tension of the solvent by a given amount. If C_{20} is the concentration of a given surfactant to lower the surface tension of the medium by 20 mN m^{-1}, pC_{20} ($=-\log C_{20}$) therefore is a measure of propensity of the amphiphile toward interfacial adsorption. The ease of a particular component toward micellization compared to interfacial adsorption is, therefore, given qualitatively by cmc/C_{20}. Table 3 shows that among pure surfactants, the surface activity by pC_{20} values is in the order of LDS<TX-100<Bj-35. It may be due to the greater degree of solvation at the LDS head group aided by an ion–dipole interaction compared to a dipole-induced dipole interaction for the nonionics. Since the former force is more efficient than the later, LDS has a greater tendency to stay in the bulk phase compared to TX-100 and Bj-35 and hence exhibits lower surface activity than the nonionics. Among the nonionics, greater numbers of polyoxyethylene linkages in Bj-35 facilitate its bulk solubilization, whereas the comparatively smaller chain in TX-100 increases its solubility in the bulk solution. Under these competing situations, it is the smaller hydrophobicity of the surfactant chain that plays the decisive role over the former situation. For all the binary mixtures, pC_{20} values decrease significantly with an increasing stoichiometric mole fraction of TX-100 (TX-100/Bj-35) and of LDS (LDS/TX-100 and LDS/Bj-35) indicating more and more surface adsorption. On the other hand, the cmc/C_{20} value for ionic/nonionic mixtures increases up to $\alpha_{\mathrm{LDS}}=0.5$ and then decreases, suggesting that for extreme compositions of LDS, interfacial adsorption is preferred, but for moderate compositions, micellization prevails over Langmuirian adsorption. However, for TX-100/Bj-35 mixtures, no such regularity is observed.

Energetics of micellization and interfacial adsorption

The standard free energy of micellization per mole of monomer unit (ΔG^0_{m}) for the nonionic binary mixture (TX-100/Bj-35) is calculated by using,

$$\Delta G^0_{\mathrm{m}} = RT\ \ln(\mathrm{cmc}) \tag{3}$$

For binary ionic/nonionic mixtures (LDS/TX-100 and LDS/Bj-35) as well as ternary combinations (LDS/TX-100/Bj-35), Eq. 3 is modified as,

$$\Delta G^0_{\mathrm{m}} = (1+g)RT\ \ln(\mathrm{cmc}) \tag{4}$$

where g is the fraction of counterions bound to the micelle obtained conductometrically and accounts for the free energy contribution arising out of counterions condensation onto the micellar interface. The ratio of slopes of post- and premicellar regions of specific conductance (κ) vs. the concentration of surfactant (C) plot gives the value of fraction of counterion dissociation (f). The degree of counterion condensation is, therefore, $g=1-f$. Although other methods of evaluation of g are available, the simplest method is often used in literature. This is a very simple method to determine g and is used in limited mixed micellar systems.

The standard free energy of interfacial adsorption (ΔG^0_{ad}) at the air/water interface is obtained from the relation [10–16],

$$\Delta G^0_{\mathrm{ad}} = \Delta G^0_{\mathrm{m}} - (\Pi_{\mathrm{cmc}}/\Gamma_{\max}) \tag{5}$$

where Π_{cmc} is the surface pressure at *cmc*.

Table 3 Interfacial parameters and counter ion binding of pure and binary surfactant combinations at 298.15 K

$\alpha_{\text{TX-100}}$ (I) or α_{LDS} (II)	$10^3\ \Pi_{\text{cmc}}$/J m^{-2}	$10^6 \Gamma_{\text{max}}$/mol m^{-2}	A_{min}/nm^2 molecule^{-1}	g	$-\Delta G^0_{\text{m}}$/kJ mol^{-1}	$-\Delta G^0_{\text{ad}}$/kJ mol^{-1}	pC_{20}	cmc/ C_{20}
TX-100/Bj-35 (I)								
0.0	29.2	2.15	0.77		34.56	48.14	5.04	5.43
0.1	30.9	1.79	0.93		33.93	51.22	5.20	16.48
0.2	32.0	1.99	0.84		33.31	49.43	5.14	16.43
0.3	33.0	2.05	0.81		32.81	48.91	5.10	15.23
0.4	34.1	2.06	0.81		32.67	49.24	5.08	15.03
0.5	34.9	2.18	0.76		32.51	48.49	5.02	14.56
0.6	36.2	2.28	0.73		32.10	48.01	5.03	15.64
0.7	37.1	2.47	0.67		31.77	46.81	4.98	16.43
0.8	37.6	2.47	0.67		31.59	46.81	4.96	15.41
0.9	38.6	2.70	0.61		31.35	45.62	4.87	13.57
1.0	39.5	2.95	0.59		30.98	44.37	4.84	14.26
LDS/TX-100 (II)								
0.0	39.5	2.95	0.56	–	30.98	44.37	4.84	14.26
0.1	38.8	8.39	0.20	0.08	33.87	38.49	4.11	2.30
0.2	38.6	7.27	0.23	0.11	34.52	39.83	4.15	2.81
0.3	38.1	6.69	0.25	0.15	35.45	41.14	4.12	2.95
0.4	37.5	6.33	0.26	0.20	36.96	42.89	4.14	3.10
0.5	37.0	6.00	0.28	0.23	37.44	43.60	4.14	3.54
0.6	37.0	5.58	0.30	0.25	37.43	44.06	4.03	3.38
0.7	36.8	5.42	0.31	0.26	37.36	44.14	3.95	3.19
0.8	36.2	5.32	0.31	0.27	36.62	43.43	3.80	3.08
0.9	35.8	5.08	0.33	0.28	35.38	42.42	3.58	3.04
1.0	28.0	3.22	0.52	0.33	29.53	38.21	2.69	4.42
LDS/Bj-35 (II)								
0.0	29.2	2.15	0.77	–	37.56	48.14	5.04	5.43
0.1	29.2	6.27	0.26	0.09	38.54	42.22	4.55	1.79
0.2	28.9	6.16	0.27	0.12	37.16	43.23	4.57	1.91
0.3	30.0	6.01	0.28	0.10	37.88	42.15	4.41	1.71
0.4	28.3	5.88	0.28	0.12	38.01	42.69	4.41	1.71
0.5	28.0	5.68	0.29	0.13	38.14	42.94	4.42	1.85
0.6	28.3	5.43	0.31	0.15	38.06	43.35	4.30	1.74
0.7	28.3	5.25	0.32	0.16	39.09	43.45	4.16	1.45
0.8	27.4	5.09	0.33	0.20	37.32	44.47	4.17	1.61
0.9	27.6	4.98	0.33	0.22	37.56	42.86	3.87	1.81
1.0	28.0	3.22	0.52	0.33	29.53	38.21	2.69	4.42

Table 4 Interfacial and thermodynamic[a] parameters of ternary combinations of LDS, TX-100, and Bj-35 at 298.15 K

$\alpha_{\text{LDS}}/\alpha_{\text{TX-100}}\alpha_{\text{Brij-35}}$	$10^3\ \Pi_{\text{cmc}}$/ J m^{-2}	$10^6\ \Gamma_{\text{max}}$/mol m^{-2}	A_{min}/nm^2 molecule^{-1}	g	$-\Delta G^0_{\text{m}}$/kJ mol^{-1}	$-\Delta G^0_{\text{ad}}$/kJ mol^{-1}	pC_{20}	cmc/ C_{20}
0.125/0.250/0.625	32.90	2.24	0.74	0.15	37.72	52.42	5.00	10.28
0.125/0.625/0.250	36.10	2.72	0.61	0.20	39.17	52.46	4.96	10.85
0.250/0.125/0.625	32.30	1.96	0.85	0.06	34.81	51.32	5.10	13.25
0.250/0.625/0.125	37.15	2.62	0.63	0.13	35.98	50.16	4.92	12.45
0.333/0.333/0.333	33.90	2.31	0.72	0.10	35.80	50.47	4.94	11.14
0.625/0.125/0.250	32.10	2.19	0.76	0.12	35.44	50.08	4.76	9.57
0.625/0.250/0.125	34.20	2.40	0.69	0.13	35.09	49.34	4.71	10.14

[a] The average errors in each of ΔG^0_{m}, and ΔG^0_{ad} are ±3%.

The values of Π_{cmc}, g, ΔG^0_{m}, and ΔG^0_{ad} for binary and ternary mixtures are presented in Tables 3 and 4, respectively. The g values for the binary mixtures of LDS with TX-100 and Bj-35 are low and increase with α_{LDS} due to the increase in the surface charge density of the mixed micelles in the presence of a higher proportion of the ionic amphiphile. For ternary mixtures, g values are low and independent of micellar composition. Figure 3 represents ΔG^0_{m} values for the TX-100/Bj-35 system, which increase (in magnitude) regularly with increasing $\alpha_{\text{TX-100}}$, indicating more spontaneous micellization. The values of ΔG^0_{m} for the LDS/TX-100 combination decrease up to $\alpha_{\mathrm{LDS}}=0.5$ and then increase, but free energy values for LDS/Bj-35 do not follow any regular trend. This parallelism in relative magnitudes of ΔG^0_{m} and ΔG^0_{ad} with the cmc/C_{20} ratio supported our earlier proposition regarding the physical significance of cmc/C_{20}. For ternaries, ΔG^0_{m} values are found to be composition dependent (Table 4) and higher for $\alpha_{\mathrm{LDS}}=0.125$ but lower for $\alpha_{\mathrm{LDS}}=0.625$. The variation in ΔG^0_{ad} with a mole fraction of surfactant of 1 (α_1) is represented in Fig. 4, which shows that for both TX-100/Bj-35 and LDS/Bj-35 mixtures, ΔG^0_{ad} values are virtually invariant to α_1. The values of ΔG^0_{ad} of the former mixture are comparatively higher in magnitude than the latter mixture. ΔG^0_{ad} of the LDS/TX-100 system increases thoroughly up to $\alpha_{\mathrm{LDS}}=0.7$ and then decreases. The values of ΔG^0_{ad} of ternary systems are comparatively higher than those of binary systems where third combination in Table 4 shows the maximum in magnitude.

In the following "Theoretical section," we considered experimental cmc of mixed systems averaged over conductometric and tensiometric values; the spectrophotometric values are not considered due to a large divergence over the entire proportion regime.

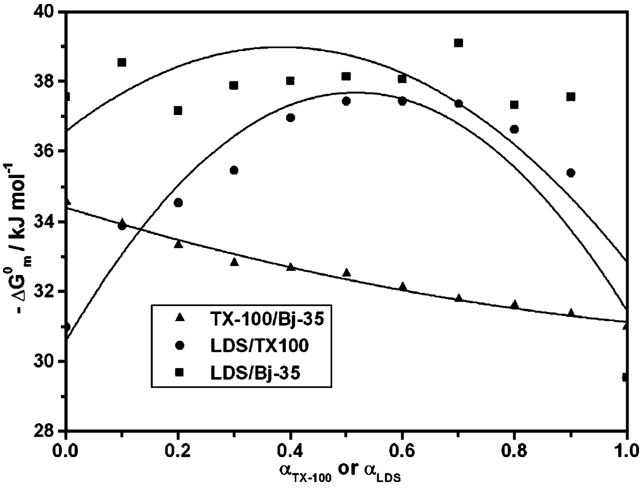

Fig. 3 Variation of ΔG^0_{m} as a function of composition in mixed system

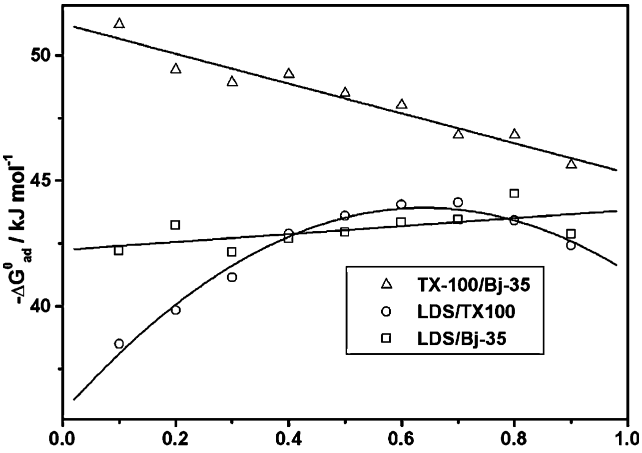

Fig. 4 Variation of ΔG^0_{ad} as a function of composition in mixed system

Theoretical section

Clint model This [17, 18] is a tool for predicting cmc of mixed surfactant systems (cmc$_{\mathrm{c}}$) with a known proportion from a knowledge of individual cmcs of the components. The involved equation is,

$$(1/\mathrm{cmc}^{\mathrm{c}}) = \sum_{i=1}^{n} (\alpha_i/\mathrm{cmc}_i) \qquad (6)$$

In this equation, α_i denotes the stoichiometric mole fraction ith component in the solution, respectively. The terms cmc$_i$ and cmc$_{\mathrm{c}}$ are the cmcs of the ith component and the mixture, respectively. Any negative deviation in experimental cmc from that of cmc$_{\mathrm{c}}$ reflects an overall synergistic (attractive) interaction, whereas overall antagonistic (repulsive) interaction is inferred from a negative deviation.

Table 1 reflects synergistic behavior in the TX-100/Bj-35 system up to $\alpha_{\text{TX-100}}=0.6$ and an antagonistic behavior thereafter. For the ionic/nonionic systems, however, synergism is evident over the entire range of composition, which may arise out of the interaction between the dodecyl sulfate ion with the ether oxygen atoms of the nonionic surfactants (TX-100 and Bj-35) through the counterion Li$^+$ of the anionic surfactant as proposed by Matsubara et al. [28].

Rosen model This model [9] focuses on the adsorbed Langmuirian mixed surfactant film at the air/solution interface and is basically an optimization algorithm. A closer resemblance with the experimental area of exclusion (A_{min}) is obtained from the A_{min} values of the respective pure components using computational iteration, which leads to the mole fraction of the component (X^{σ}_1) and an interaction parameter at the interface among the components (β^σ) as the optimization parameters. The two equations involved in the iteration procedure are,

$$\frac{(X^\sigma)^2\ln\left[\mathrm{cmc}_{\mathrm{mix}}\alpha_1/C_1^0X^\sigma\right]}{(1-X^\sigma)^2\ln\left[\mathrm{cmc}_{\mathrm{mix}}(1-\alpha_1)/C_2^0(1-X^\sigma)\right]} = 1 \qquad (7)$$

and

$$\beta^\sigma = \left(\left(\ln\left[\mathrm{cmc}_{\mathrm{mix}}\alpha_1/C_1^0X^\sigma\right]\right)\Big/\left((1-X^\sigma)^2\right)\right) \qquad (8)$$

where $\mathrm{cmc}_{\mathrm{mix}}$, C_1^0, and C_2^0 are the molar concentrations of the mixture and pure surfactants 1 and 2, respectively, at a fixed γ value corresponding to tensiometric cmc of pure component 1 and α_1 is the stoichiometric mole fraction of surfactant 1 in the solution.

The β^σ and X_1^σ values of the binary mixtures are presented in Table 5. The negative β^σ values for the ionic/nonionic combinations indicate a synergistic interaction. In TX-100/Bj-35 mixtures, Table 5 shows that the mole fraction of TX-100 in the mixed interfacially adsorbed monolayer is always greater than the corresponding stoichiometric proportion reflecting a greater tendency of TX-100 to be adsorbed at the air/solution interface as compared to Bj-35, and the interaction parameter suggests antagonism among the surfactant monomers in the adsorbed film and the extent of antagonism increases with an increasing stoichiometric proportion of TX-100 in the mixture. In LDS/TX-100 and LDS/Bj-35 mixtures, a smaller proportion of LDS in the mixed adsorbed film compared to its analytical bulk proportion suggests that LDS is relatively reluctant toward interfacial adsorption, which is probably due to the greater degree of solvation of the head group of ionic surfactants through an ion–dipole interaction compared to a dipole-induced dipole interaction of water dipoles with polarizable ether head groups of nonionic surfactants under use. The interaction parameter in either case evidenced synergism, which may arise from the ion–dipole interaction between the head groups of an ionic/nonionic surfactant pair, or as a result of dispersion

Table 5 Molecular interaction parameters of binary mixtures in aqueous medium and 298.15 K

$\alpha_{\text{TX-100}}$ or α_{LDS} (II)	Rosen model		Rubingh model			Motomura model		Georgiev model
	X_1^σ	β^σ	X_R	β^R	f_1/f_2	X_M	f_1	X_G
TX-100/Bj-35 (I)								
0.1	0.32	0.78	–	–	0.11/0.90	0.01	0.46	0.08
0.2	0.34	0.93	–	–	0.31/0.96	0.07	0.49	0.12
0.3	0.30	2.35	–	–	0.64/0.99	0.12	0.46	0.17
0.4	0.29	3.26	–	–	7.30/1.00	0.21	0.46	0.24
0.5	0.63	3.33	–	–	2.43/1.01	0.32	0.50	0.32
0.6	0.72	5.35	–	–	2.69/1.02	0.44	0.50	0.41
0.7	0.78	10.53	0.09	2.08	5.05/1.02	0.58	0.59	0.54
0.8	0.88	18.90	0.47	1.01	1.31/1.22	0.71	0.56	0.69
0.9	0.95	26.33	0.75	0.65	1.06/2.21	0.85	0.59	0.86
LDS/TX-100 (II)								
0.1	0.05	−3.62	0.14	−5.44	0.02/0.90	0.17	1.08	0.21
0.2	0.15	−5.30	0.15	−4.58	0.04/0.90	0.24	1.01	0.36
0.3	0.14	−4.36	0.16	−4.12	0.05/0.90	0.25	1.02	0.43
0.4	0.20	−5.27	0.21	−4.53	0.06/0.82	0.16	0.77	0.59
0.5	0.23	−5.46	0.23	−4.23	0.08/0.80	0.10	0.69	0.49
0.6	0.20	−3.91	0.24	−3.83	0.11/0.80	0.01	0.61	0.49
0.7	0.24	−4.00	0.28	−4.10	0.12/0.73	0.17	0.62	0.52
0.8	0.25	−3.13	0.31	−3.70	0.17/0.70	0.43	0.84	0.54
0.9	0.31	−2.83	0.38	−3.39	0.27/0.61	0.80	1.90	0.64
LDS/Bj-35 (II)								
0.1	0.14	−7.03	0.05	−4.76	0.01/0.99	0.27	1.29	0.26
0.2	0.20	−7.68	0.09	−4.84	0.02/0.96	0.31	1.23	0.30
0.3	0.11	−4.35	0.07	−3.75	0.04/0.98	0.06	1.02	0.39
0.4	0.17	−5.35	0.12	−4.38	0.03/0.94	0.02	0.83	0.43
0.5	0.18	−4.76	0.17	−5.06	0.03/0.86	0.11	0.81	0.46
0.6	0.20	−4.85	0.20	−5.26	0.03/0.81	0.32	1.03	0.47
0.7	0.19	−3.74	0.24	−5.57	0.04/0.73	0.51	1.23	0.50
0.8	0.29	−5.58	0.27	−5.76	0.05/0.66	0.68	1.41	0.52
0.9	0.32	−4.59	0.29	−4.43	0.11/0.69	0.90	1.01	0.57

interaction between the hydrophobic tail or through the participation of the Li^+ in coordination, which acts as a bridge between the two kinds of surfactants.

Rubingh model This is another iterative algorithm [20] similar to the Rosen model, but the focus is in the micellar phase formed in the bulk solution. The micellar mole fraction (X_R) of a surfactant in the mixed aggregated state and the molecular interaction parameter (β^R) can be calculated solving the coupled equations,

$$\frac{(X_R)^2 \ln[\mathrm{cmc_{mix}}\,\alpha_1/\mathrm{cmc_1}X_R]}{(1-X_R)^2 \ln[\mathrm{cmc_{mix}}(1-\alpha_1)/\mathrm{cmc_2}(1-X_R)]} = 1 \tag{9}$$

and

$$\beta^R = \left((\ln[\mathrm{cmc_{mix}}\,\alpha_1/\mathrm{cmc_1}X_R])\Big/(1-X_R)^2\right) \tag{10}$$

where $\mathrm{cmc_1}$, $\mathrm{cmc_2}$, and $\mathrm{cmc_{mix}}$ are the cmcs of surfactants 1 and 2 in their pure state and their mixture under the same physicochemical conditions, respectively, at a stoichiometric mole fraction α_1.

The activity coefficients of surfactants 1 and 2 in the mixed micelle (f_1 and f_2) can be evaluated from the equations,

$$f_1 = \exp\left[\beta^R(1-X_R)^2\right] \tag{11}$$

and

$$f_2 = \exp\left[\beta^R(X_R)^2\right] \tag{12}$$

The values of X_R, β_R, f_1, and f_2 for the binary mixtures are tabulated in Table 5. For TX-100/Bj-35 mixtures, the Rubingh model is insolvable up to $\alpha_{\text{TX-100}}$=0.6 due to the divergence in series. For compositions with $\alpha_{\text{TX-100}}$>0.6, the relative proportion of TX-100 in the micellar phase is lower compared to its stoichiometric proportion, and the interaction parameter reflects an antagonistic behavior with the extent of antagonism increasing with increasing $\alpha_{\text{TX-100}}$. The antagonism predicted by the Clint model is therefore also reflected in the Rubingh model.

For ionic/nonionic combinations, the population of LDS in the micellar phase is less compared to its stoichiometric proportion with the exception of α_{LDS}=0.1 for the LDS/TX-100 system. The lower cmc of the nonionics as compared to LDS reflects relatively lower affinity of LDS toward self-aggregation in comparison to the nonionics, which is reflected in the above computation. The interaction parameter over the entire composition regime is negative, implying a synergistic behavior as also obtained from the Clint model.

Motomura model This model [21, 22] considered mixed micelles as a macroscopic bulk phase from a thermodynamic point of view. In this model, excess thermodynamic quantities are used to evaluate various energetic parameters. The fundamental equation is,

$$X_{\text{Mo}} = \widehat{X_2} - \left(\widehat{X_1 X_2}\Big/\widehat{\mathrm{cmc}}\right)\left(\partial\widehat{\mathrm{cmc}}\Big/\partial\widehat{X_2}\right)_{\mathrm{T,P}} \tag{13}$$

where $\widehat{X_2} = \nu_2\alpha_2/(\nu_1\alpha_1 + \nu_2\alpha_2)$ and $\widehat{\mathrm{cmc}} = (\nu_1\alpha_1 + \nu_2\alpha_2)\mathrm{cmc}$. Subscripts 1 and 2 denote surfactants 1 and 2, respectively, and α and ν represent the stoichiometric mole fraction and the number of dissociated ions by a surfactant in solution. The micellar mole fractions (X_{Mo}) of a surfactant in the binary mixtures evaluated by the Motomura equation are shown in Table 5.

The mean activity coefficient of surfactant 1 in the micelle (f_1) according to this model [29] is presented by the equation,

$$\widehat{X_1}\widehat{\mathrm{cmc}}\Big/\mathrm{cmc}_1^0 = f_1 X_{1(\text{Mo})} \tag{14}$$

and the f_1 values of all binary mixtures are shown in Table 5. For the TX-100/Bj-35 system, the mole fraction of TX-100 found to be less than its stoichiometric proportion signifying the greater propensity of Bj-35 toward micelle formation compared to TX-100 as expected from a lower cmc of Bj-35 compared to TX-100. For the LDS/TX-100 system, LDS prefers the micellar phase in a lower stiochiometric proportion (α_{LDS}=0.1 and 0.2), and thereafter, TX-100 dominates the micellar phase over LDS when the stoichiometry and micellar mole fraction are considered. Moreover, there exists a minima at α_{LDS}=0.6 in the X_{Mo} vs. α_{LDS} profile. For the LDS/Bj-35 system, again the micellar proportion of LDS overweighs its stoichiometric proportion for α_{LDS}=0.1 and 0.2, and thereafterm it is Bj-35 that wins the competition toward micellization forming minima in the X_{Mo} vs. α_{LDS} profile at α_{LDS}=0.4. A strong deviation in f_{Mo} from unity for ionic/nonionic mixtures represents the participation of counterion in micellar phase [29].

Georgiev model On the basis of Markov's chain model for the polymerization process of mixed micelles [23], this theory relates the micellar composition (X_G) with α_1 and other two parameters, G_1 and G_2, as follows,

$$\left(X_1^G/X_2^G\right) = (\alpha_1/\alpha_2)\,[(G_1\alpha_1 + \alpha_2)/(G_2\alpha_2 + \alpha_1)] \tag{15}$$

where G_i represents the ratio between the equilibrium constants for the formation of micelles constructed by the same type of surfactants (K_{ii}) and different types of surfactants (K_{ij}). For the binary mixtures, X_G values are presented in Table 5.

For all the binary mixtures, X_G increases with increasing α_1 except α_{LDS}=0.4 of the LDS/TX-100 system. For nonionic/nonionic mixed micelles, X_G values are much lower compared to α_1, whereas those for ionic/nonionic systems are greater at a lower mole fraction and smaller at a higher mole fraction of LDS.

Maeda model This model is based on the short-range electrostatic interaction in the ionic/nonionic mixed micellar system. The concept of this model is that the presence of nonionic species in the micellar phase can reduce the head group repulsion in the ionic/nonionic mixed micelle. The standard free energy change due to the micellization process as a polynomial function of the mole fraction of component 2 in the micellar phase is,

$$\Delta G^0_{\mathrm{Ma}} = RT\left(B_0 + B_1\alpha_2 + B_2\alpha_2^2\right) \tag{16}$$

where

$$B_0 = \ln X_{C_1} \tag{17}$$

X_{C1} is the cmc of surfactant 1 in the mole fraction unit. If component 1 self-assembles, the micellar free energy change is expressed as a dimensionless quantity, B_0 (=$\ln X_{C1}$=$\Delta G^0_{\mathrm{m}}/RT$). The parameter B_1 is related to the standard free energy change associated with the introduction of one ionic species into a nonionic micelle coupled with the release of one nonionic species from the micelle; that is, B_1 plays an essential role for a change of cmc values of nonionic micelles when an ionic species enters the micelle [24]. B_2 is the interaction parameter in the micellar phase. R and T denote the universal gas constant and absolute temperature, respectively. Again,

$$B_1 + B_2 = \ln\left(X_{C_2}/X_{C_2}\right) \tag{18}$$

($X_{C_2}$is the cmc of surfactant 2 in mole fraction unit),

$$B_2 = -\beta_{\mathrm{R}} \tag{19}$$

(β_{R} being the interaction parameter in the micellar phase obtained from Eq. 10).

The values of ΔG^0_{Ma}, B_0, B_1, and B_2 are presented in Table 6. B_0 is constant for a binary mixture. B_1 and B_2 values do not follow any pattern with respect to α_{ionics}. ΔG^0_{Ma} values decrease regularly with increasing α_{LDS} in both binary mixtures, and they deviate more than the free energy (ΔG^0_{M}) values obtained from the Gibbs Helmohltz equation, reflecting the importance of counterion binding to the ionic/nonionic mixed micelles.

Very recently, Maeda used the Gibbs Duhem relation considered by Hall to predict another theoretical model [25] of excess free energy (g^{ex}) of the ionic/nonionic mixed micelle. The useful relations are,

$$g^{\mathrm{ex}} = X_{\mathrm{Ma}} \ln f_1 + (1 - X_{\mathrm{Ma}}) \ln f_2 \tag{20}$$

where X_{Ma} is the micellar mole fraction according to this model and f_1 and f_2 hold the same rationale as before. X_{Ma}

Table 6 Free energy and interaction parameters of ionic/nonionic binary mixtures obtained from Maeda models in aqueous medium and 298.15 K

α_{LDS}	Maeda model [24]				Maeda model [25]				
	$-B_0$	B_1	$-B_2$	$-\Delta G^0_{\mathrm{Ma}}$	X_{Ma}	f_1	f_2	$-g^{\mathrm{ex}}$	β^{Ma}
LDS/TX-100									
0.1	12.50	9.21	5.44	28.84	0.11	0.02	0.86	0.55	−5.82
0.2		8.35	4.58	27.30	0.14	0.03	0.83	0.64	−5.39
0.3		7.89	4.12	26.03	0.13	0.06	0.86	0.50	−4.48
0.4		8.30	4.53	24.55	0.10	0.11	0.78	0.45	−5.02
0.5		8.00	4.23	23.69	0.08	0.18	0.68	0.50	−6.74
0.6		7.60	3.83	23.10	0.09	0.24	0.67	0.50	−6.11
0.7		7.87	4.10	22.31	0.17	0.17	0.62	0.70	−5.04
0.8		7.47	3.70	22.04	0.33	0.13	0.71	0.89	−4.04
0.9		7.16	3.39	21.82	0.59	0.13	0.95	1.21	−5.03
LDS/Bj-35									
0.1	13.94	9.97	4.76	32.20	0.15	0.004	1.10	0.73	−5.87
0.2		10.05	4.84	30.05	0.20	0.006	1.10	0.94	−5.90
0.3		8.96	3.75	28.73	0.19	0.011	1.13	0.77	−4.94
0.4		9.59	4.38	26.78	0.15	0.020	0.98	0.61	−4.74
0.5		10.27	5.06	24.96	0.11	0.036	0.81	0.55	−5.60
0.6		10.47	5.26	23.68	0.11	0.050	0.73	0.60	−6.29
0.7		10.78	5.57	22.61	0.16	0.045	0.67	0.83	−6.21
0.8		10.97	5.76	21.94	0.30	0.034	0.68	1.30	−6.13
0.9		9.64	4.43	21.94	0.57	0.042	1.16	1.75	−7.17

ΔG^0_{Ma}in kJ mol^{-1} unit can be calculated by plotting ln(cmc) vs. α_1 using the relation,

$$X_{\mathrm{Ma}} = \frac{\alpha_1\left[1-(1-\alpha_1)\left(\partial(\ln \mathrm{cmc})/\partial\alpha_1\right)\right]}{\left[1+\nu(1-\alpha_1)\left\{\alpha_1\left(\partial(\ln \mathrm{cmc})/\partial\alpha_1\right)+1\right\}\right]} \tag{21}$$

The degree of counter ion binding (ν) is negligible in our case in the aqueous medium, and the Equation becomes

$$X_{\mathrm{Ma},(\nu=0)} = \alpha_1\left[1-(1-\alpha_1)\left(\partial(\ln \mathrm{cmc}_{\mathrm{mix}})/\partial\alpha_1\right)\right] \tag{22}$$

The activities of the components 1 and 2 are given by,

$$a_1 = X_{\mathrm{Ma}}f_1 = \alpha_1\left(\mathrm{cmc}_{\mathrm{mix}}/C_1\right)$$

and

$$a_2 = (1-X_{\mathrm{Ma}})f_2 = (1-\alpha_1)\left(\mathrm{cmc}_{\mathrm{mix}}/C_2\right)$$

β^{Ma} can be calculated from,

$$\beta^{\mathrm{Ma}} = g^{\mathrm{ex}}/[X_{\mathrm{Ma}}(1-X_{\mathrm{Ma}})] \tag{23}$$

Table 6 shows the X_{Ma}, f_1, f_2, g^{ex}, and β^{Ma} values related to this theory. It is observed that X_{Ma} does not follow any trend with α_1 up to $\alpha_{\mathrm{LDS}}=0.6$ and then increases. The value of f_1 increases up to $\alpha_{\mathrm{LDS}}=0.6$ and then decreases, but f_2 follows the reverse trend. The value of g^{ex} initially decreases and then increases at a higher mole fraction of LDS. β^{Ma} is composition independent. A similar trend is observed in the case of thermodynamic parameters (g^{ex} and β^{Ma}). In all cases, X_{Ma} is much lower than α_1.

SPB model Another thermodynamic theory developed by Blankschtein (SPB) et al. [26, 27] also predicts quantitatively the cmc, micellar composition, shape, and phase behavior on the basis of hydrophobic, structural, and

Table 7 Micellar compositions (X_{SPB}), interaction parameter (β_{SPB} [kT]), activity coefficient (*f*), and cmcs of binary mixtures at 298.15 K at different stoichiometric compositions (X)

$\alpha_{\text{TX-100}}$ or α_{LDS} (II)	X_{SPB}	β_{SPB} (kT)	f_1	f_2	10^4 cmc/(mol dm^{-3}) observed/SPB/Clint
TX-100/Bj-35 (I)					
0.1	0.03	0.21	1.22	1.00	0.63/0.53/0.53
0.2	0.06	0.38	1.40	1.00	0.81/0.59/0.58
0.3	0.09	0.54	1.56	1.00	0.99/0.66/0.64
0.4	0.14	0.54	1.49	1.01	1.05/0.74/0.71
0.5	0.19	0.53	1.41	1.02	1.12/0.85/0.79
0.6	0.26	0.70	1.46	1.05	1.32/1.02/0.90
0.7	0.36	0.87	1.43	1.12	1.51/1.28/1.05
0.8	0.49	0.96	1.29	1.25	1.62/1.60/1.26
0.9	0.68	1.32	1.14	1.84	1.79/2.04/1.57
LDS/TX-100 (II)					
0.1	0.07	−3.99	0.03	1.00	1.78/2.09/2.29
0.2	0.11	−4.10	0.04	1.00	1.98/2.16/2.57
0.3	0.14	−4.02	0.05	1.00	2.21/2.32/2.92
0.4	0.17	−4.16	0.07	1.00	2.23/2.47/3.38
0.5	0.20	−4.12	0.08	1.00	2.58/2.76/4.02
0.6	0.23	−4.02	0.11	1.00	3.15/3.21/4.96
0.7	0.26	−4.13	0.15	1.00	3.55/3.76/6.46
0.8	0.30	−4.00	0.20	1.00	4.93/4.97/9.28
0.9	0.37	−3.85	0.37	1.00	7.99/7.82/16.4
LDS/Bj-35 (II)					
0.1	0.03	−4.03	0.02	1.00	0.51/0.53/0.54
0.2	0.05	−4.08	0.02	1.00	0.54/0.58/0.61
0.3	0.07	−3.93	0.03	1.00	0.64/0.64/0.70
0.4	0.09	−4.09	0.03	1.00	0.68/0.71/0.81
0.5	0.11	−4.18	0.04	1.00	0.71/0.82/0.97
0.6	0.13	−4.16	0.04	1.00	0.80/0.97/1.21
0.7	0.16	−4.28	0.06	1.00	0.92/1.19/1.61
0.8	0.20	−4.65	0.06	1.00	1.16/1.50/2.38
0.9	0.26	−4.25	0.13	1.00	2.42/2.67/4.62

electrical interactions between the binary components. Thus, the Clint equation is written in the form,

$$(1/\mathrm{cmc}_{\mathrm{mix}}) = (\alpha_1/f_1\mathrm{cmc}_1) + ((1-\alpha_1)/f_2\mathrm{cmc}_2) \quad (24)$$

where the term *f* is the activity coefficient of the surfactant in the mixed micelle and is expressed by the relations given below,

$$f_1 = \exp\left[\left\{\beta_{12}\left(1-\alpha^*\right)^2\right\}\Big/kT\right] \quad (25)$$

and

$$f_2 = \exp\left[\left\{\beta_{12}\left(\alpha^*\right)^2\right\}\Big/kT\right] \quad (26)$$

where β_{12} is the predicted interaction parameter between surfactants 1 and 2 and α^* is the optimal micellar composition (denoted by X_{SPB}, where the free energy of mixed micellization reaches its minimum value). The following equation,

$$\frac{\beta_{12}\left(1-2\alpha^*\right)}{kT} + \ln\left(\frac{\alpha^*}{1-\alpha^*}\right) = \ln\left(\frac{\alpha_1\,\mathrm{cmc}_2}{(1-\alpha_1)\,\mathrm{cmc}_1}\right) \quad (27)$$

is solved iteratively to obtain α^* and β_{12}, and by using these values, *f* can be calculated according to Eqs. 25 and 26. It is observed from Table 7 that X_{SPB} increases with increasing α_1 for all the binaries and the values are much lower than α_1. In most of the compositions of all mixtures, X_{SPB} is lower than X_{R}, X_{Mo} or X_{G}. In the LDS/TX-100 and LDS/Bj-35 combinations, $\beta_{\mathrm{SPB}}<\beta_{\mathrm{R}}$ (in most cases) and negative values of β_{SPB} indicate attractive interaction. In the case of TX-100/Bj-35 system, positive β_{SPB} value denotes repulsive interaction between the surfactants. The activity coefficients of surfactants in nonionic systems are unity while these values of LDS are very low compared to those of TX-100 and Bj-35 for other two combinations. In case of ionic–nonionic systems, the activity coefficients of nonionic surfactants are nearly unity for Rubingh, Maeda, and SPB methods. The cmc values of TX-100/Bj-35 mixtures obtained by the SPB method are lower than those obtained experimentally except $\alpha_{\mathrm{TX\text{-}100}}=0.9$ and higher than those obtained by the Clint method. Again, in case of ionic/nonionic combinations, the cmc values follow the reverse order (observed<SPB<Clint). There are more deviations of the cmc value found in case of LDS/TX-100 mixtures particularly at a higher mole fraction of LDS denoting the presence of nonideality for mutual interaction of amphiphiles in the micelle. This deviation of cmc is the limitation of the SPB theory.

Conclusions

The experimental cmc values of TX-100/Bj-35 mixtures are higher than those predicted from Clint's equation, while the reverse trend is observed in case of LDS/TX-100 and LDS/Bj-35 combinations indicating the presence of nonideality in the micelles. This is also true in case of ternary combinations. In this study, the mixed micelle is also interpreted theoretically. The mole fraction of a particular component in the micelle is generally lower than the stoichiometric mole fraction of that component indicating the low extent of transfer of that component (surfactant) from the solution into the micelle. The binary mixtures of the LDS/TX-100 and LDS/Bj-35 systems denote synergistic interaction due to the indirect interaction between dodecyl sulfate ions of LDS and ether oxygen atoms of TX-100 and Bj-35 through the Li^+ counterions.

The Clint model is an idealization that neglects the interaction among different surfactants in the aggregated state. The Rubingh model treats mixed micelle as a regular solution, which is questionable when the counterion condensation at the micellar interface is considered in the presence of ionic surfactants. The Motomura model considers the mixed micelle as a macroscopic phase, and the micellar mole fraction and activity coefficients are defined in terms of excess thermodynamic quantities defined in reference to the spherical dividing surface, which makes the excess number of water molecules outside the dividing surface equal to zero. With the advent of continuous modification and incorporation of newer physicochemistry, the theoretical hierarchy turned more realistic. The variation in the molecular interaction parameter in different theories either arises from oversimplification of some assumption necessary for the development of the theory or a continuous source of discrepancy arising out of different scaling in different theories.

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