Micellization and Related Behavior of Binary and Ternary Surfactant Mixtures in Aqueous Medium: Cetyl Pyridinium Chloride (CPC), Cetyl Trimethyl Ammonium Bromide (CTAB), and Polyoxyethylene (10) Cetyl Ether (Brij-56) Derived System

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Mixed micelles formed with cetyl pyridinium chloride (CPC), cetyl trimethylammonium bromide (CTAB), and polyoxyethylene (10) cetyl ether (Brij-56) mixed in different combinations in aqueous medium have been studied in detail by tensiometric, conductometric, calorimetric, spectrophotometric, and fluorimetric techniques. Different physicochemical properties such as critical micellar concentration (cmc), micellar dissociation, energetic parameters (free energy, enthalpy, and entropy) of micellization, interfacial adsorption, and micellar aggregation number have been determined. The results have been analyzed in terms of the equations of Clint, Motomura, Rosen, Rubingh, Blankschtein et al., and Rubingh and Holland for justification of the experimental cmc, determination of micellar composition parameters, quantification of interaction among the mixed micelle components, and estimation of their activity coefficients.

Introduction

Mixed micelles are often used in technical, pharmaceutical, and biological fields, since they work better than pure micelles.[1,2] They have importance in industrial preparation, pharmaceutical and medicinal formulation, enhanced oil recovery process, and so forth, by way of efficient solubilization, suspension, dispersion, and transportation influenced by temperature, pressure, pH, nature of solvent, additives, etc.[3] In an aqueous medium, surfactants in pure and mixed states self-assemble to form micelles. The threshold concentration of its formation called the critical micellar concentration (cmc) is an important criterion for understanding the fundamentals of the self-organizing process.

The mixtures of the surfactant types, nonionic/nonionic,[4–6] anionic/nonionic,[7–10] cationic/nonionic,[10–12] anionic/biosurfactant,[13] anionic/anionic,[14,15] cationic/cationic,[16,17] and cationic/anionic,[18,19] have been studied and the theories of Clint,[20] Motomura,[21] Rosen,[22,23] Rubingh,[24] and Blankschtein[25] have been used to analyze and compare the experimental results to understand the synergism and antagonism of the binary combinations. In addition to this, a theoretical approach of regular solution and molecular thermodynamic theory[25,26] (considering the contributions of the hydrophilic head and hydrophobic tail structures of the amphiphiles) has been applied on ternary mixtures of amphiphiles[27] to predict the cmc and other micellar parameters on the basis of solution composition.

In the past, we have investigated several mixed multicomponent systems, namely, (1) cetyl trimethylammonium bromide (CTAB), tetradecyl trimethylammonium bromide (TTAB), and dodecyl trimethylammonium bromide (DTAB),[28] (2) cetyl trimethylammonium bromide (CTAB), *tert*-octyl phenyl polyoxyethylene ether (Triton X-100), and polyoxyethylene sorbitan monooleate (Tween-80),[29] (3) sodium dodecyl sulfate (SDS), polyoxyethylene sorbitan monolaurate (Tween-20), and polyoxyethylene (23) lauryl ether (Brij-35),[30] and (4) cetyl pyridinium chloride (CPC), polyoxyethylene sorbitan monopalmitate (Tween-40), and polyoxyethylene (10) cetyl ether (Brij-56).[31] Their mixed micelle formation and related physicochemical properties and thermodynamics have been assessed in detail. Compared to binary surfactant systems, ternaries are less studied and quantification of results in terms of the mutual interaction of components and ideality/nonideality states has been only limitedly done. It has been observed that the proportion of the nonionic surfactant components and their activity coefficients in the ternary mixed micelles is higher than that of the ionic components. In the present study, we have used CPC, CTAB, and Brij-56 in binary and ternary mixtures in an aqueous medium and studied their micellization and related behaviors (counterion binding, aggregation number, interfacial adsorption and thermodynamics of the self-aggregation process, mutual interaction, and micellar composition) in detail. The theories of Rosen, Rubingh, Rubingh and Holland, and Blankschtein et al. have been used to understand the interaction among the components in the mixed micelles. Such a detailed study with dissimilar headgroups of surfactants in binary and ternary combinations has not been assessed in the light of the existing theories of mixed micelle formation. It has been observed that the CPC/CTAB system produced two cmc's like other cationic systems recently reported[16,17,28,32] which cannot be accommodated in the proposed theories on mixed micelle formation. The predictions about the micellar composition, interaction parameter, and cmc of the studied systems were theory dependent. The ternary micelles were found to be mainly composed of the nonionic species having activities close to unity.

Experimental Section

Materials. The cationic amphiphiles used cetyl pyridinium chloride (CPC) and cetyl trimethylammonium bromide (CTAB) were products of Sigma (U.S.A.), and the nonionic amphiphile

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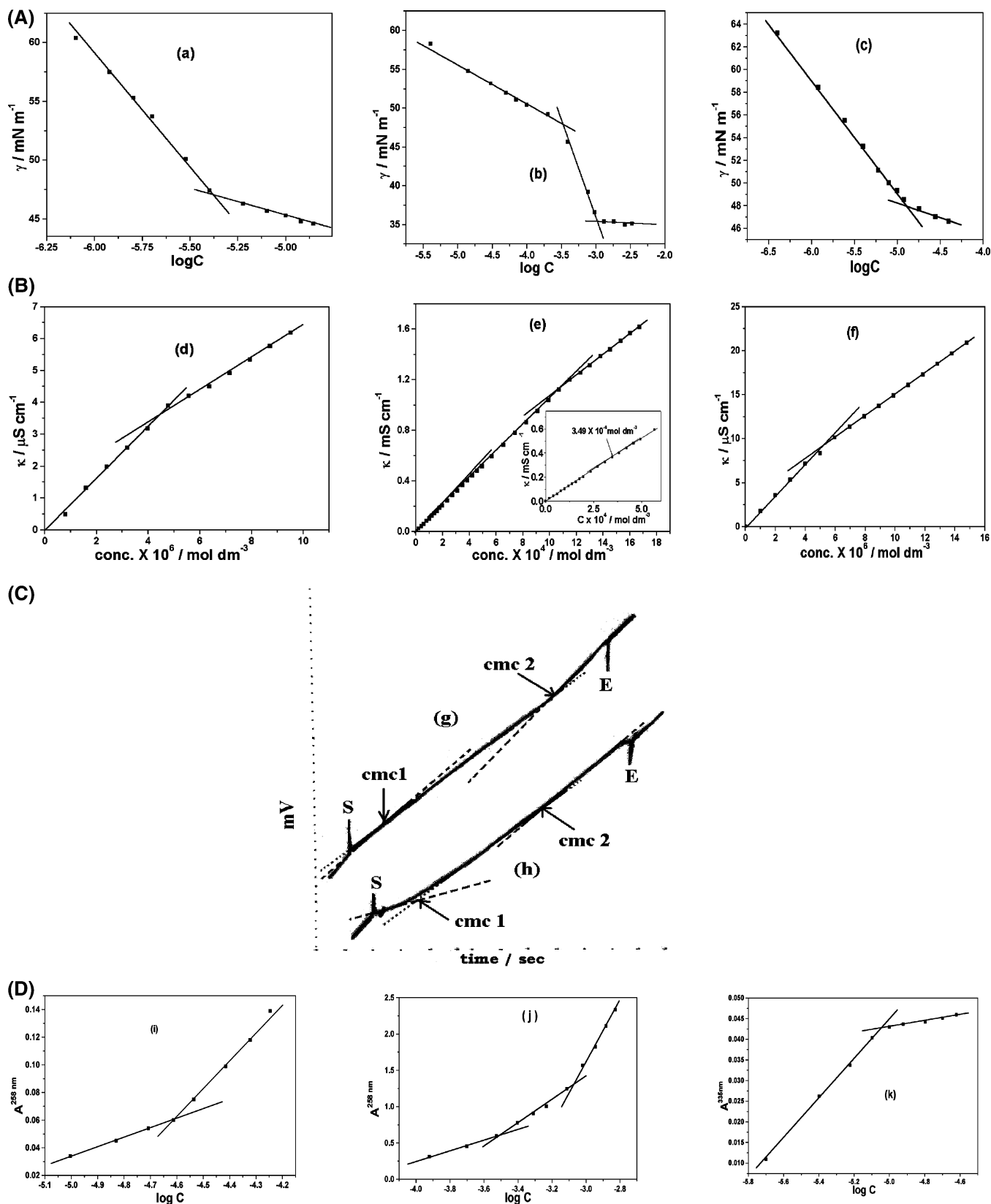
Figure 1. Determination of the cmc of binary and ternary combinations of CPC, CTAB, and Bj-56 at different mole ratios at 300 K. (A) Tensiometry: (a) [CPC]/[CTAB]/[Bj-56] = 1:2:5; (b) [CPC]/[CTAB] = 1:1; (c) [CTAB]/[Bj-56] = 5:1. (B) Conductometry: (d) [CPC]/[CTAB]/[Bj-56] = 2:1:5; (e) [CPC]/[CTAB] = 1:2 (inset shows the first cmc); (f) [CTAB]/[Bj-56] = 1:1. (C) Calorimetry: (g) [CPC]/[CTAB] = 1:1; (h) [CPC]/[CTAB] = 1:5. (D) Spectrophotometry: (i) [CPC]/[CTAB]/[Bj-56] = 5:2:1; (j) [CPC]/[CTAB] = 5:1; (k) [CTAB]/[Bj-56] = 2:1. Ordinate scales are denoted on the plots.

polyoxyethylene (10) cetyl ether (Brij-56 or Bj-56) was the same as the sample used previously.[31,33] They were used as received.

The dye pyrene (Sigma, U.S.A.) was crystallized twice from an ethanol/water mixture.

TABLE 1: Critical Micellar Concentration^a (cmc) of Pure, Binary, and Ternary Mixtures at 300 K

α_{CPC} (I) or α_{CTAB} (II)	ST	cond	calcd	spectro	average
		CPC/CTAB (10^4 cmc/mol dm^{-3}) (I)			
0.00	8.15	8.12	8.54		8.27
0.17	3.64, 11.35	3.70, 11.21	3.91, 12.48	3.43, 9.08	3.67, 11.03 (8.40)
0.33	3.46, 11.12	3.49, 10.90	3.67, 12.05	3.40, 8.91	3.51, 10.74 (8.40)
0.50	3.33, 10.54	3.30, 10.80	3.43, 11.60	3.36, 8.83	3.36, 10.44 (8.55)
0.67	3.23, 10.33	3.16, 10.58	3.19, 11.19	3.31, 8.71	3.22, 10.20 (8.55)
0.83	3.07, 9.64	3.01, 9.58	2.95, 10.53	3.15, 8.57	3.04, 9.58 (8.70)
1.00	8.71	8.90	8.70		8.77
		CTAB/Bj-56 (10^6 cmc/mol dm^{-3}) (II)			
0.00	3.20				3.20
0.17	3.63	3.65		3.57	3.62 (3.90)
0.33	4.57	4.10		4.04	4.24 (4.80)
0.50	6.25	5.14		6.21	5.87 (6.40)
0.67	8.99	7.00		8.93	8.31 (9.60)
0.83	13.90	14.80		16.60	15.10 (18.80)
1.00	815.00	812.00	854.00		827.00

$\alpha_{CPC}/\alpha_{CTAB}/\alpha_{Bi}$	ST	cond	spectro	average
		CPC/CTAB/Bj-56 (10^6 cmc/mol dm^{-3})		
0.125/0.25/0.625	4.20	4.88	4.73	4.60 (5.11)
0.125/0.625/0.25	11.45	12.30	10.90	11.55 (12.60)
0.25/0.125/0.625	4.68	4.50	4.90	4.69 (5.11)
0.25/0.625/0.125	19.86	21.80	24.30	21.99 (24.90)
0.33/0.33/0.33	8.11	9.25	9.31	8.89 (9.60)
0.625/0.125/0.25	11.60	12.00	11.70	11.77 (12.60)
0.625/0.25/0.125	21.90	21.50	24.30	22.57 (25.00)

^{a} The values in parentheses are calculated from Clint's equation (eq 12). The average error in the cmc is ±3%.

All solutions were prepared in doubly distilled water and measured under thermostated conditions at 300 K with an accuracy of ±0.01 K.

Methods. *Tensiometry.* Tensiometric measurements were taken with a calibrated du Noüy tensiometer (Krüss, Germany) by the ring detachment technique, and the measured surface tension (γ) values were corrected following the procedure of Harkins and Jordan.[34] The detailed procedure has been reported earlier.[28-31,34] The γ values were accurate within ±0.1 mN m^{-1}.

Conductometry. The conductance measurements were taken with a Jenway (U.K.) conductometer using a stoppered cell with a cell constant of 0.6 cm^{-1}. The accuracy of the measurements was within ±0.5%. The measurement details can be found in earlier reports.[28-31]

Calorimetry. A Tronac 458 isoperibol titration calorimeter (U.S.A.) was used for the study. The instrument was calibrated by measuring the heat of neutralization of hydrochloric acid with sodium hydroxide solution. The enthalpy of micellization of the surfactant mixtures was measured. The enthalpy values were accurate within ±2%. The measurement details can be found elsewhere.[28,35]

Spectrophotometry. A UV−visible (1601) Shimadzu (Japan) spectrophotometer was employed for spectral measurements using silica cells of 1 cm thickness. A series of surfactant mixtures were prepared, and their absorbances were measured. The absorbance of the binary (CPC/CTAB) and ternary (CPC/CTAB/Bj-56) mixtures were measured at 258.5 nm, the maximum wavelength of CPC. For another binary mixture of CTAB/Bj-56, pyrene was used as a probe and the absorbance was monitored at 335 nm.

Fluorimetry. The aggregation number of micelle was determined by the steady-state fluorescence quenching method using a Spex Fluorolog spectrophotometer with a slit width of 1.25 mm. Pyrene ($\sim$10 μM) was used as a probe and CPC as a quencher. Excitation was made at 335 nm, and emission was measured at 385 nm.

Results and Discussion

Determination of the Critical Micellar Concentration (cmc). The cmc values of different combinations of the binary (CPC/CTAB and CTAB/Bj-56) and ternary (CPC/CTAB/Bj-56) mixtures have been determined from the surface tension (γ)−log[surfactant], specific conductance (κ)−[surfactant], change in bridge voltage (electrical manifestation of change in temperature)−time (only for CPC/CTAB), and absorbance (A)−[surfactant] plots (Figure 1) and are presented in Table 1. The results on the other binary combination of CPC/Bj-56 reported earlier[31] have been used in the analysis. Treiner et al.[16,17] have reported two cmc's for CPC. Two cmc values of binary mixtures of CPC with other cationic surfactants[28] and of alkyl phosphonium bromides and their mixtures[32] are also available in literature. Our results in the case of the binary mixtures of CPC/CTAB (Table 1) have corroborated these findings. The cmc's have decreased systematically with an increasing proportion of CPC in the mixture. For the binary mixtures of CPC with the nonionic surfactants Tween-40 and Bj-56, the formation of a single cmc has been reported.[31] The CTAB/Bj-56 combination herein studied has also produced one cmc intermediate between the cmc's of the component surfactants. From Table 1, it is evident that the cmc's of the ternary mixtures were composition dependent and increased with an increasing proportion of the ionic surfactant in the system.

The cmc values of the binary and ternary surfactant mixtures were comparable with the trends observed earlier[29-31] for the mixed surfactants with CTAB, Triton X-100, and Tween-80; SDS, Tween-20, and Brij-35; and CPC, Tween-40, and Brij-56. The average values of the cmc determined by tensiometric, conductometric, calorimetric (only for CPC/CTAB), and spectrophotometric methods have been used for data analysis. The dependence of cmc on different combinations of the ternary mixture of CPC/CTAB/Bj-56 has been illustrated in Figure 2. The base points of the prism represent the compositions of surfactants on triangular coordinates, and the heights show the
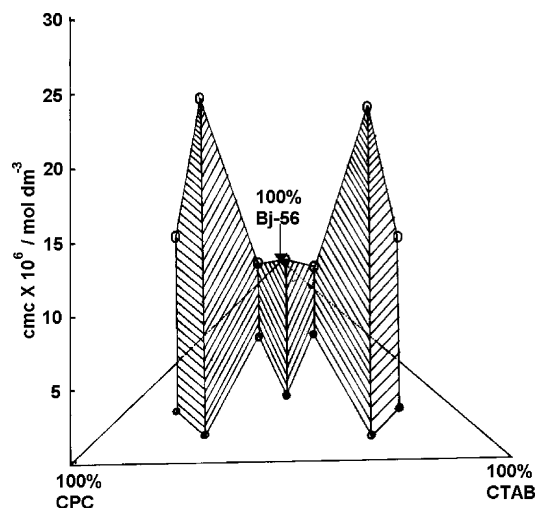
Figure 2. Composition dependent cmc values of ternary mixtures of CPC, CTAB, and Bj-56 at 300 K. The base points are in terms of component mol % compositions.

magnitudes of the cmc. The profile was multifolded: the trend of the molecular interaction dependent micellization process of the ternary mixtures was evident from the figure.

Adsorption at the Air/Water Interface. Amphiphiles orient at the air/water interface and decrease the surface tension. The Gibbs adsorption equation helps to calculate the interfacial adsorption per unit area of surface at different concentrations. For a multicomponent system, the equation has the form

$$-d\gamma = \Sigma \Gamma_i \, d\mu_i \tag{1}$$

where γ, Γ_i, and μ_i denote the surface tension, surface excess or effectiveness of adsorption of the ith component, and chemical potential of the ith component in solution, respectively.

The change in γ with respect to the change in the log of the total concentration of multicomponent surfactant mixtures can be used[28] to determine the total surface excess (Γ^{tot}). For a surfactant system having n species and the total concentration C, eq 1 takes the general form as

$$-d\gamma = nRT\Gamma^{tot} \, d \ln C \tag{2}$$

In the present context, for the binary mixtures (CTAB/Bj-56 and CPC/CTAB), the values of n were 3 and 4, respectively, and for the ternary mixture (CPC/CTAB/Bj-56), n was 5.

For the multicomponent combination of surfactants, eq 2 may be written as

$$\Gamma^{tot}_{max} = \frac{1}{2.303nRT} Lt_{C \to C_{cmc}} \frac{d\Pi}{d \log C} \tag{3}$$

where π stands for the surface pressure ($\gamma_{H_2O} - \gamma_{solution}$) and R is the gas constant. It may be mentioned here that instead of the total concentration (C) of all the species, the concentration of any one species in the mixture (with a constant composition) can also be used in eq 3 to obtain the total surface excess.[31,36] The value of Γ^{tot}_{max} at the cmc has been calculated from the least-squares slope of the π versus log C plot (figure not shown). At the cmc, the total area minimum value (A^{tot}_{min}) has been estimated from the equation

$$A^{tot}_{min} = 10^{18}[N_A(\Gamma^{tot}_{max})]^{-1} \tag{4}$$

where N_A is Avogadro's number and Γ^{tot}_{max} and A^{tot}_{min} are expressed in mol m^{-2} and nm^2 molecule^{-1}, respectively.

The values of Π_{cmc}, Γ^{tot}_{max}, and A^{tot}_{min} for the binary and ternary mixtures are presented in Tables 2 and 3, respectively. For the combination CPC/CTAB, the Γ^{tot}_{max} values given in parentheses increased with increasing mole fraction of CPC, whereas the values corresponding to the first cmc essentially decreased. The internal conditions of the two kinds of micelles were different; it was synergistic in the first and antagonistic in the second. For the CTAB/Bj-56 combination, the Γ^{tot}_{max} values decreased with increasing concentration of CTA$^+$, comparable with the reported trend of the CPC/Bj-56 combination.[31] The A_{min} values of these mixtures nearly followed a reverse order. For the ternaries, both Γ^{tot}_{max} and A^{tot}_{min} were practically independent of sample compositions except for the first two. The A^{tot}_{min}−composition profile in 3-D form has been presented in Figure 3. This pattern was also folded like the cmc−composition profile (Figure 2). The Γ^{tot}_{max} values were obviously of a similar pattern (illustration not shown).

The efficiency of interfacial adsorption is an important criterion of the solution behavior of a surfactant. It is thus useful to know the required molar concentration (C) of a surfactant to produce maximum adsorption. It has been empirically considered that maximum adsorption of a surfactant generally occurs[23] when the surface tension is reduced to 20 mN m^{-1}. The molar concentration of the surfactant at this point in the aqueous phase is called its C_{20} value, and its negative logarithmic value, symbolized as pC_{20}, is a measure of its efficacy of adsorption at the air/water interface. The larger the pC_{20} value, the better the efficiency of the amphiphile is to be adsorbed at the interface and more efficiently it reduces the surface tension. The cmc/C_{20} ratio is considered as a measure of the tendency of the surfactant to adsorb at the interface relative to its micellization tendency.[22,37] The values of pC_{20} and cmc/C_{20} for the binary and ternary combinations are given in Tables 2 and 3, respectively. For the CPC/CTAB mixtures, both pC_{20} and cmc/C_{20} values were the highest at a 1:1 molar ratio. In the binary combination of CTAB/Bj-56, the pC_{20} value mildly decreased with increasing mole fraction of CTAB, indicating a declining tendency of adsorption at the air/water interface relative to the solubilizing tendency in aqueous medium. On the other hand, the cmc/C_{20} values were virtually independent of the compositions. For the ternary combinations, the pC_{20} values were independent of composition. The cmc/C_{20} values have also shown the same trend except for the compositions 2, 6, and 7 where the values were much higher. The varied behavior of the surfactant mixtures in reducing the surface tension and self-organization in solution has been envisaged from the above analysis.

Thermodynamics of Micellization and Interfacial Adsorption. The standard free energy of micellization per mole of monomer unit ($\Delta G_m°$) for the binary and ternary combinations was evaluated from the relation

$$\Delta G_m° = (1 + g)RT \ln X_{cmc} \tag{5}$$

where g is the fraction of counterions bound to the micelle determined conductometrically[28-31] and X_{cmc} is the cmc expressed in mole fraction unit. The standard state was the hypothetical state of unit mole fraction.

The standard enthalpy of micellization ($\Delta H_m°$) was determined calorimetrically, and the standard entropy of micellization ($\Delta S_m°$) was calculated applying the Gibbs−Helmholtz equation.

$$\Delta G_m° = \Delta H_m° - T\Delta S_m° \tag{6}$$

Micellization of Binary and Ternary Surfactant Mixtures

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TABLE 2: Interfacial and Thermodynamic[a] Parameters of Pure and Binary Combinations at 300 K

α_{CPC} (I) or α_{CTAB} (II)	$10^3\Pi_{cmc}$ (J m^{-2})	$10^6\Gamma^{tot}_{max}$ (mol m^{-2})	A^{tot}_{min} (nm^2/molecule)	g	$-\Delta G_m°$ (kJ mol^{-1})	$-\Delta G_{ad}°$ (kJ mol^{-1})	$-\Delta H_m°$ (kJ mol^{-1})	$\Delta S_m°$ (J mol^{-1} K^{-1})	pC_{20}	cmc/C_{20}
					CPC/CTAB[b] (I)					
0.00	22.4	0.73	2.28	0.18	32.7	63.5	8.31	81.3	3.4	2.1
0.17	13.6	0.18	9.04	0.04	30.9	105.0	1.74	97.3	3.2	0.6
	(25.4)	(0.84)	(1.97)	(0.23)	(33.2)	(63.2)	(15.65)	(58.4)		(1.7)
0.33	20.1	0.28	6.04	0.08	32.2	105.3	1.06	104.0	3.5	1.2
	(32.5)	(0.99)	(1.67)	(0.26)	(34.1)	(66.9)	(9.07)	(83.4)		(3.8)
0.50	23.8	0.23	7.20	0.08	32.4	135.7	1.33	103.5	4.2	5.4
	(36.0)	(1.03)	(1.61)	(0.36)	(36.9)	(71.8)	(12.68)	(80.7)		(17)
0.67	19.6	0.21	7.90	0.08	32.5	125.7	2.40	100.2	3.5	1.0
	(32.9)	(1.14)	(1.46)	(0.46)	(39.7)	(68.7)	(8.88)	(103.0)		(3.1)
0.83	16.6	0.19	8.67	0.07	32.3	119.1	1.55	102.6	3.4	0.8
	(33.2)	(1.48)	(1.12)	(0.48)	(40.5)	(62.9)	(18.38)	(73.6)		(2.5)
1.00	32.0	1.31	1.27	0.47	40.5	64.9	6.87	112.2	3.8	5.3
					CTAB/Bj-56 (II)					
0.00	32.7	4.95	0.34	-	41.6	48.2		138	5.8	2.1
0.17	27.2	0.97	1.71	0.47	60.7	88.8		202	5.9	2.6
0.33	26.7	0.80	2.08	0.35	55.2	88.7		184	5.8	3.1
0.50	25.5	0.76	2.17	0.28	51.3	84.6		171	5.6	2.7
0.67	25.2	0.74	2.25	0.19	46.6	80.8		155	5.5	2.5
0.83	23.3	0.58	2.89	0.17	44.1	84.7		147	5.3	2.9
1.00	22.4	0.73	2.28	0.18	32.7	63.5	8.31	81.3	3.4	2.1

[a] The average errors in $\Delta G_m°$, $\Delta G_{ad}°$, $\Delta H_m°$, and $\Delta S_m°$ are ±3%. [b] The values in parentheses correspond to the formation of the second cmc.

TABLE 3: Interfacial and Thermodynamic[a] Parameters of Ternary Combinations of CPC, CTAB, and Bj-56 at 300 K

$\alpha_{CPC}/\alpha_{CTAB}/\alpha_{Bj}$	$10^3\Pi_{cmc}$ (J m^{-2})	$10^6\Gamma^{tot}_{max}$ (mol m^{-2})	A^{tot}_{min} (nm^2/molecule)	g	$-\Delta G_m°$ (kJ mol^{-1})	$-\Delta G_{ad}°$ (kJ mol^{-1})	$\Delta S_m°$ (J K^{-1} mol^{-1})	pC_{20}	cmc/C_{20}
0.125/0.25/0.625	24.7	6.86	2.42	0.30	52.9	88.9	176	5.6	1.7
0.125/0.625/0.25	25.2	4.07	4.08	0.24	47.6	109.5	158	5.4	3.0
0.25/0.125/0.625	24.9	5.09	3.26	0.39	56.5	105.3	188	5.7	2.2
0.25/0.625/0.125	23.6	5.63	2.95	0.23	45.2	87.2	151	4.9	1.7
0.33/0.33/0.33	20.9	5.15	3.22	0.33	51.9	92.5	173	5.2	1.2
0.625/0.125/0.25	28.2	5.34	3.11	0.27	48.7	101.5	162	5.5	3.4
0.625/0.25/0.125	28.2	4.87	3.41	0.21	44.4	103.8	148	5.3	4.5

[a] The average errors in $\Delta G_m°$, $\Delta G_{ad}°$, and $\Delta S_m°$ are ±3%.

For the binary cationic/nonionic mixtures (CTAB/Bj-56) as well as the ternary combinations (CPC/CTAB/Bj-56), the value of $\Delta H_m°$ was too low to be determined by the TRONAC isoperibol calorimeter. Even it could not be measured in the ITC microcalorimeter of OMEGA (U.S.A.), and hence, the enthalpy values were considered to be small and negligible. Thus, for these mixtures, $\Delta S_m°$ was equivalent to $-\Delta G_m°/T$. The process of micellization was virtually entropy controlled.

The standard free energy of interfacial adsorption ($\Delta G_{ad}°$) at the air/saturated monolayer interface of micelle has been evaluated from the relation

$$\Delta G_{ad}° = \Delta G_m° - \left(\frac{\Pi_{cmc}}{\Gamma^{tot}_{max}}\right) \qquad (7)$$

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

The values of g, $\Delta G_m°$, $\Delta H_m°$, $\Delta S_m°$, and $\Delta G_{ad}°$ for binary and ternary combinations have been represented in Tables 2 and 3, respectively. The g values of CPC/CTAB mixtures were almost the same and very low for the first break, and they increased with increasing mole fraction of CPC for the second break. For CTAB/Bj-56, the g values decreased with increasing mole fraction of CTAB. For ternary mixtures, the g values were moderate by the presence of Bj-56 and did not depend much on micellar composition.

In the case of CPC/CTAB mixtures, the values of $\Delta G_m°$ were almost constant for the first cmc and low and increase with α_{CPC} for the second cmc. The combinations of CTAB/Bj-56 had shown decreasing spontaneity with increasing fraction of

CTAB. For CPC/CTAB/Bj-56, $\Delta G_m°$ remained practically constant, showing equal spontaneity of the micellization process. The values of $\Delta H_m°$ were low and independent of composition for the first cmc of CPC/CTAB; for the second cmc, these $\Delta H_m°$ values were reasonable. The $\Delta S_m°$ values for the first process were positive and larger than the second. The values of $\Delta S_m°$ for the CTAB/Bj-56 mixtures decreased with increasing mole fraction of CTAB. For the ternaries, the values were more or less independent of composition.

For the CPC/CTAB pair, the value of $\Delta G_{ad}°$ was at its maximum at $\alpha_{CPC} = 0.50$ for both the first and second cmc's, and in comparison, the magnitude for the first cmc was higher than the second. For the CTAB/Bj-56 combination, $\Delta G_{ad}°$
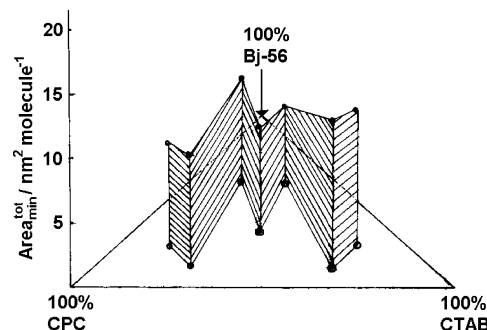

Figure 3. Composition dependent A^{tot}_{min} values of ternary mixtures of CPC, CTAB, and Bj-56 at 300 K. The base points are in terms of component mol % compositions.
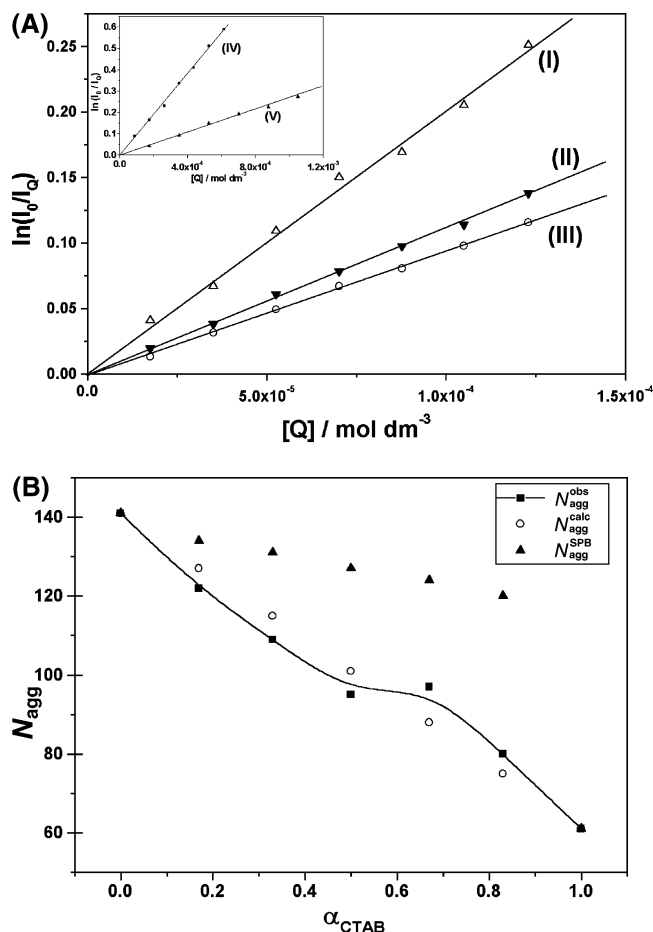
Figure 4. (A) Determination of aggregation numbers of CTAB/Bj-56 binary mixtures fluorimetrically at 300 K by plotting $\ln(I_0/I_Q)$ vs [Q] according to eq 8 for (I) 1:5, (II) 1:2, (III) 1:1, (IV) 2:1, and (V) 5:1. (B) Plot of aggregation number (N_{agg}) vs mole fraction of CTAB (α_{CTAB}).

decreased with increasing mole fraction of CTAB. For the ternary mixtures, the $\Delta G_{ad}°$ values remained on the whole nonvariant.

Micellar Aggregation Number. The aggregation number of the binary mixtures CTAB/Bj-56 was determined by the static fluorescence quenching method using the following equation:

$$\ln\left(\frac{I_0}{I_Q}\right) = \frac{[Q]N_{agg}}{([surf.] - cmc)} \tag{8}$$

The Stern−Volmer equation was used to get the equilibrium constant for the interaction between the quencher and the fluorescence probe.

$$\frac{I_0}{I_Q} = 1 + K_{SV}[Q] \tag{9}$$

In eqs 8 and 9, I_0 and I_Q are the fluorescence intensities in the absence and presence of quencher (Q), N_{agg} is the aggregation number, and K_{SV} is the Stern−Volmer constant. For [surf.] ≫ cmc, eq 8 gets simplified. Under that condition, K_{SV} should be affected as well as N_{agg}, but the effect on the latter may be considered small.[29,38] In the present study, good linear plots have been realized satisfying eqs 8 and 9, suggesting constancy of both N_{agg} and K_{SV} in the concentration range ($10-80$ times that of the cmc) used in the study.

TABLE 4: Aggregation Number[a] and Stern−Volmer Constant for Binary Mixtures of CTAB and Bj-56 at 300 K

α_{CTAB}	aggregation number $N_{agg}^{obsd}/N_{agg}^{calcd}/N_{agg}^{SPB}$	$10^{-4}K_{SV}$
0.00	141/-/-	
0.17	122/127/134	22.4
0.33	109/115/131	38.8
0.50	95/101/127	9.8
0.67	87/87/124	12.0
0.83	80/75/120	3.0
1.00	61/-/-	

[a] The N_{agg} values for pure micelles of CTAB and Bj-56 were taken from refs 28−30 and 38, respectively. N_{agg}^{calcd} and N_{agg}^{SPB} for CTAB/Bj-56 mixtures were calculated using eq 10 and mole fractions obtained from the SPB method, respectively.

The plot, according to eq 8, to obtain N_{agg} from the slope is exemplified in Figure 4A. K_{SV} was found from the slope of the plot of (I_0/I_Q) versus [Q] according to eq 9 (plot not shown). The values are presented in Table 4. The aggregation number of the CTAB/Bj-56 system decreased with decreasing mole fraction of Bj-56 which was reasonable in terms of the aggregation number of the pure micelles. Although the K_{SV} values were significantly high, they did not follow a trend with [CTAB] in the mixture like N_{agg}; other factors (for example, concentration and composition effect) were responsible for it. Here, determination of N_{agg} for mixtures with CPC could not be done because it itself acted as a good quencher of fluorescence. The N_{agg} values of CPC and alkyl triphenyl phosphonium bromide cannot be determined by the fluorescence quenching method, as has been recently reported.[32,39] In column 2 of Table 4, N_{agg} values calculated according to the mixing rationale (eq 10) are presented.

$$N_{agg}^{calcd} = \alpha_{CTAB}N_{agg}^{CTAB} + \alpha_{Bj-56}N_{agg}^{Bj-56} \tag{10}$$

The terms in the equation are all explicit. It has been found that, although the N_{agg}^{calcd} values were mostly greater than the experimental values, the agreement was good particularly for $\alpha_{CTAB} > 0.5$. Apparently, it meant maintenance of stoichiometric composition in micelles as in solution. However, the results obtained from different theories discussed in the following section proved it otherwise; the calculated N_{agg} values differed much from the experimental results. Further work is warranted to account for the difference. In Figure 4B, the experimental N_{agg} values are compared with N_{agg} values calculated using eq 10 on the basis of stoichiometric compositions as well as micellar compositions realized from the SPB equation (Table 5). The latter has shown a very poor correlation.

We mention here the nonavailability of a time-resolved fluorescence measuring facility, so we have used the static quenching method for the determination of N_{agg}. They were thus to some extent underestimated numbers.

Mutual Interaction of Surfactants in Micelles. The mixed micelles can be both ideal and nonideal. The formation of mixed micelle may be represented by the relation[23]

$$\frac{1}{cmc_{mix.}} = \sum_{i=1}^{n}\frac{\alpha_i}{f_i cmc_i} \tag{11}$$

where cmc_i and $cmc_{mix.}$ denote the critical micellar concentrations of the ith component and the mixture, respectively; α_i is the mole fraction of component i in solution; and f_i is its activity coefficient.

For ideal conditions, $f_i = 1$, and eq 11 becomes Clint's equation.[20]

$$\left(\frac{1}{\text{cmc}_{\text{mix.}}}\right) = \sum_i^n \left(\frac{\alpha_i}{\text{cmc}_i}\right) \qquad (12)$$

This equation is straightforward to predict cmc_{mix} from the knowledge of the cmc's of the individual surfactants in the mixture and is useful for comparison between ideal and nonideal mixtures. The term f_i makes the determination complex and challenging.

The ideal cmc values for the mixtures evaluated from eq 12 are presented in parentheses in the last column of Table 1. For the CPC/CTAB system, the calculated cmc was much larger than the first cmc but smaller than the second cmc. For CTAB/Bj-56 mixtures, the experimental cmc's were lower than the calculated values. The ternary mixtures of CPC/CTAB/Bj-56 produced lower experimental cmc's than the expected values. The combinations, thus, evidenced synergism in their mutual interaction behavior. The higher second cmc for the CPC/CTAB combination could not be assessed by the mixed cmc rule of Clint (eq 12); it was a special feature of the mixed system.

Motomura,[21] Rosen,[22,23] Rubingh,[24] and Blankschtein (SPB) et al.[25] have proposed equations to analyze molecular interaction in the mixed micelles of binary combinations as well as predicting cmc and f_i. Motomura's thermodynamic treatment considers mixed micelles like a macroscopic bulk phase, and the associated energetic parameters are obtained from the excess thermodynamic quantities similar to those associated with the adsorbed film of surfactant. The treatment has been used by us earlier.[5,9,31] The basic equation has the following form:[21]

$$X_2^M = \hat{X}_2 - (\hat{X}_1\hat{X}_2/\hat{\text{cmc}})(\partial\,\hat{\text{cmc}}/\partial\hat{X}_2)_{T,p} \qquad (13)$$

where

$$\hat{X}_2 = \frac{\nu_2 X_2}{\nu_1 X_1 + \nu_2 X_2}$$

and

$$\hat{\text{cmc}} = (\nu_1 X_1 + \nu_2 X_2)\text{cmc}$$

The subscripts 1 and 2 denote surfactants 1 and 2, respectively; X denotes the mole fraction; and ν denotes the number of ions dissociated by a surfactant. The mole fractions of a surfactant in the mixed micelle (X_M) (simpler symbol of X_2^M) evaluated by the Motomura equation are presented in Table 5. For the

CPC/CTAB combinations, X_M values were all greater than the stoichiometric mole fractions. For CTAB/Bj-56, the X_M values were all much lower than the stoichiometric mole fractions: similar was the finding for CPC/Bj-56.[31] Motomura's model does not depend on the nature of the surfactants and their counterions and helps to predict micellar composition only.

Rosen's model for binary surfactant mixtures provides the mole fraction of a surfactant (X_{RO}) as well as the molecular interaction parameter (β_{RO}) at the air/solution interface (Table 5). The value of β_{RO} can be obtained from surface tension−concentration data following the equation[22,23]

$$\beta_{RO} = \frac{\ln(\alpha_1 C_{12}/X_1 C_1)}{(1 - X_1)^2} \qquad (14)$$

and

$$\frac{X_1^2 \ln(\alpha_1 \ln[(1 - \alpha_1)C_{12}/X_1 C_1])}{(1 - X_1)^2 \ln[(1 - \alpha_1)C_{12}/(1 - X_1)C_2]} = 1 \qquad (15)$$

where α_1 is the mole fraction of component 1, X_1 is the mole fraction of component 1 at the air/solution interface, C_1 is the concentration of component 1, and C_{12} is the concentration of their mixture in solution.

In the evaluation procedure, γ is plotted against log(or ln) C for each of the pure surfactant components of the mixture and also for at least one mixture of them at the fixed mole fraction of component 1 (i.e., α_1). A value of γ_1 close to the minimum common value is selected. The values C_1, C_2, and C_{12} are the concentrations of surfactant 1, surfactant 2, and their mixture, respectively, required to obtain γ_1 in their respective solutions.[23] The mole fraction of a surfactant in the mixture at the aqueous solution/air interface (X denoted as X_{RO}) is obtained by solving eq 15 iteratively.

It is observed from Table 5 that the value of X_{RO} for the CPC/CTAB mixture increased with the increasing value of α_{CPC}, while for the CTAB/Bj-56 combination the trend with α_{CTAB} was not regular. The interaction parameter (β_{RO}) of CPC/CTAB was positive, indicating repulsive interaction between CPC and CTAB in the micelle. The parameter was negative for CTAB/Bj-56 mixtures, indicating synergism. In Rosen's model, since counterion effects are neglected, all solutions containing ionic surfactants should have the same total ionic strength with a swamping excess of any counterions.[22] In this model, since surfactant mixtures are generally used above their cmc, β_{RO}

TABLE 5: Micellar Compositions ($X_M/X_{RO}/X_R/X_{SPB}$), Interaction Parameters [$\beta_{RO}/\beta_R/\beta_{SPB}$ (kT)], Activity Coefficients (f_R/f_{SPB}), and cmc's of Binary Mixtures at 300 K and at Different Stoichiometric Compositions (α)

		CPC/CTAB			
α_{CPC}	$X_M/X_{RO}/X_R/X_{SPB}$	$\beta_{RO}/\beta_R/\beta_{SPB}$ (kT)	f_R^{CPC}/f_{SPB}^{CPC}	$f_R^{CTAB}/f_{SPB}^{CTAB}$	10^4cmc/(mol dm^{-3}) obsd/SPB/Clint
0.17	0.20/0.12/-/0.16	−0.88/-/−0.001	−/1.0	−/1.0	3.67, 11.03/8.40/8.40
0.33	0.37/0.04/0.16/0.32	1.55/1.32/0.002	2.6/1.0	1.0/1.0	3.51, 10.74/8.40/8.40
0.50	0.55/0.05/0.48/0.49	2.02/0.82/0.044	1.3/1.0	1.2/1.0	3.35, 10.44/8.55/8.55
0.67	0.72/0.11/0.74/0.66	2.18/0.80/0.001	1.1/1.0	1.6/1.0	3.22, 10.20/8.55/8.55
0.83	0.86/0.44/0.90/0.82	2.23/0.83/0.005	1.0/1.0	2.0/1.0	3.04, 9.58/8.70/8.70

		CTAB/Bj-56			
α_{CTAB}	$X_M/X_{RO}/X_R/X_{SPB}$	$\beta_{RO}/\beta_R/\beta_{SPB}$ (kT)	$f_R^{CTAB}/f_{SPB}^{CTAB}$	f_R^{Bj}/f_{SPB}^{Bj}	10^4cmc/(mol dm^{-3}) obsd/SPB/Clint
0.17	0.01/0.08/0.05/0.09	−6.1/−4.7/−5.97	0.02/0.01	0.99/0.95	3.62/3.32/3.90
0.33	0.01/0.13/0.08/0.13	−6.6/−4.6/−5.98	0.02/0.01	0.97/0.90	4.24/3.72/4.80
0.50	0.03/0.02/0.07/0.17	−1.9/−3.4/−5.96	0.05/0.02	0.98/0.85	5.87/4.49/6.40
0.67	0.04/0.03/0.11/0.21	−1.7/−3.5/−5.98	0.06/0.03	0.96/0.77	8.31/5.94/9.60
0.83	0.51/0.09/0.14/0.26	−2.4/−3.1/−5.98	0.11/0.04	0.94/0.67	15.10/9.44/18.80

should be determined using C_1, C_2, and C_{12} values taken from the γ−log C plots at such a lowest possible value of γ that the slopes are almost linear.

According to the theory of Rubingh,[24] the mole fraction of a surfactant in the mixed micelle (X_R) can be iteratively obtained using the equation

$$\frac{X_R^2 \ln[cmc_{mix.}\alpha_1/cmc_1 X_R]}{(1 - X_R)^2 \ln[cmc_{mix.}(1 - \alpha_1)/cmc_2(1 - X_R)]} = 1 \quad (16)$$

where cmc_1 and cmc_2 are the critical micellar concentrations of surfactants 1 and 2, respectively, and $cmc_{mix.}$ is the cmc of the mixed micelle. X_R is used in eq 17 to evaluate the molecular interaction parameter (β_R).

$$\beta_R = \frac{\ln(cmc_{mix.}\alpha_1/cmc_1 X_R)}{(1 - X_R)^2} \quad (17)$$

The activity coefficients of components 1 and 2 in the mixed micelle (f_R^1 and f_R^2, respectively) can be calculated from the equations

$$f_R^1 = \exp[\beta(1 - X_R)^2] \quad (18)$$

and

$$f_R^2 = \exp[\beta X_R^2] \quad (19)$$

The values of X_R, β_R, and activity coefficients (f_R) for the binary mixtures are presented in Table 5. For CPC/CTAB mixtures, the X_R values of CPC were found to be higher than those of CTAB in the CTAB/Bj-56 pair. The values of β_R for both the mixtures were found to be constant for the first pair (except for composition 2) but fairly so for the second (the first two compositions produced different magnitudes from the rest). These values for CPC/CTAB were positive, and the magnitudes indicated minor antagonism. The fairly large negative β_R values for CTAB/Bj-56 suggested synergism similar to β_{RO}. Such a behavior was also shown by other surfactant mixtures.[8,9,29−31] The antagonism between CPC and CTAB has been considered to be a major reason for higher CPC content in the mixed micelle compared to CTAB/Bj-56 mixtures where the CTAB population was less disproportioned with a manifestation of synergism. The role of other factors in controlling the phenomenon cannot be ruled out. In CPC/CTAB combinations, the activity coefficients of both CPC and CTAB were greater than unity, which for the first decreased while for the latter increased with increased α_{CPC} in the mixture. In the CTAB/Bj-56 system, the activity coefficients of CTAB were very low and those of Bj-56 were nearly unity which were similar to those of the CPC/Bj-56 and CPC/Tw-40 systems.[31] The ionic/ionic and ionic/nonionic mixed micelles have manifested different activity characteristics.

Blankschtein (SPB) et al.[25] also have developed a molecular thermodynamic theory to quantitatively predict the cmc, micellar composition, shape, and phase behavior on the basis of hydrophobic, structural, and electrical interactions between the binary components. According to this theory, eq 11 is written in the form

$$\frac{1}{cmc_{mix.}} = \frac{\alpha_1}{f_{SPB}^1 cmc_1} + \frac{1 - \alpha_1}{f_{SPB}^2 cmc_2} \quad (20)$$

where the terms f_{SPB}^1 and f_{SPB}^2 are the activity coefficients of surfactants 1 and 2 in the mixed micelle. These activity coefficients can be expressed as

$$f_{SPB}^1 = \exp\left[\frac{\beta_{12}(1 - \alpha^*)^2}{kT}\right] \quad (21)$$

and

$$f_{SPB}^2 = \exp\left[\frac{\beta_{12}\alpha^{*2}}{kT}\right] \quad (22)$$

where β_{12} is the predicted interaction parameter between surfactants 1 and 2, k is the Boltzmann constant, T is the absolute temperature, and α^* is the optimal micellar composition (where the free energy of mixed micellization reaches its minimum value). β_{12} and α^* are related by the following equation:

$$\frac{\beta_{12}(1 - 2\alpha^*)}{kT} + \ln\left(\frac{\alpha^*}{1 - \alpha^*}\right) = \ln\left[\frac{\alpha_1 cmc_2}{(1 - \alpha_1)cmc_1}\right] \quad (23)$$

Equation 23 was solved by iterative procedure to obtain α^* and β_{12} and hence f_{SPB}^1 and f_{SPB}^2. The results are presented in Table 5. It has been observed that, for the CPC/CTAB system, X_{SPB} (i.e., α^*) fairly agreed with both X_M and X_R. For the CTAB/Bj-56 system, X_{SPB} was higher than X_M, X_{RO}, and X_R except at $\alpha_{CTAB} = 0.83$ where $X_M > X_{SPB}$. Other cationic/nonionic combinations such as CPC/Tw-40 and CPC/Bj-56 have also produced similar results.[31] Π_{cmc} versus average X and α are plotted in Figure 5, showing the variation of cmc of different compositions. In the case of CPC/CTAB combinations, β values were positive and very small, denoting marginal repulsive interactions between the surfactants except for $\alpha_{CPC} = 0.17$, where β_{SPB} was slightly negative. In the comparative measurement with other theories, $\beta_{RO} > \beta_R \gg \beta_{SPB}$. For the CTAB/Bj-56 pair, at $\alpha_{CTAB} = 0.17$ and 0.33, $\beta_{RO} > \beta_{SPB} > \beta_R$; for the other combinations ($\alpha_{CTAB} = 0.50, 0.67$, and 0.83), $\beta_{SPB} > \beta_R > \beta_{RO}$. Here, all the interaction parameters were large. For the system of CPC/CTAB (pairs having similar charges), $\beta_{12}/kT = 0$ and consequently $cmc_{Clint} = cmc_{SPB}$. The equivalence of cmc_{Clint} and cmc_{SPB} has suggested ideal mixing behavior of CPC and CTAB. The observed double cmc's have restricted comparison of the experimental values with the theory. The $f_{SPB}^{CPC} = f_{SPB}^{CTAB} = 1$ also advocated ideal behavior. The deviation of f_R^{CPC} and f_R^{CTAB} from unity meant an inadequacy of Rubingh's formula to treat the data. This inadequacy was also reflected on the interaction parameters β_R and β_{SPB} where the latter was significantly lower (showing negligibly small antagonistic interaction) than the former (showing a fair degree of antagonism). For the other binary system of CTAB/Bj-56, $cmc_{obsd} \neq cmc_{Clint} \neq cmc_{SPB}$. The cationic/nonionic combination was nonideal. The activity coefficients also supported nonideality for the ionic component: the nonionic component has shown nonideality by the SPB model at $\alpha \geq 0.5$. However, the model of Rubingh has produced ideality for the nonionic component in the mixed micelles. Both of the models have consequently evidenced synergistic interaction and $\beta_{SPB} > \beta_R$. The SPB derived results deviated from Rubingh's results. They represent the mixed micellar behavior better than Rubingh's results, being rigorous and more quantitative. The consideration of the molecular and geometrical properties of surfactants in their mutual interaction in mixed micelles with the SPB procedure has been considered to be the reason for the disagreement between the findings of SPB and Rubingh.
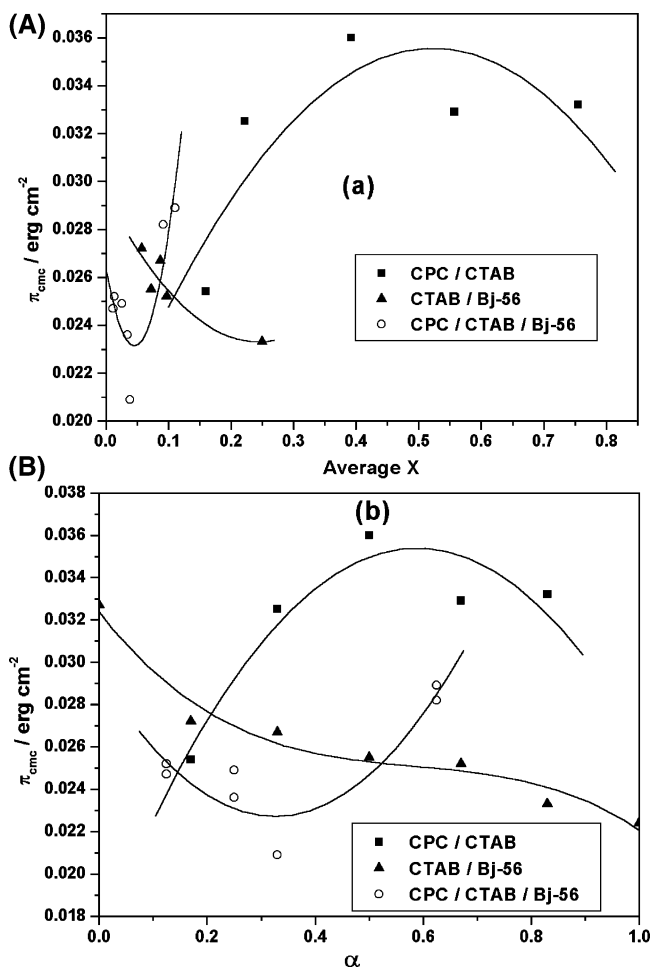
Micellization of Binary and Ternary Surfactant Mixtures

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(A)

(B)

Figure 5. (a) Plot of Π_{cmc} vs average X. (b) Plot of Π_{cmc} vs mole fraction (α) of CPC/CTAB, CTAB/Bj-56, and CPC/CTAB/Bj-56.

Theoretical treatment of surfactant mixtures of more than two components is very limited.[40,41] The theory of Rubingh and Holland[40] (RH) has been properly tested to determine the micellar composition, activity coefficient, and cmc of a ternary system. The activity coefficients of surfactants in a binary mixed micelle can be estimated from relations 18 and 19. In a multi n-component mixture, the activity coefficients f_i, f_j, f_k, and so forth, of mixed micelle forming amphiphilic species i, j, k, and so forth, can be expressed by the RH equation[40]

$$\ln f_i = \sum_{\substack{j=1 \\ (j \neq i)}}^{n} \beta_{ij} x_j^2 + \sum_{\substack{j=1 \\ (i \neq j \neq k)}}^{n} \sum_{k=1}^{j-1} (\beta_{ij} + \beta_{ik} - \beta_{jk}) x_j x_k \quad (24)$$

where β_{ij} denotes the net (pairwise) interaction between components i and j and x_j is the mole fraction of the jth component in the micelles; β_{ik}, β_{jk}, and x_k have similar significances.

Equation 25 is valid at the cmc

$$x_i = \alpha_i C f_j x_j / (C_i \alpha_j f_i) \quad (25)$$

where the new terms C_i and C_j represent the cmc's of the ith and jth components, respectively, and α_i and α_j are the mole fractions of the ith and jth components in the micelle.

The average values of the interaction parameter (β_R) obtained by Rubingh's method[24] for the binaries CPC/CTAB and CTAB/Bj-56 herein studied and that for CPC/Bj-56 studied earlier[31] were used in eq 24 to calculate the activity coefficients f_1, f_2,

and f_3 for the ternary system (CPC/CTAB/Bj-56) using the method of "successive substitution" in a computer. Then, the cmc of the mixed micelle was evaluated by using these f values in eq 25. The results are presented in Table 6. The mole fractions of the individual amphiphiles in the mixed micelles have been found to be different from the stoichiometric compositions: both X_{CPC} and X_{CTAB} were much lower than α_{CPC} and α_{CTAB}, but X_{Bj-56} was fairly higher than α_{Bj-56}. The micelle was mainly composed of the nonionic component. A similar trend was observed for the CPC/Tw-40/Bj-56 system.[31] The activity coefficients (f_{CPC} and f_{CTAB}) were very low, whereas f_{Bj-56} was high and close to unity. In the reported case of the CPC/Tw-40/Bj-56 system,[31] f_{Tw-40} was moderately high and f_{Bj-56} was close to unity, while f_{CPC} was very low. The nonionic surfactant suppressed the activity of the ionic surfactant in the mixed micelle. The cmc values evaluated by the RH method were lower than the experimental results except for the first and third compositions; the maximum difference was observed for the fourth composition. Both cmc$_{obsd}$ and cmc$_{RH}$ were lower than cmc$_{Clint}$, denoting the synergistic nonideal nature of the mixed ternary micellar system. The deviation of cmc$_{RH}$ from cmc$_{obsd}$ can be attributed to the inadequacy of the RH theory wherein the contributions of the molecular parameters of the component surfactants, counterion binding by mixed micelles, and so forth, have been left out from consideration.

In the case of structural considerations of the micelles, Israelachvili[42] showed that the geometry or "packing" properties of the aggregates depend on three parameters: (i) the surface area (A) of the polar headgroup, (ii) the volume (v) of the hydrophobic chain which can be considered to be fluid and incompressible, and (iii) the maximum effective length, called the critical chain length (l_c), a semiempirical parameter which is applicable only for smaller extensions of the hydrophobic chain and not for larger extensions, prevented by a sharp rise in the interaction energy among carbon and hydrogen molecules. Tanford[43] demonstrated that for a saturated hydrophobic chain with the n_c number of carbon atoms:

$$l_c \leq l_{max} \approx (0.154 + 0.1265 n_c) \text{ nm} \quad (26)$$

and

$$v \approx (0.0274 + 0.0269 n_c) \text{ nm}^3 \quad (27)$$

The surface area (A) of the pure amphiphile can be obtained from Table 2. According to Israelachvili,[42] the geometry of the micellar aggregates can be estimated by the value of the packing parameter (P) which can be expressed as

$$P = v/A l_c \quad (28)$$

while micellar radius, $R = (3v/A)$ nm $\quad (29)$

The packing parameter will determine whether micelles will be spherical ($P < 1/3$), nonspherical ($1/3 < P < 1/2$), vesicles or bilayers ($1/2 < P < 1$), or "inverted" structures ($P > 1$). These types of structures indicate the minimum-sized aggregates in solutions which minimize the Gibbs free energy of micellization. Since all of the amphiphiles taken have the same number (16) of carbon atoms in the linear hydrophobic chain, the values of l_c and v calculated from eqs 26 and 27 are represented in Table 7. With the values of v, A, and l_c, the values of P and R have been evaluated using eqs 28 and 29. For these surfactants, the ratio v/l_c is a constant due to the same tail length and only the area (A) makes the difference in their packing parameters. For spherical micelles, the surface area (A) should be large and the

TABLE 6: Micellar Composition (X^{RH}), Component Activity Coefficient (f^{RH}), and cmc$_{RH}$ in Ternary Mixtures of CPC/CTAB/ Bj-56 by the RH Method at 300 K and at Different Stoichiometric Compositions (α)

| $\alpha_{CPC}/\alpha_{CTAB}/\alpha_{Bj\text{-}56}$	$X^{RH}_{CPC}/X^{RH}_{CTAB}/X^{RH}_{Bj}$	$f^{RH}_{CPC}/f^{RH}_{CTAB}/f^{RH}_{Bj}$	10^6cmc/(mol dm^{-3}) RH/obsd/Clint
0.125/0.25/0.625	0.012/0.044/0.944	0.054/0.032/0.989	4.77/4.60/5.11
0.125/0.625/0.25	0.014/0.129/0.857	0.105/0.059/0.923	10.13/11.55/12.60
0.25/0.125/0.625	0.026/0.023/0.950	0.051/0.031/0.991	4.82/4.69/5.11
0.25/0.625/0.125	0.035/0.160/0.805	0.145/0.084/0.862	17.75/21.99/24.90
0.33/0.33/0.33	0.039/0.069/0.890	0.079/0.047/0.955	8.26/8.89/9.60
0.625/0.125/0.25	0.092/0.029/0.878	0.081/0.054/0.947	10.63/11.77/12.60
0.625/0.25/0.125	0.111/0.069/0.819	0.118/0.079/0.884	18.52/22.57/25.00

TABLE 7: Values of Critical Chain Length (l_c), Volume of Hydrophobic Chain (v), Surface Area of Polar Head Group (A), Packing Parameter (P), and Radius (R) of Pure CPC, CTAB, and Bj-56 Micelles

surfactant	l_c (nm)	v (nm^3)	A (nm^2)	P	R (nm)
CPC	2.178	0.4578	1.27	0.13	1.08
CTAB	2.178	0.4578	2.28	0.07	0.60
Bj-56	2.178	0.4578	0.34	0.50	4.04

radius of the micelle (R) will not exceed the critical chain length (l_c).[42] Table 7 shows that pure cationic CPC and CTAB are able to pack into the spherical micelles with their micellar radius (R) not exceeding the critical chain length (l_c). However, nonionic Bj-56 cannot be accommodated within spheres and thus it should be slightly nonspherical with the micellar radius exceeding l_c. In a similar way, the binary and ternary mixed micelles can be evaluated in terms of the effective packing parameter (P_{effect}) described as[11,44]

$$P_{effect} = (v/Al_c)_{effect} = \sum v_i X^{mic}_i / \left(\sum A_i X^{mic}_i\right) l_c \quad (30)$$

where X^{mic}_i is the average mole fraction of the ith component in the micelle of binary mixtures taken from Table 5. In the case of CPC/Bj-56, the values are taken from ref 31. For ternary mixtures, the mole fraction values of the particular component are taken from Table 6. The plot of packing parameter (P) versus mole fraction (α) of different binary mixtures is exemplified in Figure 6 which indicates that the mixed micelles formed by CPC/CTAB systems are spherical ($P < {}^1/_3$). However, in the cases of the CTAB/Bj-56 and CPC/Bj-56 systems, the micelles formed are nonspherical, excepting $\alpha_{CTAB} = 0.83$ for the CTAB/ Bj-56 mixture. In the case of pure Tween-40 ($P = 0.15$ and $R = 1.002$), the CPC/Tw-40 and Tw-40/Bj-56 systems studied earlier,[31] spherical micelles are formed, excepting $\alpha_{Tw\text{-}40} = 0.17$
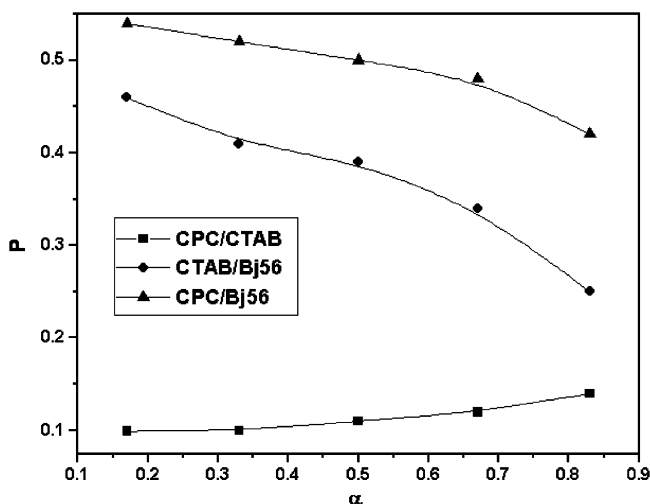
Figure 6. Profile of packing parameter (P) vs mole fraction (α) of different binary mixtures.

TABLE 8: Values of Packing Parameter (P) in Ternary Mixed Micelles of CPC/CTAB/Bj-56 at Different Stoichiometric Compositions (α)

$\alpha_{CPC}/\alpha_{CTAB}/\alpha_{Bj\text{-}56}$	P
0.125/0.25/0.625	0.48
0.125/0.625/0.25	0.36
0.25/0.125/0.625	0.51
0.25/0.625/0.125	0.31
0.33/0.33/0.33	0.41
0.625/0.125/0.25	0.44
0.625/0.25/0.125	0.36

($P = 0.346$) for the Tw-40/Bj-56 combination. The packing parameters of the ternary mixtures have been presented in Table 8. This shows that the mixed micelles formed herein are nonspherical, excepting the fourth composition where the mole fraction of Bj-56 is at a minimum. However, for the systems of CPC/Tw-40/Bj-56 combinations,[31] the micelles formed are spherical with the exception of the first and third compositions where the mole fraction of Bj-56 is at a maximum.

The above rationale has given an idea about the expectation from the concept of Israelachvili.[42] The scattering experiments (DLS or SANS) would be useful for verification of the shapes which is at present not possible for the lack of facility. We contemplate taking up the matter in a future occasion.

Conclusions

The binary combinations of CPC/CTAB produced two cmc values; one is lower and another is higher than that predicted by the Clint equation.[20] The CTAB/Bj-56 system has produced a cmc lower than that of Clint. The aggregation number of CTAB/Bj-56 micelles can be calculated with a fair degree of agreement by a simple additive rule considering stoichiometric composition. The binary system of CPC/CTAB has shown minor repulsive interaction (small positive β) due to similar positive charge on the headgroups of the amphiphiles, whereas the components of the CTAB/Bj-56 system have evidenced fair a degree of attractive interaction with negative β values.

In the studied ternary combination CPC/CTAB/Bj-56, the surfactant tails contained 16 carbon atoms, whereas the headgroups were different. The cmc$_{RH}$ values were lower than the ideal values according to Clint. However, they were less lower than cmc$_{obsd}$ except for the first and third compositions. An overall nonideality by way of synergistic interaction among the components resulted. The cationic headgroups of CPC and CTAB interacted favorably with the oxygen centers of the headgroup of Bj-56. The mole fractions of the components in the mixed micelle were different from the stoichiometric composition; the extents of transfer of both CPC and CTAB from solution to the micelles were much lower than that of Bj-56. The much higher proportion of Bj-56 in the mixed micelle produced a lower effective charge density at the micelle/solution interface with a consequence of lower ($\sim$30%) counterion binding as against 47% for pure CPC micelles.

Micellization of Binary and Ternary Surfactant Mixtures

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Both the cationic amphiphiles CPC and CTAB form spherical micelles, while the nonionic amphiphile Bj-56 forms nonspherical micelles. According to the values of the packing parameter, the two binary mixtures CTAB/Bj-56 and CPC/Bj-56 form nonspherical micelles, excepting $\alpha_{CTAB} = 0.83$ for the CTAB/Bj-56 combination, while the CPC/CTAB systems form spherical micelles. For ternary combinations of CPC/CTAB/Bj-56, nonspherical micelles are formed with the exception of the fourth composition.

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