



## Micellar Properties of Cationic Surfactants in Pure and Mixed States

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The solution properties of the surfactants dodecyl-, tetradecyl-, and hexadecyl(cetyl)trimethylammonium bromide (DTAB, TTAB, and CTAB, respectively) as well as hexadecylpyridinium chloride (CPC) in pure and mixed states (binary and ternary combinations) have been studied. The critical micelle concentration (cmc), counterion binding, aggregation number, polarity, thermodynamics of micellization, interfacial adsorption, etc., have been quantitatively estimated by surface tension, conductance, spectrophotometry, fluorescence, and calorimetric methods. The micellar compositions, activities of the components in the micelle, and their mutual interactions have been estimated from Rubingh's theory. The surfactant mixtures have been found to be nonideal, with a lower degree of counterion association compared to pure states, but possess more or less comparable micellar polarity and energetic parameters.

### Introduction

In aqueous medium, surfactants in pure and mixed states form micelles after a critical concentration, called cmc (critical micelle concentration). Formation of a micelle and its dependence on environmental factors (pH, temperature, additives, pressure, etc.), thermodynamics of formation, counterion binding (for ionic surfactants), aggregation number, solubilization property, catalyzing functions, etc., are important physicochemical aspects that need detailed and intensive attention for both fundamental understanding and application prospects. Mixed surfactants producing mixed micelles are very often used in industrial preparations and pharmaceutical and medicinal formulations for the purpose of solubilization, suspension, dispersion, etc. Much attention has been directed in recent years toward understanding the detailed behaviors of surfactant (amphiphile) mixtures yielding mixed micelles.<sup>1–15</sup> Fundamental properties of mixed amphiphiles have, therefore, been studied by a number of workers, and relevant (useful) theories have been proposed and used.<sup>15–22</sup> However, none of the theories are yet adequately perfect to predict the micellization properties on the basis of intra- or intersurfactant interactions including modifications therein by counterions (salts), other additives, solvents, temperature, pressure, and other effective perturbants. The recent molecular thermodynamic theory<sup>19–22</sup> in this direction is of considerable advancement and needs detailed testing on carefully collected data by different techniques. The dimensions of such exploration (investigation) have also been extended by workers in this field examining the effects of chain length<sup>23–27</sup> and hydrophilic and hydrophobic groups in the surfactant molecules<sup>28–31</sup> on the micellization and solution behaviors of different kinds of amphiphiles.

Out of the three types (nonionic, ionic, and zwitterionic) of amphiphiles, it is known that in the mixed state nonionics show ideal behavior, while other combinations exhibit nonideality resulting from synergistic (attractive) or antagonistic (repulsive) interactions between the amphiphiles of different types. The factors guiding the interactions are of various origin; their quantitative (preferably exact) accounting remains a matter of continued research interest.

Investigations on the mixed micelle formation between binary combinations of cationic surfactants are scanty.<sup>12,26,35</sup> Solubi-

lization behaviors of different solubilizates in the mixed micellar solution of cationic surfactants have been studied by several workers.<sup>35–37</sup> It may be mentioned that similarly charged amphiphiles of different molecular architecture may exhibit both ideal<sup>12,26</sup> and nonideal<sup>14</sup> behaviors in solutions forming micelles. A literature survey shows that considerable efforts have been made on the study of mixed surfactant systems<sup>14,33,38</sup> to characterize micelles and their formation. The significant contributions of Rosen et al. deserve special mention in this context.<sup>39,40</sup> Extensive investigations on the thermodynamics of micellization and adsorption, counterion binding, polarity, and aggregation number have been reported, but systematic studies are limited.

In this presentation, results of the detailed exploration of the above mentioned physicochemical properties of mixed cationic surfactants (in binary and ternary combinations) using dodecyltrimethylammonium bromide (DTAB), tetradecyltrimethylammonium bromide (TTAB), hexadecyl(cetyl)trimethyl ammonium bromide (CTAB), and hexadecyl(cetyl)pyridinium chloride (CPC), adopting conductometric, calorimetric, spectrophotometric, and fluorimetric methods have been reported. The results have been analyzed in the light of the existing theories. It may be mentioned that although comprehensive studies on binary mixtures of cationic surfactants are reported in the literature, fundamental investigations on ternary combinations most probably have not yet been addressed.

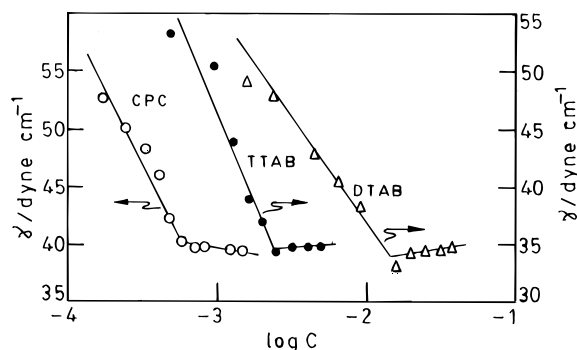
### Experimental Section

**Materials.** The amphiphiles DTAB, TTAB, and CTAB were products of Aldrich, Fluka, and E-Mark (Germany), respectively. They were 99% pure and, therefore, used as received. The CPC was a gift sample which was recrystallized from ethanol and stored in a desiccator. Pyrene (Aldrich) was purified by gel chromatography with cyclohexane as the solvent medium.

**Methods and Measurements.** All solutions were prepared in doubly distilled water of specific conductance 1.5–2.0  $\mu\text{S cm}^{-1}$  at 303 K. Measurements were taken under thermostated condition at 303  $\pm$  0.01 K.

**Conductivity.** Conductance measurements were taken with a Jenway, U.K., conductometer at 10 mHz using a dip-type cell of cell constant 1.0  $\text{cm}^{-1}$ . The errors in the conductance measurements were  $\pm$  0.50%. The surfactant solution was

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**Figure 1.** Surface tension ( $\gamma$ ) vs  $\log C$  plots for pure cationic surfactants at 303 K.

progressively added with the help of a Hamilton microsyringe to water (taken in a small beaker), and the conductance was measured after thorough mixing and temperature equilibrium.

**Surface Tension.** A du Nouy tensiometer Model K8 of Krüss, Germany, was used for the purpose. Tensions were measured by the principle of detachment of a platinum ring. Progressive addition of surfactant to water with the help of a microsyringe was made, and the tension was measured after thorough mixing and equilibrium, as described earlier.<sup>14</sup> The results were accurate within  $\pm 0.1 \text{ N m}^2$ .

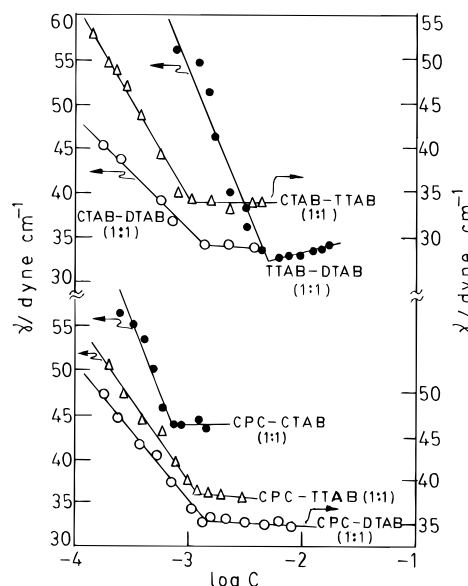
**Calorimetry.** The enthalpy of micellization was measured in a Tronac isoperibol titration calorimeter (at  $303 \pm 0.0002 \text{ K}$ ) whose calibration was checked by measuring the heat of neutralization of hydrochloric acid with sodium hydroxide. The experimental procedure was the same as described in earlier publications.<sup>14,41,42</sup> The accuracy of the instrument was  $\pm 0.5\%$  on 2 cal.

**Spectrophotometry.** A UV-visible Shimadzu (Japan) spectrophotometer was used for spectral measurements. A series of surfactant solutions of different concentrations were prepared, and their absorbances were measured at 258.5 nm using 0.5 cm silica cells. Since the surfactant CPC shows an absorption peak (by virtue of the pyridinium ion), the measurements were restricted to samples containing this surfactant only.

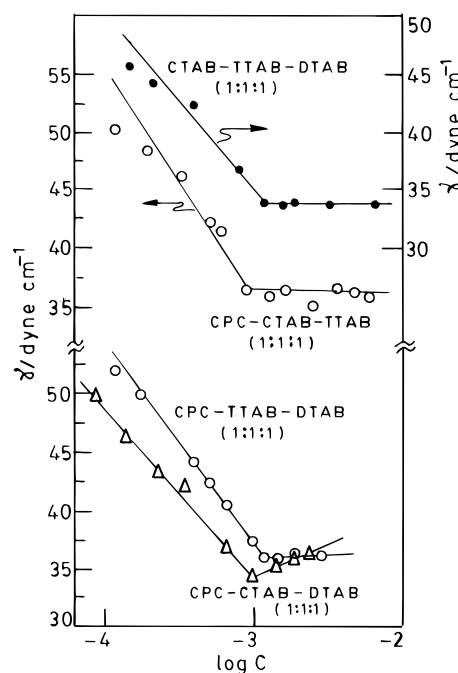
**Fluorimetry.** The fluorescence emission measurements were taken in a Perkin-Elmer Model MPF 44B fluorimeter by exciting the pyrene ( $10 \mu\text{mol dm}^{-3}$ ) at 335 nm and monitoring the emission in the range 350–550 nm. Fluorescence quenching was measured using CPC as the quencher. A series of surfactant solutions were prepared and their fluorescence intensities measured following the procedure used in spectrophotometry.

## Results and Discussion

**Critical Micelle Concentration (cmc).** The characteristic features of all the physical measurements employed are distinct breaks in the course of the physical properties with respect to concentration recognized as the cmc's of the surfactants. Representative illustrations are presented in Figures 1–6. The comprehensive results are presented in Table 1 along with the available literature reports. It is seen that the cmc's of the pure surfactants and their binary mixtures agree with literature values. Except for a few, all the methods have yielded comparable cmc values for the mixtures; method dependent variations are apparent. The mixtures of CPC with DTAB, TTAB, and CTAB have shown two cmc values by the spectrophotometric method. The second cmc is on the average 2–3 times higher than the first. The cmc's obtained by the other methods agree with the higher cmc. In an earlier work, we have reported<sup>14</sup> two cmc's of CTAB–bile salt mixtures. Treiner et al.<sup>26,35</sup> have reported that binary mixtures of some cationic surfactants show two cmc's by the conductance method; the second one is nearly 3

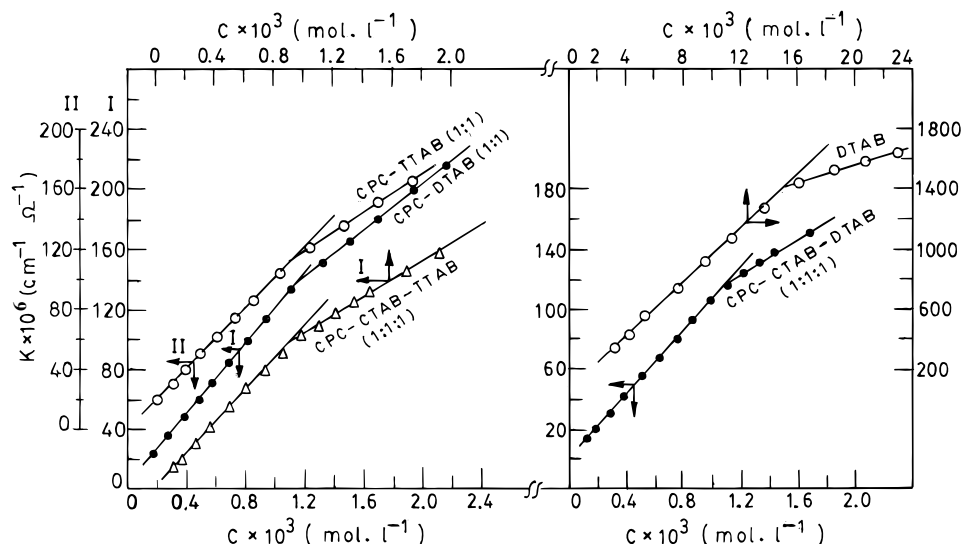


**Figure 2.** Surface tension ( $\gamma$ ) vs  $\log C$  plots for mixed cationic surfactants (1:1) at 303 K.

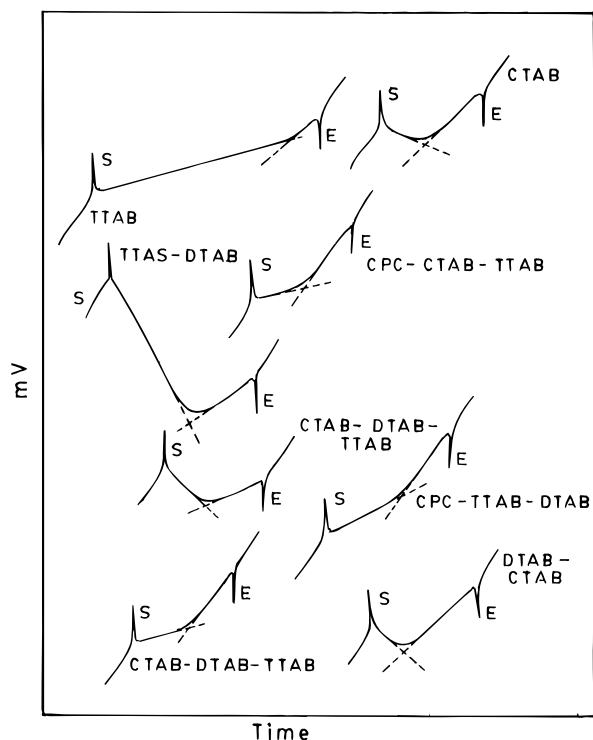


**Figure 3.** Surface tension ( $\gamma$ ) vs  $\log C$  plots for ternary mixed cationic surfactants (1:1:1) at 303 K.

times higher than the first. The binary mixtures of CTAB–DTAB, TTAB–DTAB, and CTAB–TTAB have also been investigated by Attwood and Patel.<sup>12</sup> It is obvious that cmc and hence cmc-derived parameters should depend on the methodology adopted; for general correlation,  $(\text{cmc})_{\text{av}}$  (average cmc) has been used. The cmc values are presented in Table 1. The cmc's determined by different methods vary, but individually the methods have shown good reproducibility. For the determination of surface tension of the surfactant solutions, sufficient time has been allowed after mixing to reach equilibrium. It is known that dewetting of cationic surfactants may pose problems in surface tension measurements. Our careful experimental measurements have produced consistent results. Usually, the cmc's of mixed surfactants fall in between the cmc's of the individual pure components. Except for the spectrophotometrically obtained first cmc's of binary mixtures of CPC, all cmc's lie in between the cmc's of the parent components for both binary and ternary mixtures.



**Figure 4.** Specific conductance ( $\kappa$ ) vs  $C$  plots for pure and mixed cationic surfactants at 303 K. The surfactant system and the ordinate scale are indicated in each plot.



**Figure 5.** Millivolt (mV) vs time of titration plots for pure and mixed cationic surfactants at 303 K. S and E represent the start and end of the run. The break point corresponds to the cmc.

The length of the hydrocarbon chain in a surfactant has been shown to be a major factor in guiding the cmc.<sup>43</sup> In a homologous series, the cmc normally decreases logarithmically with the number of carbon atoms ( $n_c$ ) in the chain according to the following relation

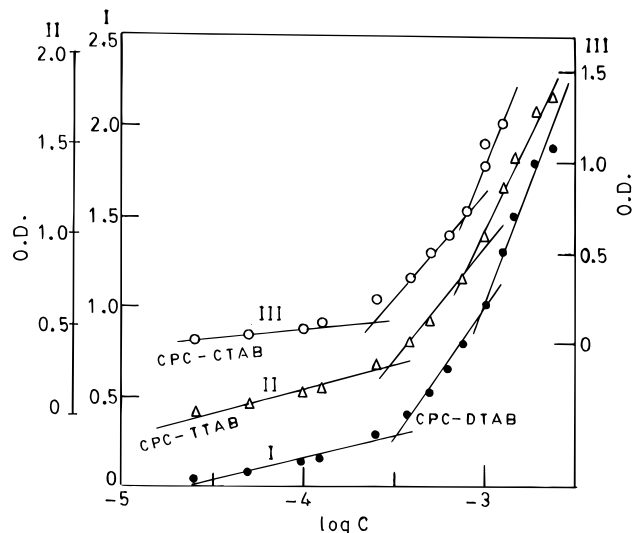
$$\log(\text{cmc}) = A - Bn_c \quad (1)$$

where  $A$  and  $B$  are constants specific to a homologous series under constant conditions of temperature, pressure, etc.

The  $\log(\text{cmc})_{\text{av}}$  vs  $n_c$  profile (where  $(\text{cmc})_{\text{av}}$  corresponds to the average of the three methods) is presented in Figure 7. It has been found that a linear relation of the form

$$\log(\text{cmc})_{\text{av}} = 6.25 - 0.427n_c \quad (2)$$

holds, and both pure and mixed surfactants can be brought under



**Figure 6.** OD vs  $\log C$  plot for CPC-CTAB, CPC-TTAB, and CPC-DTAB at 303 K. The surfactant system and the ordinate scale are indicated in each plot.

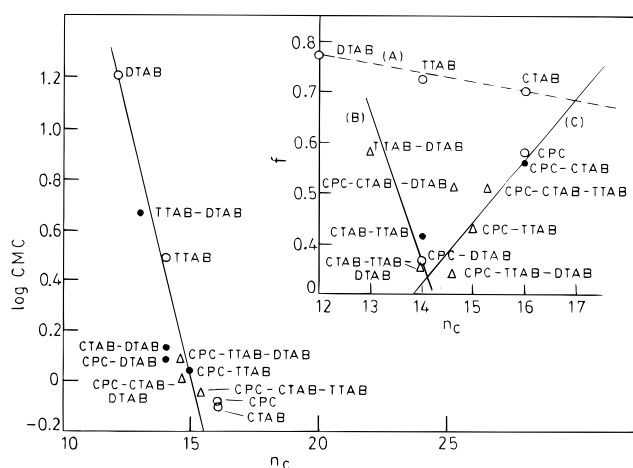
one rationale. For the mixtures, the average of the carbon numbers of the surfactants has been used in constructing Figure 7. Except CPC, all the surfactants in the present study are members of the same homologous series; they are, therefore, expected to follow eq 1. CPC has been found not to deviate from the trend; the pyridinium head group is thus not markedly different from the alkylammonium head group in the micellization behavior. The agreement of the measured  $(\text{cmc})_{\text{av}}$  with eq 2 suggests that the averaging procedure smooths out the deviations in the cmc.

**Counterion Binding.** Ionic micelles bind a considerable amount of counterions, which can be estimated by electrochemical measurements. Following the procedure of Evans,<sup>44</sup> the counterion association ( $f$ ) properties of the pure and mixed micelles (herein studied) have been evaluated from the ratio of the postmicellar and premicellar slopes obtained from the plots of specific conductance of the surfactant solution at different concentrations. The results are presented in Table 1. The  $f$  values are plotted with  $n_c$  in the inset of Figure 7. The pure micelles of DTAB, TTAB, and CTAB have shown higher but decreasing dependence (line A) of  $f$  on  $n_c$ ; the CPC deviates much from the line. The binary and ternary combinations have also shown such a linear but decreasing dependence of  $f$  on  $n_c$

**TABLE 1: Critical Micelle Concentration of Pure and Mixed Surfactants (Equimolar Proportion) at 303 K by Different Methods**

system	cmc $\times 10^3/\text{mol dm}^{-3}$					(cmc) <sub>av</sub>
	conductivity	ST	calorimetry	spectrophotometry	<i>f</i> %	
CPC	0.98 (0.90) <sup>63</sup>	0.60 (0.85) <sup>61</sup>	1.06	0.66	57.8	0.83
TTAB	3.60 (3.80) <sup>59</sup>	2.34 (3.40) <sup>60</sup>	3.31		73.4 (80) <sup>27</sup>	3.08
DTAB	15.8 (15.60) <sup>59</sup>	14.45 (14.0) <sup>62</sup>	17.85		76.6 (77) <sup>27</sup>	16.03
CTAB	0.90 (0.92) <sup>59</sup>	0.80 (0.80) <sup>60</sup>	0.70		70.0 (84) <sup>27</sup>	0.80
CPC-CTAB	0.92 (0.94) <sup>a</sup>	0.74 (0.68)	0.78 (0.84)	0.76	56.3	0.82
CPC-TTAB	1.15 (1.54)	1.20 (0.95)	1.14 (1.61)	0.78	43.4	1.10
CPC-DTAB	1.17 (1.84)	1.45 (1.15)	1.22 (3.78)	0.96	35.8	1.20
CTAB-TTAB	1.01 (1.44) <sup>b</sup>	1.04 (1.19)	1.18 (1.16)		58.3	1.08
CTAB-DTAB	1.36 (1.70) <sup>b</sup>	1.38 (1.51)	1.24 (1.35)		40.7	1.33
TTAB-DTAB	5.42 (5.86) <sup>b</sup>	4.57 (4.02)	6.11 (5.58)		57.8	5.37
CPC-CTAB-TTAB	0.96 (1.25)	0.87 (0.89)	0.85 (1.13)		51.0	0.89
CPC-CTAB-DTAB	1.03 (1.37)	0.95 (1.03)	1.09 (1.25)		51.6	1.02
CPC-TTAB-DTAB	1.23 (2.20)	1.20 (1.39)	1.23 (2.33)		33.4	1.22
CTAB-TTAB-DTAB	1.46 (2.07)	1.10 (1.72)	1.43 (1.70)		35.5	1.33

<sup>a</sup> The values in parentheses without references are obtained from the Clint equation (13). <sup>b</sup> cmc's 1.20, 1.40, and 5.41 for CTAB-TTAB, CTAB-DTAB, and TTAB-DTAB, respectively (ref 12).

**Figure 7.** Log(cmc)<sub>av</sub> vs  $n_c$  plot for pure and mixed cationic surfactants. Inset shows counterion binding (*f*) vs  $n_c$  plot for pure and mixed systems.

(line B). CPC and its binary and ternary mixture have shown a reverse trend (only CPC-CTAB-DTAB mixtures appreciably deviate). Whatever may be the trend, the *f* values of the mixed micelles are lower than the pure micelles. According to a previous report,<sup>27</sup> in the alkyltrimethylammonium bromide series, *f* increases with the chain length. We have found an opposite trend. The lower counterion association (lower *f*) found in the mixed systems compared to pure micelles means lowering of effective surface charge density in the mixed micelles. It will be seen in a subsequent section that the aggregation numbers of the pure and mixed micelles remain more or less the same; only a minor variation is observed. The lowering of the surface charge density of micelles in binary and ternary combinations of the studied amphiphiles thus appears to be unexpected.

**Properties at the Air–Water Interface.** Amphiphiles orient at the air–water interface and decrease surface tension. The amounts of their adsorption per unit area of the surface at various concentrations can be calculated with the help of the Gibbs adsorption equation. For surfactant mixtures in water, the Gibbs surface excess (relative to zero excess of water per unit area of surface) is related to the surface pressure  $\pi$  (=surface tension of water ( $\gamma_0$ ) – surface tension of surfactant solution ( $\gamma$ )) by the relation

$$d\pi = \sum \Gamma_i RT d \ln a_i \quad (3)$$

where  $\Gamma_i$  is the surface excess and  $a_i$  is the activity of the *i*th component, respectively, at temperature *T*. For a constant

**TABLE 2:  $\Gamma_{\max}$ ,  $A_{\min}$ , and  $\pi_{\text{cmc}}$  for Pure and Mixed Systems (Equimolar Proportion) at 303 K by Surface Tension**

system	$\Gamma_{\max} \times 10^6/\text{mol m}^{-2}$	$A_{\min}/\text{nm}^2$	$\pi_{\text{cmc}}/\text{erg cm}^{-2}$
CPC	$2.34 \pm 0.04$	$0.71 \pm 0.01$	32.0
CTAB	$1.12 \pm 0.02$	$1.48 \pm 0.02$ (1.40) <sup>14</sup>	31.4
TTAB	$2.32 \pm 0.05$	$0.72 \pm 0.02$ (0.75) <sup>27</sup>	32.0
DTAB	$1.40 \pm 0.12$	$1.18 \pm 0.06$ (0.77) <sup>27</sup>	39.0
CPC-CTAB	$1.21 \pm 0.11$	$1.37 \pm 0.13$ (1.04) <sup>a</sup>	26.5
CPC-TTAB	$1.64 \pm 0.06$	$1.01 \pm 0.04$ (0.67)	37.0
CPC-DTAB	$1.39 \pm 0.05$	$1.19 \pm 0.05$ (0.83)	36.5
CTAB-TTAB	$2.16 \pm 0.02$	$0.77 \pm 0.01$ (1.04)	39.0
CTAB-DTAB	$1.13 \pm 0.02$	$1.46 \pm 0.03$ (1.19)	37.5
TTAB-DTAB	$1.73 \pm 0.02$	$0.96 \pm 0.01$ (0.83)	38.0
CPC-CTAB-TTAB	$1.56 \pm 0.02$	$1.06 \pm 0.01$ (0.91)	34.5
CPC-CTAB-DTAB	$1.28 \pm 0.01$	$1.30 \pm 0.01$ (1.01)	37.5
CPC-TTAB-DTAB	$0.81 \pm 0.01$	$2.04 \pm 0.02$ (0.70)	35.5
CTAB-TTAB-DTAB	$1.20 \pm 0.01$	$1.38 \pm 0.05$ (1.01)	37.5

<sup>a</sup> Values in parentheses are by eq 7.

composition of the ionic surfactant mixture with total concentration *C*,

$$\Gamma = 1/4.61RT[d\pi/(d \log C + d \log \gamma_{\pm})] \quad (4)$$

Dilute solutions of surfactants can be considered ideal (as in the present study), and the activity coefficient containing term  $d \log \gamma_{\pm}$  can thus be neglected in the calculation.

The maximum surface excess ( $\Gamma_{\max}$ ) and the minimum area per molecule of a surface active compound ( $A_{\min}$ ) can be estimated from the relations<sup>41,42</sup>

$$\Gamma_{\max} = (1/4.61RT) \lim_{C \rightarrow \text{cmc}} (d\pi/d \log C) \quad (5)$$

and

$$A_{\min} = 10^{18}/N\Gamma_{\max} \quad (6)$$

where *N* is the Avogadro number.

$\Gamma_{\max}$  and  $A_{\min}$  have been evaluated for the present systems from the least squares slopes of the  $\pi$  vs  $\log C$  plot (figure not shown). The results are presented in Table 2 with errors in  $\Gamma_{\max}$  and  $A_{\min}$ . The  $\Gamma_{\max}$  values are on the same order as reported for cationic surfactants of various chain lengths<sup>45,46</sup> and CTAB–bile salt mixtures recently studied by us.<sup>14</sup> On the whole,  $(A_{\min})_{\text{pure}} < (A_{\min})_{\text{binary}} < (A_{\min})_{\text{ternary}}$ . Decreased surface charge density of the micelles with increased molecular heterogeneity of the mixed surfactants may occur due to increased micellar size by interamphiphile repulsive interaction.

**TABLE 3:  $\Delta G_m^\circ$ ,  $\Delta H_m^\circ$ ,  $\Delta S_m^\circ$ , and  $\Delta G_{ad}^\circ$  of the Pure and Mixed Surfactant Systems (Equimolar Proportion) at 303 K<sup>a</sup>**

system	$\Delta G_m^\circ$ / kJ mol <sup>-1</sup>	$\Delta H_m^\circ$ / kJ mol <sup>-1</sup>	$\Delta S_m^\circ$ / J K <sup>-1</sup> mol <sup>-1</sup>	$\Delta G_{ad}^\circ$ / kJ mol <sup>-1</sup>
CPC	-28.2	-5.60	74.6	-41.2
CTAB	-30.5	-8.57	72.4	-57.1
TTAB	-25.3	-7.35	59.2	-38.2
DTAB	-18.4	-1.77	54.9	-41.3
CPC-CTAB	-28.0	-11.33	55.0	-41.3
CPC-TTAB	-24.6	-5.67	62.5	-44.6
CPC-DTAB	-23.0	-5.69	57.1	-48.2
CTAB-TTAB	-27.2	-5.40	71.9	-45.3
CTAB-DTAB	-23.5	-4.92	61.3	-55.5
DTAB-TTAB	-20.8	-4.42	54.1	-41.0
CPC-CTAB-TTAB	-26.7	-5.45	70.1	-50.7
CPC-CTAB-DTAB	-26.3	-5.90	67.3	-54.1
CPC-TTAB-DTAB	-22.5	-5.56	53.9	-65.8
CTAB-TTAB-DTAB	-22.6	-3.19	64.1	-50.4

<sup>a</sup> The (cmc)<sub>av</sub> values from Table 1 have been used for the free energy calculation.

Since the head groups of the surfactants herein used are the same (except CPC), the origin of the increased repulsion with increased number of components eludes a straightforward explanation. Assuming ideal mixing, the minimum area occupied by an amphiphile molecule at the interface has been calculated by the equation

$$A_{\min}^{\text{mix}} = \sum \alpha_i A_{\min}^i \quad (7)$$

where  $\alpha_i$  is the mole fraction of the  $i$ th component and  $A_{\min}^i$  is its minimum area at the interface in the pure state.

The calculated values of  $A_{\min}^i$  are given in parentheses in column 3 of the Table 2. Except CPC, the amphiphiles have identical head groups. The calculated  $A_{\min}^{\text{mix}}$  values according to eq 7 are different from the experimental values. Except CPC-CTAB and CTAB-TTAB, the latter values are higher than the calculated ones; the disagreements are more than the experimental uncertainties. The composition of the adsorbed mixed surfactant layer may not be equal to the bulk composition;<sup>47</sup> the calculated values based on  $\alpha_i = 0.5$  may thus be erroneous. However, this cannot account for higher experimental values for mixtures having components each with  $A_{\min}^i$  of lower magnitude than  $A_{\min}^{\text{mix}}$ . Increased charge repulsion among amphiphiles of similar head groups leading to increased values of  $A_{\min}^{\text{mix}}$  is also ruled out. Factors other than interfacial composition are responsible for the unexpected surface behavior. The results show that the mixing is not ideal with different surface composition. A critical examination of the phenomenon is needed.

**Thermodynamics of Interfacial Adsorption and Micelle Formation.** The standard free energy of adsorption ( $\Delta G_{ad}^\circ$ ) of the surfactants at the air-water interface has been evaluated by the equation<sup>48</sup>

$$\Delta G_{ad} = \Delta G_m^\circ - (\pi_{\text{cmc}}/\Gamma_{\text{max}}) \quad (8)$$

where  $\Delta G_m^\circ$  is the free energy of micellization (discussed below),  $\pi_{\text{cmc}}$  is the surface pressure at cmc, and  $\Gamma_{\text{max}}$  is the maximum surface excess of the amphiphile.

The  $\Delta G_{ad}^\circ$  values are given in column 5 of Table 3. It is seen that except CTAB, CTAB-DTAB, CPC-CTAB-DTAB and CTAB-TTAB-DTAB, all systems on the whole have exhibited comparable spontaneity of adsorption. Critically, the adsorption of the mixed amphiphiles is more favorable than the pure amphiphiles. The  $\Delta G_{ad}^\circ$  values realized in the present study are comparable to the results recently reported on CTAB-bile salt mixtures<sup>14</sup> as well as on pure and mixed nonionic

surfactants.<sup>48</sup> The  $\Delta G_m^\circ$  and  $\Delta G_{ad}^\circ$  are both negative. Their magnitudes reveal the latter to be more spontaneous than the former. The hydrophobicity of the amphiphiles primarily leads them toward the air-water interface, and the formation of micelles occurs above a critical concentration (cmc); the latter process is secondary and less spontaneous.

The standard free energy of micellization per mole of monomer unit ( $\Delta G_m^\circ$ ) of ionic surfactants is related to the cmc by the following relation:

$$\Delta G_m^\circ = (1 + f)RT \ln \text{cmc} \quad (9)$$

Equation 9 is very frequently used both for pure and mixed surfactants.<sup>45,49</sup> Using the (cmc)<sub>av</sub> and the  $f$  values presented in Table 1, the  $\Delta G_m^\circ$  values for the studied pure and mixed surfactant systems have been computed and listed in Table 3. For a complete thermodynamic understanding, the enthalpy of micellization ( $\Delta H_m^\circ$ ) has been evaluated from the calorimetric runs following the procedure described earlier.<sup>14</sup> From the Gibbs equation ( $\Delta S_m^\circ = (\Delta H_m^\circ - \Delta G_m^\circ)/T$ ) the entropy of micellization has been obtained. The estimated energetic parameters are reasonably accurate since the  $\Delta H_m^\circ$  values are directly obtained by calorimetry and not from the temperature coefficient of  $\Delta G_m^\circ$  according to the van't Hoff equation. The thermodynamic parameters given in Table 3 are not vastly different in a particular mixture; they have on the whole a mild variation. The formation of the different micelles is energetically comparable. As expected, all the micellization processes end up with a considerable positive entropy change.<sup>50</sup> For the pure micelles, entropy increase follows the order DTAB > TTAB > CTAB > CPC. In the cases of binary and ternary mixtures a specific trend in the thermodynamic parameters has not been witnessed. The  $\Delta H_m^\circ < T\Delta S_m^\circ$  results manifest the micellization process to be entropy controlled. Randomness produced by the melting of the icebergs around the nonpolar tail during micelle formation and increased randomness of the tails in the micellar interior act in conjunction for the entropy increase.

**Fluorescence Behavior and Micellar Aggregation.** The quenching of fluorescence of a suitable probe by a quencher has been successfully utilized to find out the micellar aggregation number<sup>51-53</sup> as well as the binding constant of the quencher with the probe. The relations used are the following:

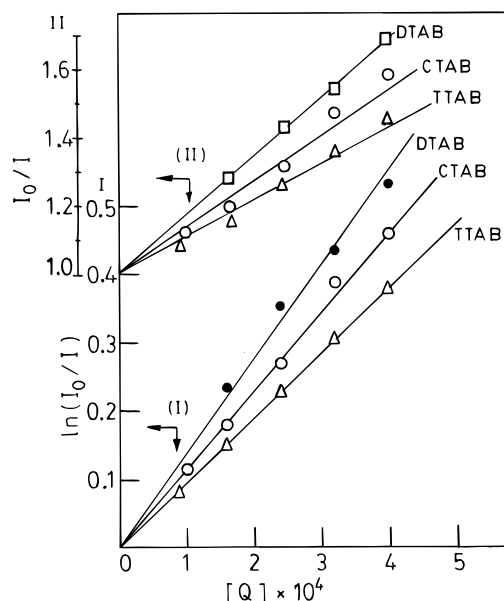
$$\ln(I_0/I) = [Q]n/([\text{surf}] - \text{cmc}) \quad (10)$$

and

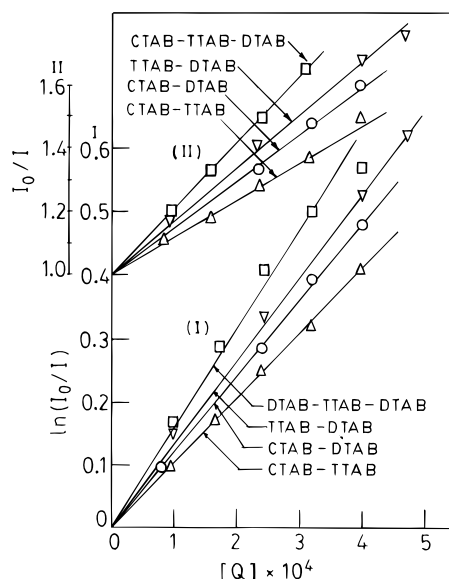
$$I_0/I = 1 + K_{SV}[Q] \quad (11)$$

where  $I_0$  and  $I$  are the fluorescence intensities in the absence and presence of a quencher (Q),  $n$  is the average aggregation number, and  $K_{SV}$  is the Stern-Volmer binding constant of the quencher with the probe (a 1:1 complex is assumed). In eq 10, a pseudophase micellization process has been assumed.

The graphical presentations of the experimental results are illustrated in Figures 8 and 9, and the  $n$  and  $K_{SV}$  are given in Table 4. The aggregation numbers of pure surfactant micelles have followed the order CTAB > TTAB > DTAB; the higher hydrocarbon chain in the surfactant homologues has yielded higher  $n$ . The binary mixtures have comparable aggregation numbers, whereas the ternary mixture has produced higher  $n$ . The reported  $n$  values<sup>54-56</sup> on the studied pure micelles of DTAB, TTAB, and CTAB agree fairly well with the present findings. In the present experimental procedure, CPC has been used as the quencher; therefore, micelles formed with CPC cannot be probed for determining  $n$  and  $K_{SV}$ . A trial of vapor



**Figure 8.** Graphical processing of fluorescence data on pure surfactants at 303 K: (I)  $\ln(I_0/I)$  vs  $[Q]$  plot according to eq 10; (II)  $(I_0/I)$  vs  $[Q]$  plot according to eq 11.



**Figure 9.** Graphical processing of fluorescence data on mixed surfactants at 303 K: (I)  $\ln(I_0/I)$  vs  $[Q]$  plot according to eq 10; (II)  $(I_0/I)$  vs  $[Q]$  plot according to eq 11.

pressure osmometry to study these unexplored samples has not been found to be adequately sensitive for obtaining  $n$  and  $K_{SV}$  with reasonable accuracy. The  $K_{SV}$  values are on the same order (a higher value has been observed for the CTAB-TTAB-DTAB ternary mixture). The  $K_{SV}$  values obtained in the cases of pure ionic and nonionic micelles (sodium dodecyl sulfate, Triton x-100, and Tweens) using anthracene sulfonate as the fluorescence probe and CPC as the quencher are reasonably higher than the present values.<sup>53</sup>

The ratio of the first and third vibronic peaks, i.e.,  $I_1/I_3$ , in the pyrene fluorescence emission spectrum can be a measure of the polarity of the micellar interior (pyrene dissolves in the core of the normal micelles). Normally, low and high values of  $I_1/I_3$  should indicate the environment to be nonpolar and polar, respectively. Such measurements have been performed at  $[\text{pyrene}] = 5 \text{ mmol dm}^{-3}$ . The  $I_1/I_3$  values for the pure, binary, and ternary systems have been found to be small and more or less similar (Table 4). In the case of pure CPC no sharp peak has been observed, which, however, has appeared in the

**TABLE 4: Micellar Polarity, Aggregation Number, and Stern-Volmer Constant for Pure and Mixed Surfactants (Equimolar Proportion) at 303 K**

system	polarity	agg. no <sup>a</sup>	$K_{VS} \times 10^{-3}$
CTAB	1.19	62 (61) <sup>56</sup>	1.36
TTAB	1.26	55 (58) <sup>56</sup>	1.33
DTAB	1.42	48 (50) <sup>54,55</sup>	1.66
CTAB-TTAB	1.20	50	1.18
CTAB-DTAB	1.22	58	1.40
TTAB-DTAB	1.23	60	1.61
CTAB-TTAB-DTAB	1.22	76	2.04
CPC-CTAB	1.20		
CPC-TTAB	1.22		
CPC-DTAB	1.33		
CPC-CTAB-TTAB	1.27		
CPC-CTAB-DTAB	1.26		
CPC-TTAB-DTAB	1.29		

<sup>a</sup> cmc by the ST method has been used in eq 10.

mixtures. Direct information on pure CPC micelles has been, therefore, restricted. On a comparative basis the polarity of its micellar interior is also considered to be low.

**Interactions of Surfactants in Micelles.** For an ideal binary mixture of surfactants, the cmc's are related by the Clint equation:<sup>15</sup>

$$1/\text{cmc}_{\text{mix}} = \alpha_1/\text{cmc}_1 + \alpha_2/\text{cmc}_2 \quad (12)$$

where  $\text{cmc}_{\text{mix}}$ ,  $\text{cmc}_1$ , and  $\text{cmc}_2$  are the cmc values of the mixture, component 1, and component 2, respectively;  $\alpha_1$  and  $\alpha_2$  are the mole fractions of the respective components in solution.

For multicomponent systems, eq 12 may be written as

$$1/\text{cmc}_{\text{mix}} = \sum \alpha_i/\text{cmc}_i \quad (13)$$

where  $\alpha_i$  and  $\text{cmc}_i$  are the mole fractions and cmc of the  $i$ th component, respectively. The  $\text{cmc}_{\text{mix}}$  obtained by eq 13 are presented in Table 1. Except for several cases, the observed cmc's are not very different from the calculated values. Equation 13 is rarely obeyed by mixed surfactant solutions: nonionic mixed surfactants may show ideal solution behavior and hence obey eq 13. The deviations of the experimentally determined cmc's from those of the calculated ones indicate the degree of nonideality.

The mutual interaction of surfactants in the mixed micelles leading to nonideality has been theoretically treated by Rubingh<sup>17</sup> in the light of regular solution theory. The mole fraction of surfactant 1 in solution ( $\alpha_1$ ), its mole fraction in the micelle ( $x$ ), and the mixed cmc ( $\text{cmc}_{\text{mix}}$ ) are related by the relation

$$\frac{x^2 \ln[\text{cmc}_{\text{mix}} \alpha_1 / \text{cmc}_1 x]}{(1-x)^2 \ln[\text{cmc}_{\text{mix}} (1-\alpha_1) / \text{cmc}_2 (1-x)]} = 1 \quad (14)$$

where  $\text{cmc}_1$  and  $\text{cmc}_2$  are the critical micelle concentrations of surfactant 1 and 2, respectively.

The intersurfactant interaction coefficient in the mixed micelle,  $\beta$ , is given by the equation

$$\beta = \ln(\text{cmc}_{\text{mix}} \alpha_1 / \text{cmc}_1 x) / (1-x)^2 \quad (15)$$

A positive  $\beta$  value means repulsion between the mixed species, while a negative  $\beta$  advocates attraction.

The activity coefficients of the components 1 and 2 in the mixed micelle,  $g_1$  and  $g_2$ , respectively are given by the relations

$$g_1 = \exp[\beta(1-x)^2] \quad (16)$$

and

$$g_2 = \exp[\beta x^2] \quad (17)$$

In Tables 5 and 6 the micellar composition  $x$  (mole fraction of the first named component) and the  $\beta$  values for the binary

**TABLE 5:  $x$ ,  $\beta$ ,  $g_1$ , and  $g_2$  Values for Binary Mixed Surfactants (Equimolar Proportion) According to Rubingh's Proposition Obtained from Conductance, Calorimetric, and Surface Tension Data at 303 K**

system	$x(\beta)$ (cond)	$x(\beta)$ (cal)	$x(\beta)$ (ST)	$x(\beta)$ (cmc <sub>av</sub> )	$g_1(g_2)$ (ST)	$g_1(g_2)$ (av)
CPC-CTAB	0.48 (-0.08)	0.41 (-0.32)	0.52 (+0.74)	0.49 (+0.03)	1.188 (1.218)	1.008 (1.007)
CPC-TTAB	0.68 (-1.44)	0.65 (-1.62)	0.74 (+4.48)	0.71 (-0.82)	1.347 (11.781)	0.933 (0.661)
CPC-DTAB	0.75 (-3.65)	0.74 (-3.67)	0.95 (+89.73)	0.75 (-0.59)	1.251 (high)	0.963 (0.717)
CTAB-TTAB	0.68 (-1.87)	0.82 (+0.84)	0.70 (-3.48)	0.72 (-0.82)	0.735 (0.187)	0.938 (0.654)
CTAB-DTAB	0.81 (-1.92)	0.90 (-1.19)	0.88 (-1.95)	0.86 (-1.73)	0.974 (0.217)	0.966 (0.278)
TTAB-DTAB	0.77 (-0.43)	0.83 (+3.66)	0.84 (+5.88)	0.86 (+0.69)	1.162 (63.367)	1.014 (1.665)

**TABLE 6: Values of  $x$ ,  $\beta$ ,  $g_1$ , and  $g_2$  for Ternary Systems (Equimolar Proportion) According to Rubingh's Proposition from Conductance, Calorimetric, and Surface Tension Data at 303 K**

system	$x(\beta)$ (cond)	$x(\beta)$ (cal)	$x(\beta)$ (ST)	$x(\beta)$ (cmc <sub>av</sub> )	$g_1(g_2)$ (av)	$g_1(g_2)$ (ST)
(CPC-CTAB)-TTAB	0.24 (-1.73)	0.22 (-1.56)	0.19 (-0.66)	0.22 (-1.37)	0.434 (0.936)	0.648 (0.976)
CPC-(CTAB-TTAB)	0.35 (-0.18)	0.41 (-1.26)	0.44 (+0.26)	0.41 (-0.42)	0.864 (0.932)	1.085 (1.052)
CTAB-(CPC-DTAB)	0.41 (-0.44)	0.47 (-0.56)	0.48 (-1.07)	0.44 (-0.58)	0.834 (0.894)	0.749 (0.784)
(CPC-CTAB)-DTAB	0.18 (-3.16)	0.06 (-1.23)	0.11 (-2.05)	0.13 (-2.41)	0.161 (0.960)	0.197 (0.975)
CPC-(CTAB-DTAB)	0.43 (-0.66)	0.38 (-0.29)	0.52 (+0.02)	0.45 (-0.34)	0.902 (0.933)	1.005 (1.005)
CTAB-(CPC-DTAB)	0.40 (-0.15)	0.40 (+0.69)	0.62 (-3.17)	0.43 (-0.07)	0.977 (0.987)	0.648 (0.284)
(CPC-TTAB)-DTAB	0.20 (-3.20)	0.19 (-3.23)	0.22 (-3.42)	0.18 (-3.20)	0.116 (0.902)	0.125 (0.847)
CPC-(TTAB-DTAB)	0.61 (-2.54)	0.61 (-3.06)	0.72 (-1.11)	0.64 (-2.14)	0.758 (0.416)	0.917 (0.562)
TTAB-(CPC-DTAB)	0.24 (-1.31)	0.26 (-1.37)	0.34 (-1.60)	0.26 (-1.26)	0.502 (0.918)	0.498 (0.831)
(CTAB-TTAB)-DTAB		0.15 (-2.40)	0.20 (-3.24)	0.14 (-2.21)	0.195 (0.958)	0.126 (0.126)
CTAB-(TTAB-DTAB)	0.65 (-1.58)	0.73 (-1.08)	0.62 (-2.16)	0.66 (-1.59)	0.832 (0.500)	0.732 (0.436)
TTAB-(CTAB-DTAB)	0.24 (-1.01)	0.21 (-0.62)	0.34 (-1.80)	0.27 (-1.20)	0.528 (0.916)	0.456 (0.812)

and ternary compositions are presented. For the ternary mixtures, the four sets of results stand for three possible pairings taking two of the components as one and the third as the other. It is seen from Table 5 that, except for CPC-CTAB, the mole fractions of the surfactants are all appreciably different from the stoichiometric composition of 1:1. The  $x$  values have a modest dependence on the methodology of cmc determination. Results on the basis of (cmc)<sub>av</sub> are also presented in Table 5. The  $\beta$  values are mostly negative; of the six binary combinations, four are positive by the surface tension method. Although repulsive interaction among similarly charged cationic surfactants yielding positive  $\beta$  is expected (and realized from the surface tension (ST) method to a small extent), they are all negative by conductance and calorimetry. This reverse trend in the  $\beta$  values is not uncommon, but this is a serious anomaly with Rubingh's<sup>15</sup> theory for the binary mixtures possessing identical quaternary ammonium ionic head groups but differing in tail lengths.

For the ternary mixtures, both  $x$  and  $\beta$  values are obviously found to depend on the way of selection of the pairing of the three components. Moreover, the  $\beta$  values are all negative, except three marginal cases, two by the ST method and one by calorimetry. The dominance of attractive interaction among the surfactants in the mixed micelles by Rubingh's approach is again contrary to expectation.

The results of the  $g$  values for the binary mixtures obtained by relations 16 and 17 are presented in Table 5. The activity coefficients of the surfactants in the ternary mixtures based on

the pairing sequence (given in Table 6) have also been obtained by relations 16 and 17. Calculations of  $g$  values by other methods would maintain a similar trend, but they would differ in magnitude. Results based on (cmc)<sub>av</sub> are also presented in Tables 5 and 6 for comparison. The individual  $g$  values indicate the deviations of the surfactants from ideality in the mixed micelle. For the pairs CPC-TTAB, TTAB-DTAB, and CPC-DTAB, the  $g_2$  values are abnormally high, and the rest are more or less of normal magnitudes. The  $g$  values of the ternary mixtures are also of normal magnitudes, and those of the CTAB-DTAB-TTAB system are fairly low. We have examined the dependence of the energetic parameters on  $\beta$ . The parameters have been found to exhibit more or less regular trends with  $\beta$ ;  $\Delta H_m^\circ$  and  $\Delta G_m^\circ$  increase with  $\beta$ , whereas  $\Delta S_m^\circ$  decreases. The trends for binary mixtures are on the whole linear with poor correlations (correlation coefficients 0.6–0.7), while the trends for ternary mixtures are distinctly nonlinear. The parameters for the mixtures relative to the corresponding pure surfactants have not shown regular trends with  $\beta$ . However,  $\Delta S_m^\circ$  has shown fairly good correlation (correlation coefficient = 0.87) with  $A_{\min}^{\text{mix}}$ , whereas for  $\Delta G_m^\circ$  and  $\Delta H_m^\circ$  poor correlations are observed. Like micellization, interfacial accommodation of surfactant mixtures also appears to be entropy directed.

In a recent publication Hoffmann et al.<sup>57</sup> have presented a critical discussion on the interaction parameter and possible errors in  $\beta$ . According to the authors, the error in the calculation



of the interaction parameter arises due to the errors in cmc values, the macroscopic micellar ratio, and the degree of the interaction between the surfactant components.

From Table 5 we observe minimum error in  $\beta$  values when the micellar mole fraction lies around 0.5. The errors in  $\beta$  values corresponding to an asymmetric mixing ratio are found to be much higher. This may be due to weak interactions between the surfactants. A similar trend was noticed in the mixed system studied by Hoffman et al.<sup>57</sup>

Interactions between the surfactants also affect the adsorption of surfactants at the interface. We have discussed this in another section (Thermodynamics of interfacial Adsorption and Micelle Formation).

Very recently, Puvvada et al.<sup>19–22</sup> have proposed a rigorous theoretical treatment for binary mixed micelle formation and relations for predicting cmc, aggregation number, counterion binding, activities of the components in the mixed micelle, etc. This molecular thermodynamic theory has been used by us for surfactant mixtures.<sup>58</sup> For hydrocarbon-based surfactant ions of similar types, the theory leads to the ideal equation (eq 12) of Clint. Puvvada et al.'s approach is thus not valid for the studied mixtures of cationic surfactants having similar charges on their head groups. Interestingly, despite inherent limitations, Rubingh's approach can be applied to the mixed cationic surfactants which show deviations from Clint's equation (i.e., from ideality), corroborated by experiments.

## Conclusions

The investigation leads to the following conclusions.

- (1) The cmc values obtained by different methods satisfactorily agree and the counterion binding capacity of the micelles is lowered when they are in the mixed states, whereas the aggregation numbers depend on the chain length.
- (2) The cmc of the mixed micelles and the activity coefficients of the components in the mixed micellar states indicate nonideality.
- (3) Except for a few cases, the micellization process is associated with comparable entropy changes.
- (4) The micellar polarities are low and comparable.

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