

CHAPTER-VI

Physicochemistry of Mixed Micellization: Binary and Ternary Mixtures of Cationic Surfactants in Aqueous Medium

INTRODUCTION

Mixed aqueous surfactant systems often exhibit better performance over the individual components^{1,2} in terms of lowering of surface tension of aqueous solution. These systems are, thus, capable of exhibiting enhanced detergency and solubilizing capacity for insoluble substances in aqueous solution, and are widely used in the areas of suspension, wetting, emulsification, and different technological, biochemical, pharmaceutical applications³. The molecular structures of amphiphiles, their concentration, and composition along with the environmental conditions, such as temperature, *pH*, pressure, presence of additives³ significantly influence the activity of the surfactant mixtures.

Owing to their amphiphilic nature, surfactants prefer to get adsorbed interfacially in the low concentration region; whereas above a certain critical concentration, they self-aggregate to form assembled structure. The size, shape and composition of these aggregated structures depend on the amphiphile concentration and other physicochemical parameters like temperature, presence of salt, etc. The critical amphiphile concentration required for the onset of formation of such aggregates (known as micelles) is referred to as the critical micellar concentration (*cmc*). Because micelles can be treated to form a separate phase within a surfactant solution, various physicochemical properties could, therefore, change dramatically depending upon whether the micelles are formed or not. Measurement of such properties with varying surfactant concentration leads to a discontinuity in the profile which allows the determination of *cmc* of the surfactant. The properties generally exploited in *cmc* determination include surface tension⁴⁻⁹, conductance⁴⁻⁹,

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Colloid and Polymer Science, 2008 (Communicated)

fluorescence intensity¹⁰, heat capacity^{11, 12}, light scattering¹³. The changes in these properties occur over a narrow range of surfactant concentration. Moreover, the concentration dependent changes in these properties in the pre- and postmicellar regions can be described by two separate straight lines and their point of intersection may be taken as the *cmc* of the surfactant.

Investigations on the interactions between the surfactants in a mixture could provide valuable information regarding the self-aggregation and association thermodynamics in such systems¹⁴⁻³¹. In this chapter, studies on the binary and ternary combinations of three cationic surfactants namely, dodecylpyridinium chloride (DPC), cetylpyridinium chloride (CPC), and tetradecyltrimethylammonium bromide (TTAB) have been reported. The first two (DPC and CPC) have the same pyridinium head groups and different tail lengths (12 and 16 C) whereas TTAB has a methyl substituted quaternary ammonium head group linked with a 14 C tail. Three binary combinations, CPC/TTAB, DPC/TTAB and CPC/DPC and the ternary mixture of CPC/DPC/TTAB have been studied using tensiometry and conductometry. Various parameters such as *cmc*, Gibbs surface excess (Γ_{\max}), minimum area of exclusion per surfactant monomer at the air/solution interface (A_{\min}), pC_{20} (where C_{20} is the surfactant concentration required to decrease the surface tension of the solvent by 20 units), degree of counterion binding (g) on micellar interface along with such thermodynamic parameters as Gibbs adsorption energy (ΔG_{ad}^0), Gibbs micellization energy (ΔG_{m}^0), can be obtained by using these two methods. Existing theories of Clint³², Rosen^{33, 34}, Rubingh³⁵, Motomura³⁶⁻³⁷, Blankshtein³⁸⁻⁴⁰, Rubingh and Holland⁴¹ are applied to evaluate the theoretical *cmc*, micellar and interfacial mole fractions and interaction parameters among the surfactants in micellar and interfacial monolayer, surface free energy, activity coefficient, etc.

EXPERIMENTAL

Materials and Methods

The cationic surfactants dodecylpyridinium chloride (DPC), cetylpyridinium chloride (CPC), and tetradecyltrimethylammonium bromide (TTAB) were purchased from Sigma (USA). All the products were used without further purification. The solutions were prepared in doubly distilled water and the experiments were performed at 298.15K.

The tensiometric experiments are performed using a platinum ring by the ring detachment method in a calibrated K9 Tensiometer (Krüss, Germany) details of which have been reported in Chapter II. Each experiment was repeated several times to achieve good reproducibility. The measured surface tension (γ) values were corrected according to the procedure of Harkins and Jordon. The uncertainties in the γ values were always within $\pm 0.1 \text{ mN m}^{-1}$.

The conductance measurements were done with a Pye-Unicam PW-9509 conductivity meter at a frequency of 2000 Hz using a conductivity cell of cell constant 1.0 cm^{-1} . The uncertainty of the measurements was within $\pm 0.1\%$. The measurement details can be found in Chapter II.

RESULTS AND DISCUSSION

Critical micellar concentration (cmc) determination

The *cmc* obtained tensiometrically corresponds to the surfactant concentration at which there is a distinct break in the air/solution interfacial tension vs. $\log[\text{surfactant}]$ isotherms (Fig. 1). Phenomenologically, this *cmc* corresponds to the saturation of interfacial adsorption. Beyond this concentration, the added surfactant molecules can hardly affect the topology of the interfacially adsorbed surfactant monolayer rather they prefer to self-associate in the bulk solution to form micelles whereby the hydrophobic tails of individual surfactant monomers are buried within hydrophilic encapsulation provided by their polar head groups^{5, 23}. On initiation of the self-association, the counterions of ionic surfactants with significantly large mobility start to adsorb onto the micelle-solution interface. This leads to a dramatic change in the electrical transport property of the solution as a result of a decrease in the number of effective charge carriers in solution and is reflected in a sharp break in the specific conductance (κ) vs. surfactant concentration isotherm (Fig. 2). The conductometric *cmc*, therefore, corresponds to the initiation of self-association of ionic surfactants in bulk solution. If the interfacial saturation and bulk association processes are coherent, the *cmc* values obtained by either method should agree with each other.

For all the pure surfactants, *cmc* determined by either method are found to be in close agreement with each other (*cf.* Tables 1 and 2). The *cmc* values were found to

increase as the tail length of the surfactants decreases. Although, CPC and DPC have the same pyridinium head groups, their *cmc* differs by a factor of ~ 19 reflecting that the hydrophobic interaction predominates over the electrostatic interaction in the micellization process.

For CPC/TTAB and DPC/TTAB binary systems, the *cmc* values obtained from conductometry and tensiometry are in reasonable agreement whereas for CPC/DPC mixed system, the tensiometric *cmc* is found to be much lower than that determined by conductometry signifying a concentration delay (lag) between interfacial saturation and self-aggregation processes. In all the mixtures, the *cmc* values are close to the component with higher tail length (lower *cmc*) and these increase with increasing stoichiometric mole fraction of the shorter-tail-component in the mixture. A detailed discussion on this aspect has been made in the theoretical section (see later).

Interfacial adsorption

The process of interfacial adsorption is mainly entropy-driven whereby there is an expulsion of water molecules solvating the monomer in bulk solution through hydrophobic hydration on micellization. In some cases, exothermic enthalpy change associated with the micellization process adds to the entropic effect to make the process thermodynamically spontaneous. The onset of interfacial saturation can be envisaged from a sharp break in the tensiometric isotherm beyond which the interfacial tension remains almost invariant with surfactant concentration. The interfacial tension at the point of *cmc* (γ_{cmc}) is a measure of efficacy of the surfactant to reduce the interfacial tension of the solution in the form of a monolayer. The same for a surfactant or a mixture of surfactants toward interfacial adsorption is quantified by the Gibbs surface excess (Γ_{max}) at the air/water interface and can be calculated using the least-squares slope of Π vs. $\log C$ plot^{4-10, 42} using Eq. (1)

$$\Gamma_{max} = -\frac{1}{2.303nRT} \text{Lt}_{C \rightarrow cmc} \frac{d\Pi}{d \log C} \quad (1)$$

where Π is the surface pressure ($\gamma_{H_2O} - \gamma_{surfactant}$), R is the universal gas constant, T is the absolute temperature, and n is the average number of ions present in solution per

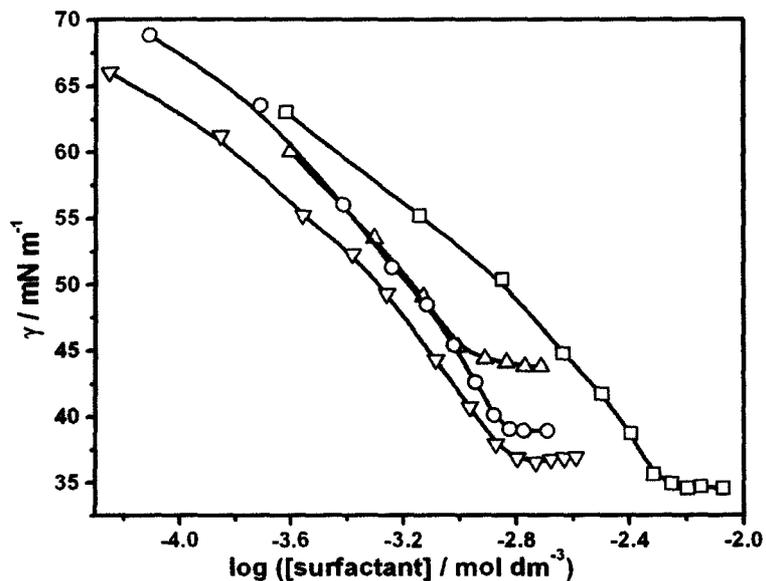


Figure 1. Tensiometric plot of binary mixtures (∇) CPC/TTAB, $\alpha_{\text{CPC}} = 0.25$; (\square) DPC/TTAB, $\alpha_{\text{DPC}} = 0.4$; (Δ) CPC/DPC, $\alpha_{\text{CPC}} = 0.9$; and ternary mixtures (\circ) DPC/CPC/TTAB (0.333/0.333/0.333) at 298.15K.

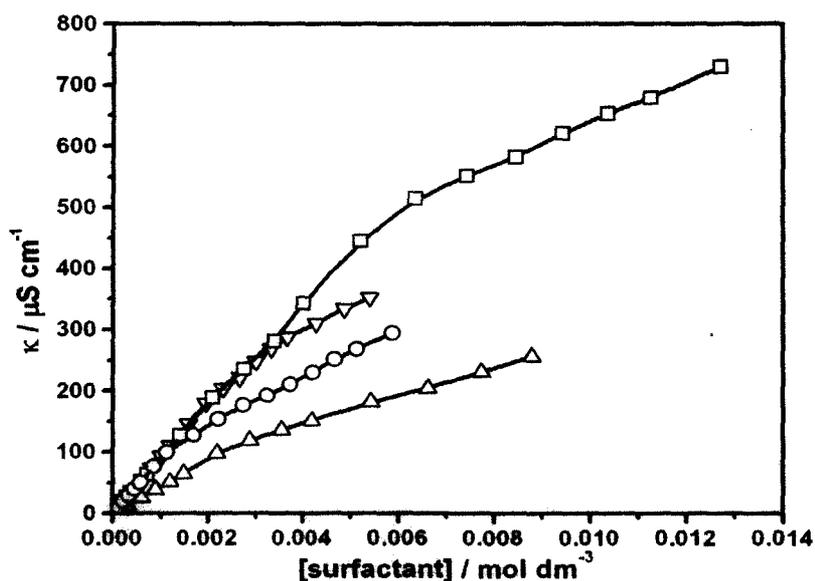


Figure 2. Conductometric plot of binary mixtures (∇) CPC/TTAB, $\alpha_{\text{CPC}} = 0.1$; (\square) DPC/TTAB, $\alpha_{\text{DPC}} = 0.4$; (Δ) CPC/DPC, $\alpha_{\text{CPC}} = 0.75$; and ternary mixtures (\circ) DPC/CPC/TTAB (0.125/0.625/0.250) at 298.15K.

surfactant monomer. Here, n is taken as unity for pure surfactants, their binary and ternary mixture, *i.e.*, the contribution of counterions of cationic surfactants has been neglected. Its estimation from the knowledge of counterion condensation at the micellar interface seems to be a crude approximation due to the large discrepancy in radius of curvature, which significantly affect the counterion condensation between the micellar interface and the air/solution interface. C is the total molar surfactant concentration⁶.

The area of exclusion (A_{\min}) per surfactant monomer at complete saturation of air/water interface near *cmc* can be calculated using the equation,

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

where the factor 10^{18} arises out of conversion from m to nm and N_A is the Avogadro's number. Γ_{\max} and A_{\min} are expressed in $\text{mol } m^{-2}$ and $nm^2 \text{ molecule}^{-1}$ units, respectively.

C_{20} is the surfactant concentration³⁶ required to reduce the surface tension of water by $20 \text{ mN } m^{-1}$ and negative logarithm of C_{20} is called pC_{20} . The higher the surface activity of a surfactant, the smaller is the C_{20} value. The cmc/C_{20} ratio dictates the preference of a surfactant blend toward micellization compared to interfacial adsorption^{35, 43}.

The values of Π_{cmc} , Γ_{\max} , pC_{20} and cmc/C_{20} of the pure surfactants as well as their binary and ternary mixtures are shown in Tables 3 and 4. Among the pure surfactants TTAB has the lowest γ_{cmc} value ($34.1 \text{ mN } m^{-1}$) followed by DPC ($39.4 \text{ mN } m^{-1}$) and CPC ($44.3 \text{ mN } m^{-1}$). The Γ_{\max} value increases with increasing tail length and eventually A_{\min} decreases with increasing tail length. The pC_{20} values also follow the same trend as Γ_{\max} as expected if the tensiometric isotherms are linear in the pre-micellar region. The increasing Γ_{\max} and pC_{20} values with increasing tail length is a consequence of increasing surface activity arising out of increasing hydrophobicity of the longer tail surfactant. The lowering in A_{\min} signifies greater compactness of the surfactant-saturated monolayer arising from an increased van der Waals attraction among the surfactant tails. The cmc/C_{20} value increases with decreasing chain length dictating the preference of the shorter-tailed surfactant toward micellization over interfacial adsorption. The ratio of the slopes of pre- to

postmicellar regions of the specific conductance (κ) vs. the surfactant concentration (c) plot gives an estimate of the fraction of counterions condensed (g)^{4,7-10, 23}. The g values for the single amphiphiles decrease in the order: TTAB<CPC<DPC. The lowering of g with decreasing tail length within a homologous series may originate from a change in micellar size.

For the CPC/TTAB mixtures, Π_{cmc} and A_{min} decrease with increasing amount of CPC; Γ_{max} , however, follows a reverse trend. There is a significant lowering in g for pure TTAB micelle even in the presence of a very small amount of CPC and g reaches a minimum at $\alpha_{CPC} = 0.5$; pC_{20} , on the other hand, reaches a maximum at $\alpha_{CPC} = 0.5$. For the DPC/TTAB blend, Π_{cmc} and Γ_{max} values pass through a maximum at around $\alpha_{DPC} = 0.4$. The pC_{20} values, however, follow no regular trend. The variation of g is found to be regular and it decreases with increasing stoichiometric proportion of DPC in the mixtures.

Π_{cmc} in CPC/DPC system slowly decreases while Γ_{max} increases with increasing α_{CPC} . The most important observation is that the g value of pure DPC is decreased drastically upon addition of CPC upto $\alpha_{CPC} = 0.5$. This indicates a decrease in surface charge density probably through stacking interaction among the π electron clouds which is operative only when there exists a disparity in the chain length of the surfactant. This lowers the extent of counterion condensation which destabilizes the micellar structure and can account for the concentration lag between interfacial saturation and bulk micellization in this system.

Energetics of micellization and interfacial adsorption

The standard free energy of micellization per mole of monomer unit (ΔG_m^0) for pure surfactants and their mixtures can be obtained from

$$\Delta G_m^0 = (1 + g) RT \ln X_{cmc} \quad (3)$$

where X_{cmc} is the cmc in mole fraction scale and the factor $(1 + g)$ accounts for the free energy contribution arising from the counterion condensation on micellar surface.

The standard free energy of interfacial adsorption (ΔG_{ad}^0) at the air/water interface can be obtained from the relation

$$\Delta G_{ad}^0 = \Delta G_m^0 - \left(\frac{\Pi_{cmc}}{\Gamma_{max}} \right) \quad (4)$$

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

The free energy changes associated with micellization (ΔG_m^0) and interfacial adsorption (ΔG_{ad}^0) for binary and ternary mixtures are given in Tables 3 and 4, respectively. The *g* values for binary mixtures of CPC/TTAB and DPC/TTAB are higher compared to those of CPC/DPC system. For ternary mixtures, *g* values are maximum for higher α_{CPC} and minimum for higher α_{DPC} . ΔG_m^0 values for CPC/TTAB and CPC/DPC systems increase with increasing α_{CPC} (Fig. 3), indicating that the micellization process becomes more and more spontaneous with CPC, but the reverse trend is observed in case of DPC/TTAB system. The values of ΔG_m^0 for the ternaries demonstrate that micellization becomes more favourable for mixtures richer in CPC. ΔG_{ad}^0 values follow the same trend as do the ΔG_m^0 values for CPC/TTAB, DPC/TTAB and for ternaries, but for CPC/DPC no such regularity is observed.

THEORETICAL SECTION

Clint Model

This model^{14, 32} predicts the *cmc* of mixed surfactant systems (cmc^C) with known composition from a knowledge of individual *cmcs* of the components according to the equation

$$\left(1/cmc^C\right) = \sum_{i=1}^n (\alpha_i / cmc_i) \quad (5)$$

Here, α_i denotes the stoichiometric mole fraction of the *i*th component in the solution. The terms cmc_i and cmc^C are the critical micellar concentrations of the *i*th component and the mixture, respectively. Any negative deviation of the experimental *cmc* from the calculated value (cmc^C) reflects an overall synergistic (attractive) interaction whereas overall antagonistic (repulsive) interaction is inferred from a positive deviation.

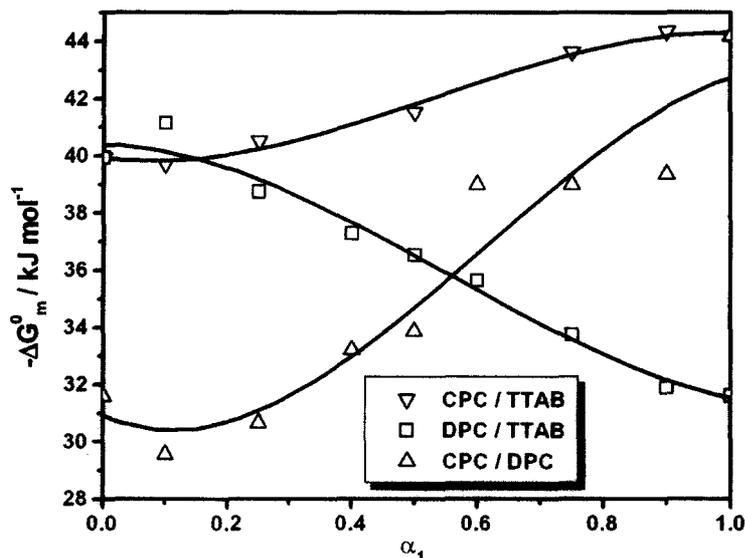


Figure 3. Variation of ΔG_m^0 as a function of composition in mixed binary systems at 298.15K.

It is observed from Table 1 that for DPC/TTAB and CPC/DPC binary systems, the Clint *cmc*s are lower than the average experimental *cmc*s whereas those for CPC/TTAB system are greater than the experimental ones indicating nonideality of these mixtures due to mutual interaction between the surfactants in the micelle. In the case of ternaries (Table 2), Clint *cmc*s do not follow any regular trend with the surfactant composition.

Rosen model

This model focuses on the adsorbed Langmuirian mixed surfactant film at the air/solution interface^{33, 34} and is basically an optimization algorithm. A closer resemblance with the experimental area of exclusion (A_{\min}) is obtained from the A_{\min} values of the respective pure components using computational iteration which leads to the mole fraction of the component (X_1^σ) and interaction parameter at the interface among the components (β^σ) as the optimization parameters. The two equations involved in the iteration procedure are,

$$\frac{(X^\sigma)^2 \ln[cmc_{\text{mix}} \alpha_1 / C_1^0 X^\sigma]}{(1 - X^\sigma)^2 \ln[cmc_{\text{mix}} (1 - \alpha_1) / C_2^0 (1 - X^\sigma)]} = 1 \quad (6)$$

and

$$\beta^\sigma = \frac{\ln[cmc_{\text{mix}} \alpha_1 / C_1^0 X^\sigma]}{(1 - X^\sigma)^2} \quad (7)$$

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

The β^σ and X^σ values of the binary mixtures are presented in Table 5. The negative β^σ values for the three binaries investigated indicate synergistic interaction in these systems. The interaction parameter decreases regularly with increasing α_1 for CPC/TTAB and DPC/TTAB mixtures, but for CPC/DPC mixture, the values are highly irregular. Higher X^σ values compared to α_1 for all cationic/cationic system indicate that surfactant 1 would tend to be adsorbed preferentially at the air/water interface compared to surfactant 2. The X^σ values for CPC/DPC system are very much higher than the other two binaries (CPC/TTAB and DPC/TTAB) reflecting more surface activity of the former system.

Rubingh Model

Following this approach³⁵, the micellar mole fraction (X_R) of a surfactant in a mixed aggregated state and the molecular interaction parameter (β^R) can be obtained by solving Eqs. (8) and (9) iteratively:

$$\frac{(X_R)^2 \ln[cmc_{\text{mix}} \alpha_1 / cmc_1 X_R]}{(1 - X_R)^2 \ln[cmc_{\text{mix}} (1 - \alpha_1) / cmc_2 (1 - X_R)]} = 1 \quad (8)$$

and

$$\beta^R = \frac{\ln[cmc_{\text{mix}} \alpha_1 / cmc_1 X_R]}{(1 - X_R)^2} \quad (9)$$

where cmc_1 , cmc_2 , and cmc_{mix} are respectively the critical micellar concentrations of surfactants 1, 2, and their mixture at a mole fraction of α_1 .

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

$$f_1 = \exp[\beta^R (1 - X_R)^2] \quad (10)$$

and

$$f_2 = \exp[\beta^R (X_R)^2] \quad (11)$$

The values of X_R , β_R , f_1 , and f_2 for the binary mixtures are listed in Table 5. It can be seen from this Table that for CPC/TTAB and CPC/DTAB mixtures, the micellar mole fraction (X_R) increases with increasing mole fraction of surfactant 1, while no such systematic variation of X_R is observed for CPC/DPC mixtures. For CPC/TTAB and CPC/DPC systems, the values of X_R are higher than those of α_{CPC} , but for DPC/TTAB mixtures, X_R values are always lower than the α_{CPC} values. For any given mole fraction of surfactant 1 in the three binary mixtures, X_R values increase in the order: DPC/TTAB < CPC/TTAB < CPC/DPC. A comparison of the X^σ and X_R values (Table 5) shows that DPC/TTAB mixtures have much greater X^σ values than X_R values thus indicating greater surface activity of the component DPC in the mixed state. On the other hand, for CPC/TTAB mixed micelles, X^σ values are slightly lower compared to X_R values (except at $\alpha_{CPC} = 0.1$) indicating equal or to some extent higher priority in surface saturation and micelle forming properties.

β_R values for all mixtures are negative (except at $\alpha_{CPC} = 0.25$ and 0.40 for CPC/DPC system) demonstrating synergistic interaction in these systems. This conclusion can also be drawn from the lower experimental *cmc* in most of the cases of these mixtures than the Clint *cmc*. For CPC/DPC binary mixtures, β_R values indicate antagonistic interaction among themselves. A comparison of the Clint *cmc* values for this system with those obtained experimentally also pointed to the same behavior.

Motomura Model

This model^{36, 37} considers mixed micelles as a macroscopic bulk phase from a thermodynamic point of view. Here, excess thermodynamic quantities are used to evaluate various energetic parameters. The fundamental equation is

$$X_{Mo} = \hat{X}_2 - \left(\hat{X}_1 \hat{X}_2 / \hat{cmc} \right) \left(\partial \hat{cmc} / \partial \hat{X}_2 \right)_{T,P} \quad (12)$$

where $\hat{X}_2 = \frac{v_2 \alpha_2}{v_1 \alpha_1 + v_2 \alpha_2}$ and $\hat{cmc} = (v_1 \alpha_1 + v_2 \alpha_2) cmc$

Subscripts 1 and 2 refer to surfactants 1 and 2, respectively, and α and ν represent the stoichiometric mole fraction and the number into which a surfactant molecule dissociates in solution. The micellar mole fractions (X_{Mo}) of a surfactant in the binary mixtures evaluated by Motomura equation are shown in Table 5.

According to this model³⁸, the mean activity coefficient of surfactant 1 in the micelle (f_1) is obtained from

$$\hat{X}_1 \hat{cmc} / cmc_1^0 = f_1 X_{1(Mo)} \quad (13)$$

and the f_1 values for all binary mixtures are shown in Table 5. For CPC/TTAB and CPC/DPC, X_{Mo} values are higher than the stoichiometric mole fraction of CPC. This signifies that for these two mixed surfactant systems, CPC prefers the micellar phase. On the other hand, for DPC/TTAB, the X_{Mo} values are always found to be lower than the α_{DPC} values. This indicates a greater affinity of TTAB toward micelle formation compared to DPC as expected from a lower cmc of TTAB than that of DPC. Motomura model is independent of the nature of surfactant and their counterions and predicts the micellar composition only.

SPB Model

Another thermodynamic theory developed by Blankschtein (SPB) *et al.*³⁸⁻⁴⁰ also predicts quantitatively the cmc , micellar composition, shape, and phase behavior on the basis of hydrophobic, structural, and electrical interactions between the binary components. Clint equation is written in the form,

$$\frac{1}{cmc_{mix}} = \frac{\alpha_1}{f_1 cmc_1} + \frac{1 - \alpha_1}{f_2 cmc_2} \quad (14)$$

where the f terms represent the activity coefficient of the surfactant in the mixed micelle and can be expressed by the following relations

$$f_1 = \exp \left[\frac{\beta_{12} (1 - \alpha^*)^2}{kT} \right] \quad (15)$$

and

$$f_2 = \exp \left[\frac{\beta_{12} (\alpha^*)^2}{kT} \right] \quad (16)$$

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

$$\frac{\beta_{12}(1-2\alpha^*)}{kT} + \ln\left(\frac{\alpha^*}{1-\alpha^*}\right) = \ln\left(\frac{\alpha_1 \text{ cmc}_2}{(1-\alpha_1) \text{ cmc}_1}\right) \quad (17)$$

is solved iteratively to obtain α^* and β_{12} and by using these values, the activity coefficients can be calculated according to equations 15 and 16. It is observed from Table 6 that X_{SPB} increases with increasing α_1 for all the binaries and the X_{SPB} values are much lower than α_1 in DPC/TTAB, but much higher than α_1 in case of CPC/TTAB and CPC/DPC systems. In most of the compositions of all these mixtures, X_{SPB} is lower than X_{R} , X_{M_0} or X_{G} . In the CPC/TTAB mixtures, $\beta_{\text{SPB}} < \beta_{\text{R}}$ (in most cases) and negative values of β_{SPB} indicate attractive interaction. In the case of DPC/TTAB (excepting $\alpha_{\text{DPC}} = 0.9$) and CPC/DPC systems, positive β_{SPB} values denote repulsive interaction between the surfactants. In case of all binary systems, the activity coefficients of component 1 are found to be nearly unity following Rubingh, and SPB models. The *cmc* values of CPC/TTAB (excepting $\alpha_{\text{CPC}} = 0.1$) and DPC/TTAB mixtures obtained by the SPB method are lower than those obtained experimentally and more or less comparable with those obtained by the Clint theory. Again, in case of CPC/DPC combination, the *cmc* values follow the reverse trend (SPB > obs > Clint). Higher deviations in the *cmc* values found in case of CPC/DPC mixture particularly at lower mole fraction of CPC indicate nonideality for mutual interaction of amphiphiles in the micelle. This is a limitation of SPB theory.

Rubingh-Holland model

Theoretical treatment of surfactant mixtures with more than two components is very limited⁴¹. The theory of Rubingh and Holland⁴¹ (RH) has been properly tested to determine the micellar composition, activity coefficient and *cmc* of ternary systems. The activity coefficients of surfactants in a binary mixed micelle can be estimated from the relations 10 and 11. In a multicomponent mixture, the activity coefficients f_i, f_j, f_k, \dots of the mixed micelle-forming amphiphilic species i, j, k, \dots can be expressed by the RH equation⁴¹.

$$\ln f_i = \sum_{\substack{j=1 \\ (j \neq i)}}^n \beta_{ij} x_j^2 + \sum_{\substack{j=1 \\ (i \neq j \neq k)}}^n \sum_{k=1}^{j-1} (\beta_{ij} + \beta_{ik} - \beta_{jk}) x_j x_k \quad (18)$$

where β_{ij} denotes the net (pairwise) interaction between components i and j , and x_j is the mole fraction of the j th component in the micelles; β_{ik} , β_{jk} , and x_k have similar significance. Equation 19 is valid at the *cmc*.

$$x_i = \alpha_i C_j f_j x_j / (C_i \alpha_j f_i) \quad (19)$$

where the terms C_i and C_j represent *cmcs* of the i th and j th components, respectively, and α_i and α_j are the mole fractions of the i th and j th components in the micelle.

The average interaction parameter (β_{av}^R) values for the binary mixtures CPC/TTAB, DPC/TTAB, and CPC/DPC obtained from the equation of Rubingh (Eq. 9), were used in equation 18 to evaluate the activity coefficients f_1 , f_2 , and f_3 for the ternary system DPC/CPC/TTAB using the computer controlled "successive substitution" method. By putting the f value in equation 19, the *cmc* of the mixed micelle was found out. The mole fractions of the individual components (X^{RH}), the activity coefficients (f^{RH}), and the cmc^{RH} values thus obtained have been presented in Table 7. It is found that X_{DPC}^{RH} values are much higher than the stoichiometric mole fraction α_{DPC} (exception in 6th combination) and X_{CPC}^{RH} values are fairly lower than α_{CPC} values, whereas most of the X_{TTAB}^{RH} values are lower than α_{TTAB} values (exception lies in 4th, 6th, and 7th sets of combinations) demonstrating that the mixed micelles mainly consists of DPC. RH theory has already been applied to various combinations of surfactants, namely, ionic/nonionic/nonionic^{7, 8, 44, 45}, ionic/ionic/nonionic^{4, 46}, ionic/ionic/ionic^{47, 48}. The activity coefficient of CPC (f_{CPC}^{RH}) is close to unity, whereas f_{DPC}^{RH} is moderately high compared to f_{TTAB}^{RH} indicating that CPC and DPC control the activity of the third component. The *cmc* values obtained by RH method are higher than those obtained experimentally (except the 2nd combination). But in all cases, the Clint *cmcs* are higher than the experimental *cmcs* and those obtained from the Rubingh-Holland model indicating synergistic interactions in these ternary systems. The deviation of Rubingh-Holland *cmcs* from the experimental values points to the limitation of this theory for the present ternary system.

CONCLUSIONS

This chapter reports the mixed micellization behavior of three cationic surfactants cetylpyridinium chloride (CPC), tetradecyltrimethylammonium bromide (TTAB), and dodecylpyridinium bromide (DPC) with different tail lengths using tensiometry and conductometry from a thermodynamic viewpoint. Increasing *cmc* with decreasing tail length signifies the dominant effect of hydrophobic interaction in dictating the self-aggregation behavior. The coherence of *cmc* values obtained by tensiometry and conductometry for pure and CPC/TTAB and DPC/TTAB binary combinations suggests concurrence of interfacial saturation by surfactant monomer and their self-aggregation in bulk solution. A finite and significant lag in *cmc* determined by those two methods for CPC/DPC binaries and the ternary systems DPC/CPC/TTAB indicates a decrease in charge density at the micellar interface arising out of π - π interaction among the pyridinium head groups of surfactants with dissimilar tail lengths. Negative deviation in the experimental *cmc* for the binary combinations again infers the van der Waals attractive interaction among the similarly charged surfactant head groups.

The Rosen model predicts the interfacially adsorbed layer and interaction parameters. Rubingh, Motomura and SPB models, on the other hand, deal with the micellar phase. For CPC/TTAB system, these three models predict more or less similar composition of the micellar phase. The interaction parameters in the micellar phase predicted by Rubingh model are all negative signifying synergistic interaction. With increasing stoichiometric amount of CPC, its proportion in monolayer and micellar phase increases. This increase in the amount of CPC in the interfacial layer is, however, less prominent than that in micellar phase. In DPC/TTAB system, the Rubingh, Motomura, and SPB models predict similar composition in the micellar phase. The variation of micellar composition with the stoichiometric composition is again more pronounced in micellar phase compared to that in the monolayer. For CPC/DPC system, however, there is a discrepancy in micellar composition as predicted by Rubingh, Motomura, and SPB models. The deviation of the experimental *cmcs* from those obtained using the RH model for the DPC/CPC/TTAB ternary system may be ascribed to the incompatibility of the three amphiphiles due to the dissimilarity in their nonpolar tail and ionic head groups.

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TABLE-1

Critical Micellar Concentrations^a (*cmc*) of Pure CPC, TTAB and DPC, and their Binary Mixtures at 298.15K

α_{CPC} (I) or α_{DPC} (II)	S.T.	Cond.	Av. <i>cmc</i>	<i>cmc</i> ^c
CPC/TTAB ($10^3 \text{ cmc} / \text{mol dm}^{-3}$) (I)				
0.00	3.715	3.524	3.620	-
0.10	2.564	2.716	2.640	2.846
0.25	1.556	2.255	1.906	2.154
0.50	1.247	1.562	1.404	1.534
0.75	0.998	1.250	1.124	1.191
0.90	0.920	1.313	1.026	1.050
1.00	0.910	1.036	0.973	-
DPC/TTAB ($10^3 \text{ cmc} / \text{mol dm}^{-3}$) (II)				
0.00	3.715	3.524	3.620	-
0.10	3.908	3.992	3.950	3.931
0.25	4.645	4.731	4.688	4.513
0.40	5.297	5.781	5.539	5.297
0.50	5.929	6.435	6.182	5.991
0.60	7.211	7.131	7.171	6.895
0.75	9.453	9.387	9.420	8.910
0.90	11.695	12.414	12.054	12.588
1.00	17.132	17.608	17.370	-
CPC/DPC ($10^3 \text{ cmc} / \text{mol dm}^{-3}$) (I)				
0.00	17.132	17.608	17.370	-
0.10	4.291	8.631	6.461	6.468
0.25	3.254	7.764	5.509	3.332
0.40	2.218	5.190	3.704	2.244
0.50	1.527	3.950	2.739	1.843
0.60	1.465	2.775	2.120	1.563
0.75	1.445	2.469	1.957	1.273
0.90	1.096	2.296	1.696	1.074
1.00	0.910	1.036	0.973	-

^aThe average uncertainty in *cmc* is $\pm 2\%$

TABLE-2

Critical Micellar Concentrations^a (*cmc*) of the Ternary Mixtures of CPC, TTAB and DPC at 298.15K

$\alpha_{DPC} / \alpha_{CPC} / \alpha_{TTAB}$	S.T.	Cond.	Av. <i>cmc</i> (Clint <i>cmc</i>)
	$10^3 \text{ cmc} / \text{mol dm}^{-3}$		
0.125 / 0.250 / 0.625	1.517	1.862	1.690 (2.289)
0.125 / 0.625 / 0.250	1.153	1.367	1.260 (1.392)
0.250 / 0.125 / 0.625	2.138	2.322	2.230 (3.169)
0.250 / 0.625 / 0.125	1.183	1.388	1.286 (1.447)
0.333 / 0.333 / 0.333	1.462	1.628	1.545 (2.206)
0.625 / 0.125 / 0.250	2.667	3.981	3.324 (4.282)
0.625 / 0.250 / 0.125	1.941	2.213	2.077 (3.054)

^aThe average uncertainty in *cmc* is $\pm 3\%$.

TABLE-3

Interfacial and Counterion Binding Parameters of Pure CPC, TTAB and DPC, and their Binary Mixtures at 298.15K

α_{CPC} (I) or α_{DPC} (II)	$10^3 \Pi_{cmc} /$ $J m^{-2}$	$10^6 \Gamma_{max} /$ $mol m^{-2}$	$A_{min} /$ $nm^2/molecule$	g	$-\Delta G_m^0 /$ $kJ mol^{-1}$	$-\Delta G_{ad}^0 /$ $kJ mol^{-1}$	pC_{20}	cmc/C_{20}
CPC/TTAB (I)								
0.00	37.9	4.52	0.37	0.645	39.94	48.33	3.09	4.41
0.10	36.1	4.63	0.36	0.583	39.70	47.50	3.19	4.09
0.25	35.7	4.89	0.34	0.564	40.50	47.81	3.36	4.38
0.50	34.0	4.97	0.33	0.557	41.52	48.36	3.38	3.38
0.75	31.5	5.19	0.32	0.602	43.62	49.69	3.36	2.59
0.90	29.2	5.50	0.30	0.615	44.34	49.65	3.34	2.23
1.00	27.7	5.99	0.28	0.601	44.17	48.79	3.28	1.84
DPC/TTAB (II)								
0.00	37.9	4.52	0.37	0.645	39.94	48.33	3.09	4.45
0.10	37.4	4.29	0.39	0.710	41.14	49.86	3.07	4.62
0.25	37.6	4.48	0.37	0.639	38.73	47.11	3.01	4.85
0.40	37.2	5.13	0.32	0.606	37.27	44.52	2.86	3.97
0.50	36.6	4.25	0.39	0.592	36.51	45.12	2.91	5.07
0.60	35.7	3.47	0.48	0.579	35.62	45.92	2.93	6.14
0.75	34.6	3.30	0.51	0.542	33.73	44.21	2.80	5.94
0.90	33.7	3.12	0.53	0.500	31.88	42.67	2.67	5.66
1.00	32.6	2.6	0.64	0.554	31.59	44.14	2.48	5.29
CPC/DPC (I)								
0.00	32.6	2.60	0.64	0.554	31.59	44.14	2.48	5.29
0.10	31.6	2.27	0.73	0.338	29.56	43.48	3.20	10.24
0.25	30.7	2.51	0.66	0.371	30.65	42.88	3.24	9.57
0.40	29.8	2.75	0.60	0.370	33.19	44.03	3.28	7.13
0.50	29.6	3.74	0.44	0.355	33.85	41.76	3.24	4.73
0.60	28.7	3.96	0.42	0.521	38.98	46.23	3.23	3.61
0.75	28.1	4.14	0.40	0.509	38.98	45.77	3.25	3.47
0.90	27.6	4.51	0.37	0.503	39.36	45.48	3.24	2.97
1.00	27.7	5.99	0.28	0.601	44.17	48.79	3.28	1.84

TABLE-4

Interfacial and Thermodynamic^a Parameters of the Ternary Combinations of DPC, CPC and TTAB at 298.15K

$\alpha_{DPC} / \alpha_{CPC} / \alpha_{TTAB}$	$10^3 \Pi_{cmc}$ / J m ⁻²	$10^6 \Gamma_{max}$ / mol m ⁻²	A_{min} / nm^2 molecule ⁻¹	g	$-\Delta G_m^0 /$ kJ mol ⁻¹	$-\Delta G_{ad}^0 /$ kJ mol ⁻¹	pC_{20}	cmc/C_{20}
0.125 / 0.250 / 0.625	34.6	5.76	0.29	0.391	-36.44	42.45	3.31	3.43
0.125 / 0.625 / 0.250	32.2	5.21	0.32	0.566	-42.19	48.37	3.33	2.68
0.250 / 0.125 / 0.625	35.4	4.45	0.37	0.338	-34.12	42.08	3.24	3.92
0.250 / 0.625 / 0.125	30.4	4.96	0.33	0.529	-41.11	47.24	3.27	2.41
0.333 / 0.333 / 0.333	33.2	5.90	0.28	0.416	-37.42	43.05	3.24	2.67
0.625 / 0.125 / 0.250	33.5	4.90	0.34	0.321	-32.36	39.20	3.06	3.81
0.625 / 0.250 / 0.125	32.1	5.34	0.31	0.328	-34.1	40.12	3.13	2.81

^aThe average uncertainty in each of ΔG_m^0 , and ΔG_{ad}^0 are $\pm 3\%$.

TABLE-5

Molecular Interaction Parameters of Binary Mixtures in Aqueous Medium and 298.15K

α_{CPC} (I) or α_{DPC} (II)	Rosen Model		Rubingh Model			Motomura Model	
	X^σ	β^σ	X_R	β^R	f_1 / f_2	X_{Mo}	f_1
CPC/TTAB (I)							
0.10	0.43	-3.49	0.34	-0.46	0.82 / 0.95	0.30	0.91
0.25	0.52	-3.48	0.55	-1.21	0.78 / 0.69	0.60	0.81
0.50	0.62	-2.71	0.73	-0.88	0.94 / 0.62	0.73	0.99
0.75	0.74	-2.16	0.84	-1.16	0.97 / 0.43	0.88	0.98
0.90	0.84	-1.94	0.92	-1.40	0.99 / 0.31	-	0.94
DPC/TTAB (II)							
0.10	0.37	-7.82	0.05	-0.89	0.45 / 1.00	0.07	0.29
0.25	0.40	-6.17	0.06	-0.09	1.08 / 1.00	0.08	0.82
0.40	0.43	-4.93	0.14	-0.18	0.87 / 1.00	0.07	1.75
0.50	0.45	-4.38	0.20	-0.19	0.88 / 0.99	0.10	1.75
0.60	0.47	-3.54	0.23	-0.16	1.10 / 1.01	0.20	1.26
0.90	0.65	-1.58	0.64	-0.32	0.96 / 0.88	0.76	0.82
CPC/DPC (I)							
0.10	0.73	-2.18	0.60	-1.56	0.78 / 0.57	0.12	7.31
0.25	0.76	-2.96	0.89	+0.33	1.00 / 1.30	0.64	3.13
0.40	0.81	-3.16	0.97	+1.16	1.00 / 3.02	-	-
0.50	0.80	-4.04	0.86	-1.51	0.97 / 0.33	-	-
0.60	0.89	-1.83	0.97	-0.01	1.00 / 1.01	0.78	1.67
0.75	0.97	-	-	-	-	0.77	1.96
0.90	0.99	-	-	-	-	0.91	1.73

TABLE-6

Micellar Compositions (X_{SPB}), Interaction Parameters [$\beta_{SPB}(kT)$], Activity Coefficients (f), and cmc s of Binary Mixtures at 298.15K at Different Stoichiometric Compositions

α_{CPC} (I) or α_{DPC} (II)	X_{SPB}	$\beta_{SPB} (kT)$	f_1	f_2	$10^3 cmc/(mol dm^{-3})$ Obs/SPB/Clint
CPC/TTAB (I)					
0.10	0.292	-0.146	0.93	0.99	2.640 / 2.760 / 2.846
0.25	0.553	-0.608	0.89	0.83	1.906 / 1.853 / 2.154
0.50	0.788	-1.962	0.92	0.30	1.404 / 0.972 / 1.534
0.75	0.918	-8.605	0.94	-	1.124 / 0.010 / 1.191
0.90	0.971	-27.221	0.98	-	0.973 / - / 1.050
DPC/TTAB (II)					
0.10	0.022	0.035	1.034	1.000	3.950 / 3.934 / 3.931
0.25	0.064	0.060	1.054	1.000	4.688 / 4.529 / 4.513
0.40	0.122	0.058	1.046	1.001	5.539 / 5.330 / 5.297
0.50	0.172	0.050	1.035	1.001	6.182 / 6.033 / 5.991
0.60	0.238	0.069	1.041	1.004	7.171 / 6.980 / 6.895
0.90	0.652	-0.358	0.958	0.859	12.054 / 11.59 / 12.588
CPC/DPC (I)					
0.10	0.665	2.567	1.334	3.112	6.461 / 10.67 / 6.468
0.25	0.856	-	2.330	-	5.509 / 9.070 / 3.332
0.40	0.923	-	1.650	-	3.704 / 4.013 / 2.244
0.50	0.947	-	1.486	-	2.739 / 2.892 / 1.843
0.60	0.964	-	1.356	-	2.120 / 2.199 / 1.563
0.75	0.982	-	1.536	-	1.957 / - / 1.273
0.90	0.994	-	1.578	-	1.696 / - / 1.074

TABLE-7

Micellar Composition (X^{RH}), Activity Coefficient (f^{RH}), and cmc_{RH} in Ternary Mixtures of DPC/CPC/TTAB by RH Model at 298.15K and at Different Stoichiometric Compositions (α)

$\alpha_{\text{DPC}} / \alpha_{\text{CPC}} / \alpha_{\text{TTAB}}$	$X_{\text{DPC}}^{\text{RH}} / X_{\text{CPC}}^{\text{RH}} / X_{\text{TTAB}}^{\text{RH}}$	$f_{\text{DPC}}^{\text{RH}} / f_{\text{CPC}}^{\text{RH}} / f_{\text{TTAB}}^{\text{RH}}$	$10^3 cmc / (\text{mol dm}^{-3})$ RH/obsd/Clint
0.125 / 0.250 / 0.625	0.574 / 0.117 / 0.414	0.835 / 1.093 / 0.707	1.791 / 1.690 / 2.289
0.125 / 0.625 / 0.250	0.830 / 0.008 / 0.162	0.972 / 1.010 / 0.489	1.236 / 1.260 / 1.392
0.250 / 0.125 / 0.625	0.450 / 0.033 / 0.517	0.749 / 1.082 / 0.798	2.492 / 2.230 / 3.169
0.250 / 0.625 / 0.125	0.713 / 0.013 / 0.274	0.923 / 1.063 / 0.587	1.301 / 1.286 / 1.447
0.333 / 0.333 / 0.333	0.700 / 0.032 / 0.267	0.921 / 1.61 / 0.590	1.833 / 1.545 / 2.206
0.625 / 0.125 / 0.250	0.547 / 0.116 / 0.336	0.857 / 1.072 / 0.682	3.453 / 3.324 / 4.282
0.625 / 0.250 / 0.125	0.741 / 0.093 / 0.166	0.958 / 1.017 / 0.524	2.707 / 2.077 / 3.054