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ORIGINAL ARTICLE

Mixed Micellization Study of Alkyltrimethylammonium and Alkyltriphenylphosphonium Bromides in Aqueous Solution

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Abstract Mixed micellization study of cationic surfactants viz. alkyltrimethylammonium bromides (C_nTAB) and alkyltriphenylphosphonium bromides (C_nTPPB) with similar hydrophobic groups (C_{12}-, C_{14}-, and C_{16}-) was performed using tensiometry and UV–visible light spectrophotometry techniques. Critical micelle concentration (CMC) values of the single and binary surfactant mixtures were obtained from a plot of surface tension versus the logarithm of surfactant concentration (C_s). The degree of synergy and various mixed micelle parameters like interaction parameter (β), activity coefficients (f^m) and interfacial parameters like surface pressure (π_{CMC}), packing parameter (P), surface excess concentration (Γ_{max}), surface tension at the CMC (γ_{CMC}), and minimum area per molecule (A_{min}) were evaluated using the regular solution theory (RST). Thermodynamic parameters were calculated using several proposed models which suggest the mixed micellar system to be more thermodynamically stable than their respective individual components. In addition, a dye solubilization study was performed using a spectrophotometric method to validate the CMC data obtained from tensiometric method. Conductometric measurements were also carried out for the mixture of $C_{12}TAB + C_{12}TPPB$ only as it showed a more negative β, indicating a higher degree of synergism.

Keywords Cationic surfactant · Mixed micellization · CMC · Synergism · Dye solubilization

Introduction

Comprehensive studies on co-micellization in binary cationic surfactant mixtures are well reported [1–5]. Mixed surfactant systems are expected to give superior surface properties compared to the corresponding pure individual components. Consequently, such surfactant blends, with synergistic behavior, cost-effectiveness due to overall reduction in the total amount of surfactant used for a particular application and environmental impact, reinforces a wide variety of industrial applications [6–10]. Furthermore, such mixed micellar systems offer a better understanding of molecular interactions in surfactant aggregates and delivery systems. For all the above noted reasons, the study of mixed surfactant systems with different physico-chemical experimental techniques viz. surface/interfacial tensiometry, conductivity, spectroscopy, microscopy or scattering techniques has become increasingly important [1–13].

Thermodynamic theories proposed by Clint, Motoumura, Rubingh and Blackschtein have described the molecular details of various binary combinations and highlighted the specific synergistic (attractive)/antagonistic, i.e., repulsive, interactions between different surfactants in mixed micelles [13–16].

Binary mixtures of non-ionic surfactants are reported to exhibit ideal behavior while other surfactant pairs usually exhibit non-ideality resulting from the synergistic or

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antagonistic interactions between the surfactant monomers. Such behavior is attributed to electrostatic and steric interactions between hydrophilic head groups and hydrophobic tails of the respective surfactant molecules [17]. The influence of the hydrophobic chain length or different head groups on the micellization of mixtures of alkyl quaternary ammonium and alkyl pyridinium halides has been studied [17–21].

With the aim to synchronize our current research with the reported literature, we have chosen the mixture of alkyltrimethylammonium and alkyltriphenylphosphonium bromides with identical hydrophobic chain length and bromide as a counterion, but with dissimilar head groups (NH_4^+ and Ph_3P^+). Our work presents a systematic investigation on the interfacial and micellar properties of these surfactants in pure and in binary mixed systems in aqueous solution at 30 °C using tensiometry and ultraviolet–visible light (UV–vis) spectrophotometry methods. The critical micelle concentration (CMC) of these surfactants in the mixed system having different compositions was determined and the results obtained herein are explained in terms of ideality of mixing and thermodynamics. The significant influence of the head group in the micelle formation process and the contribution that comes from the hydrocarbon tails is also explained.

Experimental

Materials

Cationic surfactants alkyltrimethylammonium bromide (C_nTAB) and alkyltriphenylphosphonium bromide (C_n-TPPB), dye (Orange OT) and a solvent (methanol, 99.8 % purity) of analytical reagent (AR) grade were procured from Sigma Aldrich. These compounds were used as received for the solubilization study. The sample solutions used in this study for the pure and the binary mixtures were prepared using Millipore water (ST = 71.4 mN m^{-1}).

Methods

UV–visible spectrophotometry

Spectrophotometry measurements were carried out on an Evolution™ 300 UV–vis spectrophotometer (Thermo-Scientific) with a matched pair of quartz cuvets having an internal thickness of 10 mm. The dye solubilization measurements using this technique were obtained at 30 °C maintained in a water bath. The temperature environment was thoroughly controlled and maintained constant within an error limit of ±0.1 °C. Considering the solubility of the dye in a particular solvent (methanol in our case), a calibration plot is drawn within the limit of dye solubility where there is no excess insoluble dye left in the solvent system. After the calibration plot is drawn, the same dye is added in excess to various concentrations of surfactant solution. The entire system was shaken for 48 h at 30 °C to let the dye solubilize completely in the micellar solution. As far as the issue of the insoluble dye accountability is concerned, the excess insoluble dye is separated using Millipore filters (pore size of ~0.22 μm) and the filtrate is diluted with an equal volume of methanol. The concentration of the solubilized dye in the surfactant solutions was determined from the absorbance study at the wavelength of maximum absorption ($\lambda_{max} = 505$ nm).

Tensiometry

The surface tension measurements for the single and mixed binary surfactant systems were performed on a K9 tensiometer (Krüss, Germany). Temperature was maintained constant throughout the experiments (30 °C within ±0.1 °C). Surfactant concentration was varied by adding small installments of the same in water. This solution mixture was kept for at least 30 min for equilibration before measuring the surface tension. Readings of the surface tension for aqueous solutions of single and mixed surfactant systems at different mole fractions was noted after careful mixing and temperature equilibration in order to obtain the CMC. The inflection or break point in the plot of surface tension as a function of surfactant concentration in mole/liter corresponded to the CMC value.

Air/water interface behavior of the binary surfactant mixture

Using the Gibbs adsorption equation, the surface pressure at the CMC (π_{CMC}), maximum surface excess concentration (Γ_{max}, mol m^{-2}), and the minimum area per molecule at the air/solution interface (A_{min}) were calculated from Eqs. 1–3.

$$\pi_{CMC} = \gamma_{water} - \gamma_{CMC} \quad (1)$$

$$\Gamma_{max} = -\frac{1}{nRT}\left(\frac{\partial\gamma}{\partial \ln c}\right) \quad (2)$$

$$A_{min}\left(\text{Å}\right) = \frac{10^{20}}{N_A \Gamma_{max}} \quad (3)$$

where $\left(\frac{\partial\gamma}{\partial \ln c}\right)$ is the maximum slope, $R = 8.314$ J mol^{-1} K^{-1}, N_A is Avogadro's number, $n = 2$ for monovalent counter ions and T is the absolute temperature in Kelvin [22, 23, 26, 27].

According to Rubingh's regular solution theory for mixed micelles, the mixed CMC obtained by mixing two surfactants is given by Eq. 4:

$$\frac{1}{C_{12}}=\frac{\alpha_1}{f_1^m C_1}+\frac{(1-\alpha_1)}{f_2^m C_2} \qquad (4)$$

where α_1 is the mole fraction of the first surfactant in the mixture, and C_1 and C_2 are the respective CMC values of the first and second surfactant in the mixture [13, 20].

The Clint equation [11, 20] was employed to understand the mixed micellization at varying mole fraction compositions. In this study, the experimental CMC of the pure components was related with the ideally mixed CMC and the activity coefficients f_1^m and f_2^m were considered to be unity. Hence Eq. 4 reduces to Eq. 5.

$$\frac{1}{C_{12}}=\frac{\alpha_1}{C_1}+\frac{(1-\alpha_1)}{C_2} \qquad (5)$$

The strength of the interaction between the two surfactants in the mixture is denoted as β, which is determined by calculating the CMCs from the curve: surface tension (γ)-log concentration (C_s) of individual surfactant and in their mixtures. Considering the phase separation model for micellization, we have employed Eq. 6 proposed by Rubingh [15]:

$$\frac{(X_1)^2\ln(\alpha_1 C_{12}/X_1 C_1)}{(1-X_1)^2\ln[(1-\alpha_1)C_{12}/(1-X_1)C_2]}=1 \qquad (6)$$

where X_1 is the mole fraction of surfactant 1 in the mixed micelle. Solving the equation iteratively gives the value of β, as shown in Eq. 7.

$$\beta=\frac{\ln(\alpha_1 C_{12}/X_1 C_1)}{(1-X_1)^2} \qquad (7)$$

β is a measure of the degree of interaction between the surfactants resulting in their deviations from mixed micelle ideal behavior. Negative β values indicated synergism in mixed micelle formation, while positive values indicate antagonism. If $\beta = 0$, then no strong interactions are observed [26, 27].

The activity coefficients highlight the contribution of the individual component in a mixed micellar system and are directly related to the interaction parameter by Eqs. 8 and 9:

$$\ln f_1^m=(1-X_1)^2 \qquad (8)$$

$$\ln f_2^m=(X_1)^2 \qquad (9)$$

where f_1^m and f_2^m are the activity coefficients of TTAB and TTPPB, respectively.

The minimum surface area of surfactants at the interface can be used to predict the shape of the micelle by calculating the packing parameter, P, given by Tanford's formula:

$$P=\frac{V_0}{l_c A_{\min}} \qquad (10)$$

where volume of exclusion per monomer in the aggregate, $V_0 = [27.4 + 26.9(n_c - 1)]$ Å^3 (n_c is the number of carbon atoms in the hydrocarbon chain), and the maximum chain length, $l_c = [1.54 + 1.26(n_c - 1)]$ Å [24, 25].

Results and Discussion

Micellization Study

Figure 1 shows the plots of surface tension (γ) versus the logarithm of surfactant concentration (C_s) for mixed micellization study of cationic surfactants with identical alkyl chain lengths but with dissimilar head groups (NH_4^+ and Ph_3P^+) at 30 °C. The surface tension of single surfactant and surfactant mixtures decreases with concentration, which is a typical signature of surfactants.

A typical non-linear decrease in surface tension is observed up to the CMC, beyond which the surface tension remains more or less constant. Mixed CMC values along with the computed results for mixed micellar composition, interaction parameter (β) and activity coefficients (f^m) are shown in Table 1. It was observed that the CMC values lie between those of the single conventional components, indicating good surface activity. The calculated CMC of single surfactants are in good agreement to the reported values [19, 20]. The β appeared to be more negative for the same set of mixtures, indicating strong non-ideal mixing in the blends, resulting in favorable synergism in mixed micelles. The lower mole fraction (X_1^m) value of the surfactant reflects a low activity coefficient (f_1^m) value, suggesting that the cationic surfactant in the mixed micelle is very far away from its respective standard state, while the higher values of (f_2^m) appear close to unity, which represents that C_nTPPB in the mixed micelle is near its standard state. Such a noticeable trend is well reported [19, 28].

The study of interfacial adsorption is an important criterion to understand the surfactant behavior in the solution. Various parameters related to the interfacial study are presented in Table 2. It can be seen that in all surfactant mixtures, the values of surface pressure (Π_{CMC}) appear lower than that of their corresponding pure surfactants, indicating a synergistic mixed micelle formation. The minimum area per molecule ($A_{\min}$) provides an insight on the assembly of the surfactant molecule at the air–water interface. It was observed that the $A_{\min}$ value of pure C_nTPPB is almost always larger than C_nTAB which may be ascribed to greater electrostatic repulsions between triphenylphoshonium bromide head groups at the interface. The $A_{\min}$ value can be used to calculate the packing parameter P which predicts the shape of the mixed micelle. Because

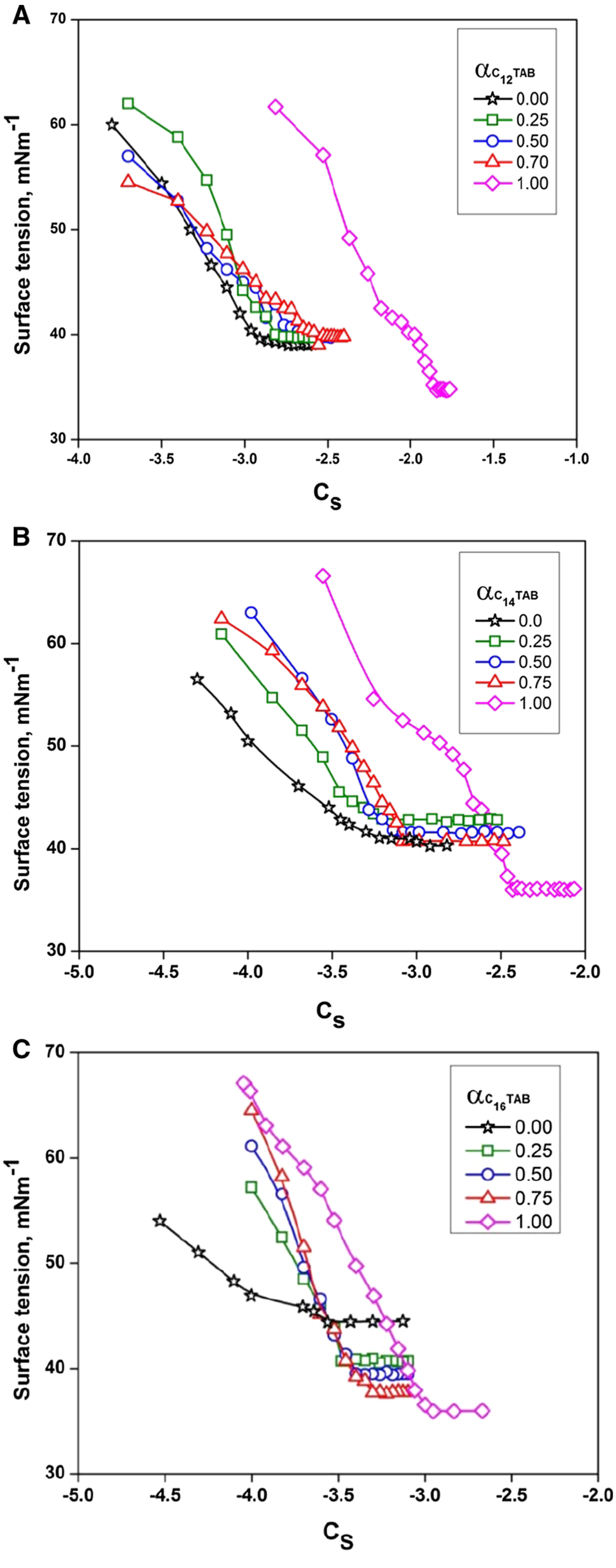

Fig. 1 Surface active behavior of binary surfactant mixtures in aqueous solution at different mole fractions at 30 °C: **a** $C_{12}TAB$ (α_{C12TAB}) with $C_{12}TPPB$, **b** $C_{14}TAB$ (α_{C14TAB}) with $C_{14}TPPB$ and **c** $C_{16}TAB$ (α_{C16TAB}) with $C_{16}TPPB$, respectively, at 30 °C

of the inverse relationship, larger $A_{\min}$ values predict smaller packing parameters, suggesting that the mixed micelles are roughly spherical in shape [21, 29].

Synergism

Synergism is a measure of the interaction between the individual surfactants in the mixture. Synergy can be measured for monolayer formation at the air–water interface and mixed micelle formation. The conditions required for synergy include: (a) β^{o} and β^{m} must be negative, (b) $|\beta^o| > |\ln(C_1^o/C_2^o)|$, where C_1^o and C_2^o are the molar concentration of the individual surfactants in the binary mixture and (c) $|\beta^m| > |\ln(C_1^m/C_2^m)|$, where C_1^m and C_2^m are the CMC values of the individual surfactants.

The terms: $1-\left({}^{c_{12,\min}}\big/{}_{c_1^o}\right)$ and $1-\left({}^{C^m_{12,\min}}\big/{}_{c_1^m}\right)$ were evaluated using Eq. (11) proposed by Liu and Rosen whose value must be maximum 1 and which determines the degree of synergism in reducing the surface tension or CMC efficiently [30–33].

$$\frac{C_{12,\min}}{C_1^o} = \exp\left\{\frac{\left[\beta^o - \ln\left(\frac{c_1^o}{c_2^o}\right)\right]^2}{4\beta^o}\right\} \tag{11a}$$

$$\frac{c^m_{12,\min}}{c_1^m} = \exp\left\{\frac{\left[\beta^m - \ln\left(\frac{c_1^m}{c_2^m}\right)\right]^2}{4\beta^m}\right\} \tag{11b}$$

where $C_{12,\min}$ and $C^m_{12,min}$ are the minimum concentrations of mixed surfactant systems.

Data presented in Table 3 predicts the appreciable level of synergism for the examined three binary surfactant mixtures as their values appear close to 1. More evidently, it was observed that $C_{12}TAB + C_{12}TPPB$ attributed a high degree of synergism and, thereby, became more efficient in reducing the surface tension. However, it was noticed that this trend decreases as the degree of hydrophobicity increases, which could be attributed to the difference in hydrophobic and hydrophilic groups resulting in a weak or low degree of synergism.

Thermodynamics of micellization and interfacial adsorption phenomenon

Our mixed surfactant systems are ionic in nature. Reported studies have rationalized such mixed systems as important as they clearly explain the role of head group–head group and chain–chain interactions which drive synergism. For mixed micelles, we have considered the thermodynamic analysis proposed by Maeda which involves ionic species

Table 1 Mixed micellar parameters: CMC (ideal and experimental), mole fraction of surfactant 1 in the mixed micelle (X_1^m), interaction parameter (β), activity coefficients (f^m)

Surfactant	CMC (mM)			X_1^m	β	f_1^m	f_2^m
	Tensiometry		UV–vis				
	Ideal	Experimental					
α_{C12TAB}							
0	2.04	1.95	2.00	–	–	–	–
0.25	2.65	1.54	1.50	0.18	−2.46	0.19	0.92
0.50	3.66	1.74	2.00	0.29	−2.69	0.26	0.80
0.75	5.90	2.28	2.50	0.41	−3.04	0.35	0.60
1.0	15.16	14.45	15.00	–	–	–	–
α_{C14TAB}							
0	0.60	0.61	0.60	–	–	–	–
0.25	0.77	0.64	0.65	0.18	−2.11	0.24	0.94
0.50	1.04	0.73	0.75	0.29	−2.17	0.33	0.84
0.75	1.65	0.82	0.85	0.43	−2.93	0.38	0.59
1.0	3.98	3.82	4.0	–	–	–	–
α_{C16TAB}							
0	0.16	0.26	0.25	–	–	–	–
0.25	0.34	0.32	0.35	0.14	−0.89	0.52	0.98
0.50	0.79	0.40	0.40	0.26	−0.65	0.70	0.96
0.75	0.92	0.50	0.50	0.45	−0.96	0.75	0.82
1.0	1.00	1.10	1.0	–	–	–	–

Table 2 Interfacial composition (X_1^o), interaction parameter (β^o), effectiveness (γ_{CMC}), surface excess (Γ_{max}), minimum area per molecule (A_{min}), packing parameter (P), and surface pressure (π_{CMC}) of binary surfactant mixture at 30 °C

Surfactant	X_1^o	β^o	f_1^o	f_2^o	γ_{CMC} (mNm^{-1})	Γ_{max} ($\times 10^6$ mol m^{-2})	A$_{min}$ (A^{o2})	P	π_{CMC} (mN m^{-1})
α_{C12TAB}									
0	–	–	–	–	39	1.55	107	0.20	32.3
0.25	0.56	−5.96	0.32	0.15	40	1.99	83	0.26	31.5
0.50	0.66	−4.4	0.60	0.15	41	1.25	132	0.16	30.5
0.75	0.81	−2.7	0.91	0.17	42	1.10	150	0.14	30.4
1.0	–	–	–	–	35	2.35	71	0.30	36.5
α_{C14TAB}									
0	–	–	–	–	41	1.40	119	0.18	30.1
0.25	0.22	−2.97	0.16	0.87	43	1.66	100	0.21	28.3
0.50	0.32	−2.84	0.26	0.75	42	2.01	83	0.26	29.4
0.75	0.43	−3.26	0.35	0.55	41	1.74	95	0.23	30.5
1.0	–	–	–	–	36	9.48	175	0.12	35.2
α_{C16TAB}									
0	–	–	–	–	44	1.16	143	0.15	26.8
0.25	0.16	−1.24	0.42	0.97	41	4.50	37	0.58	30.5
0.50	0.30	−1.33	0.52	0.89	39	3.53	47	0.45	32.0
0.75	0.46	−1.42	0.66	0.74	38	2.60	64	0.34	33.5
1.0	–	–	–	–	36	3.09	54	0.40	35.3

based on the phase separation model [34, 35]. Table 4 presents the free energy of micellization ($\Delta G_{\mathrm{Maeda}}$) as a function of the mole fraction of the ionic component in the mixed micelle which is given by:

$$\Delta G_{\mathrm{Maeda}} = RT(B_0 + B_1X_1 + B_2X_1^2) \tag{12}$$

where B_o is related to the CMC of the second surfactant within the mixture and is given by $B_o = \ln C_2$ (where C_2 is

Table 3 Parameters predicting the interaction and synergism in a binary surfactant mixture with varying hydrophobic environments at 30 °C

Mix system	β^o	$\ln\left(\frac{C_1^o}{C_2^o}\right)$	$1-\left({c_{12,min}}/{c_1^o}\right)$	β^m	$\ln\left(\frac{C_1^m}{C_2^m}\right)$	$1-\left({C_{12,min}^m}/{c_1^m}\right)$
C_{12}TAB + C_{12}TPPB	−13.1	2.02	0.99	−10.95	2.00	0.98
C_{14}TAB + C_{14}TPPB	−9.07	1.96	0.97	−7.21	1.85	0.94
C_{16}TAB + C_{16}TPPB	−3.99	1.50	0.85	−2.50	1.44	0.79

Table 4 Chain–chain interaction parameters of binary surfactant mixtures at 30 °C

Surfactant	B_0	B_1	B_2
α_{C12TAB}			
0	–	–	–
0.25	0.67	−0.46	2.46
0.50	0.67	−0.60	2.69
0.75	0.67	−1.04	3.04
1.0	–	–	–
α_{C14TAB}			
0	–	–	–
0.25	−0.49	−0.28	2.11
0.50	−0.49	−0.34	2.17
0.75	−0.49	−1.10	2.93
1.0	–	–	–
α_{C16TAB}			
0	–	–	–
0.25	−1.28	0.48	0.89
0.50	−1.28	0.72	0.65
0.75	−1.28	0.41	0.96
1.0	–	–	–

the CMC of C_nTPPB). The second term, B_1 relates to the standard free energy change, and the last coefficient, B_2, is equivalent to β^n as per the regular solution theory (RST), specifically, as $B_2 = -\beta^m$. Thus, once B_2 is calculated, we can obtain B_1 using

$$B_1 + B_2 = \ln\frac{C_1}{C_2} \tag{12a}$$

Negative values of B_1 indicate chain–chain interaction also plays an important role in mixed micellization.

The transfer of surfactant molecules from the bulk phase to the surface phase depends on the free energy change. As the value of free energy decreases, the surface becomes more stable thermodynamically, leading to more actives at the adsorbed surface. Thus, synergism in a mixed surfactant system depends on the extent of lowering of the measured free energy change [36, 37].

Thermodynamic parameters during micellization in terms of free energy such as surface free energy (ΔG_{min}), free energy of micellization (ΔG_{M}), and free energy of adsorption (ΔG_{ads}) were evaluated using the equations below, as described in the literature [24–26].

$$\Delta G_{\mathrm{min}} = A_{\mathrm{min}}\gamma_{\mathrm{CMC}}N_{\mathrm{A}} \tag{13}$$

$$\Delta G_{\mathrm{M}} = [X_1 \ln X_1 f_1 + X_2 \ln X_2 f_2]RT \tag{14}$$

$$\Delta G_{\mathrm{ads}} = \Delta G_{\mathrm{M}} - \frac{\pi_{\mathrm{CMC}}}{\Gamma_{max}} \tag{14a}$$

The last term $\left(\frac{\pi_{\mathrm{CMC}}}{\Gamma_{max}}\right)$ in Eq. (14a) expresses the work involved in transferring the surfactant molecule from a monolayer at a zero surface pressure to the micelle. Here, for all the binary mixtures, the last term of the Eq. (14a) is very small as compared to ΔG_{M}, which suggests that the work involved in transferring the surfactant molecule from a monolayer at zero surface pressure to the micelle is negligible.

According to RST, the excess free energy of micellization, (ΔG_{ex}) is calculated by using Eq. 15 which is related to excess enthalpy and the entropy of micellization as

$$\Delta G_{\mathrm{ex}} = \Delta H_{\mathrm{ex}} = \Delta H_{\mathrm{M}} = [X_1 \ln f_1 + (1 - X_1)\ln f_2]RT \tag{15}$$

$$\Delta S_{\mathrm{M}} = \frac{\Delta H_{\mathrm{M}} - \Delta G_{\mathrm{M}}}{T} \tag{15a}$$

Table 5 presents the data of the free energy change for all three systems, which appeared to be very low, indicating a more stable system and high surface activity which could be attributed to the evolution of synergism in the mixed surfactant system.

Solubilization study in mixed micellar system

Solubilization in surfactant micelles influences the absorption spectra of dyes. Such spectral change is typical dye behavior in the presence of cationic surfactants of opposite charge and a varying headgroup/hydrophobic environment. This phenomenon involves a consistent equilibrium existing between surfactant monomers and their respective micelles, the aggregation of the dye in the solution, the premicellar dye–surfactant complex and dye incorporated in the surfactant micelle. Studies have explained the role of hydrophobic interaction and electrostatic effect which results in the dye–surfactant complex formation in aqueous solution. However, such behavior is

Table 5 Thermodynamic parameters [free energy micellization by Maeda's approach ($\Delta G_{\mathrm{Maeda}}$), surface free energy ($\Delta G_{\min}$), free energy of micellization (ΔG_{M}), excess free energy (ΔG_{ex}), entropy of micellization (ΔS_{M})] of binary surfactant mixtures at 30 °C

Surfactant	$\Delta G_{\min}$ (KJ mol^{-1})	ΔG_{ads} (KJ mol^{-1})	ΔG_{M} (KJ mol^{-1})	$\Delta G_{\mathrm{ex}} = \Delta H_{\mathrm{M}}$ (KJ mol^{-1})	ΔS_{M} (J mol^{-1} K^{-1})
α_{C12TAB}					
0	25.11		–	–	–
0.25	19.92	−20.95	−5.14	−3.41	5.70
0.50	32.42	−28.03	−3.70	−2.11	5.27
0.75	36.94	−29.01	−1.45	−0.48	3.21
1.0	14.76		–	–	–
α_{C14TAB}					
0	29.40		–	–	–
0.25	25.91	−19.06	−1.96	−0.78	3.89
0.50	20.84	−17.29	−2.63	−1.12	4.96
0.75	23.37	−21.03	−3.52	−1.81	5.67
1.0	37.99		–	–	–
α_{C16TAB}					
0	38.29		–	–	–
0.25	9.05	−9.67	−1.28	−0.27	3.35
0.50	11.11	−10.38	−1.74	−0.31	4.75
0.75	14.49	−16.24	−2.34	−0.60	5.73
1.0	11.62		–	–	–

strongly connected with the chemical structure of the surfactant and the dye and also the way they assemble themselves in the micellar solution [38–40].

A dye solubilization study was performed to validate the CMC obtained from the surface tension measurements. For the solubilization study, we have used the hydrophobic dye, Orange OT which exhibits high affinity towards cationic surfactants. Figure 2 reveals the influence of surfactant hydrophobicity on the process of dye solubilization. A negligible amount of the Orange OT gets solubilized at low surfactant concentration while a sudden and steep rise was observed after the CMC. This value was noted as the CMC, the data of which are presented in Table 1.

In our study, the degree of dye solubilization followed the order of $C_{16}^{-} > C_{14}^{-} > C_{12}^{-}$ as the degree of hydrophobicity of the cationic surfactant had a major effect on micellization and aggregation. Our findings were similar to reported work which related the solubilization power with N_{agg} [40–43]. A reverse trend was observed for the $\mathrm{C_nTPPB}$ series, though, having a lower aggregation number than the $\mathrm{C_nTAB}$ series, the former was able to solubilize a larger amount of dye. The higher solubilization power and lower CMC of the $\mathrm{C_nTPPB}$ series could be explained by the three phenyl groups in the polar head group region which occupies a large area per molecule at the interface, imparting additional hydrophobicity, thereby promoting favorable conditions for micellization [38]. Figure 3 shows negative deviation from ideal behavior, indicating attractive interaction amongst all the three mixed surfactant systems. This behavior is agrees well with the negative values of β^{m} [24].

Conclusion

A detailed study of interfacial and micellar behavior for a single and binary mixture of quaternary, salt-based cationic surfactants in aqueous solution using surface tension and dye solubilization measurements was performed. The selected binary surfactant mixtures belonging to the family of *n*-alkyltrimethylammonium bromide and *n*-alkyltriphenylphosphonium bromide with alkyl chain length ($n = 12$, 14 and 16 carbon atoms) exhibited good surface activity. The composition of the mixed micelles and the negative value of the interaction parameters, β^{o} and β^{m} from Rubingh's theory, indicated an attractive interaction, i.e., synergistic mixing between each pair of surfactant. Further it was also inferred that the interaction decreased with an increase in the concentration of $\mathrm{C_nTPPB}$ which could be due to electrostatic repulsion between the ionic species of $\mathrm{C_nTPPB}$. Activity coefficients (f_1 and f_2) of mixed surfactant systems exhibited the ideality of the individual surfactant in the binary mixture. Out of our examined systems, the $\mathrm{C_{12}TPPB} + \mathrm{C_{12}TAB}$ mixture showed significant deviation from ideality with an average negative value of β as ~ -2.7. Such behavioral change in the ideality for the mixed micellar system could be attributed to the weakening of the electrostatic head group

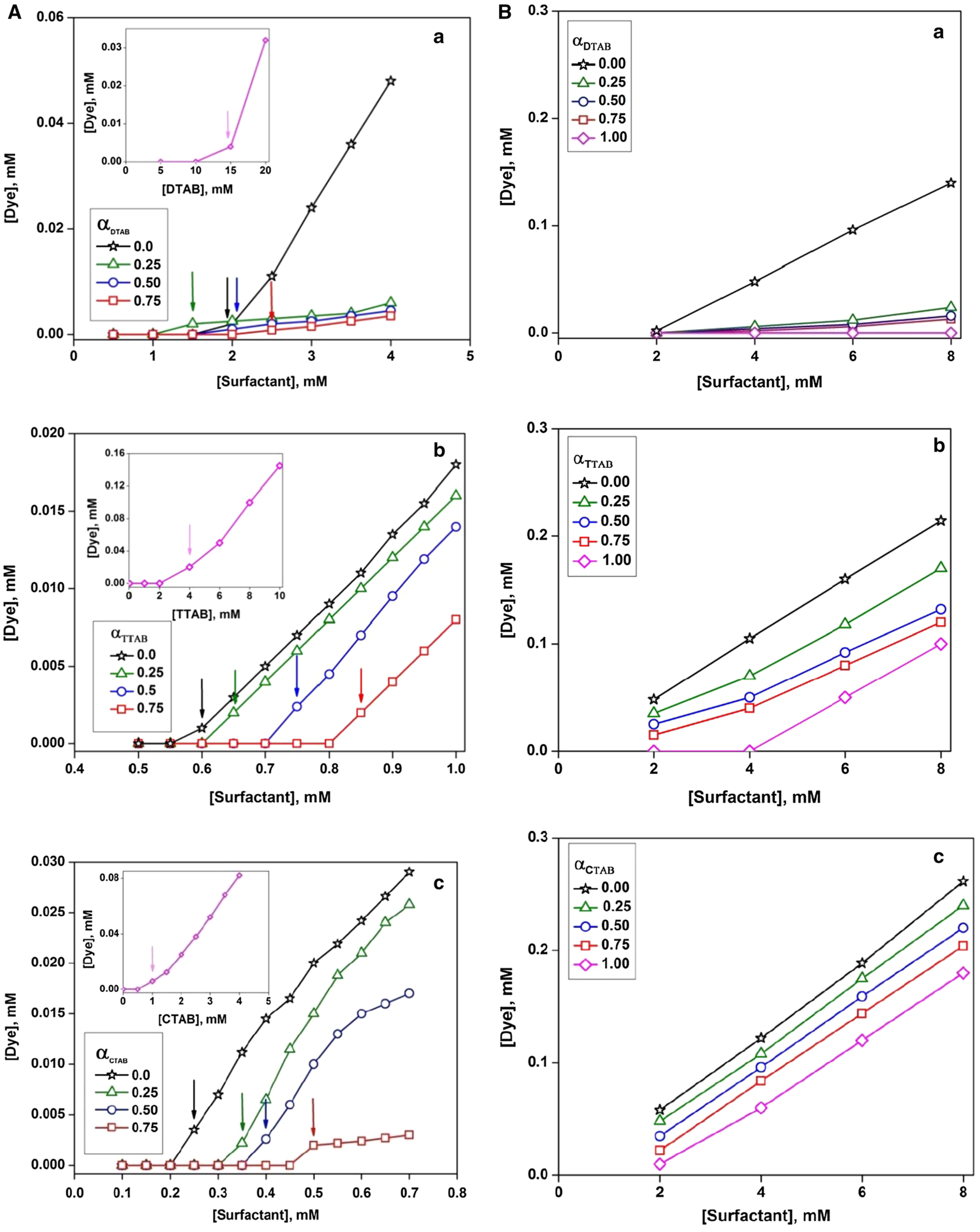

Fig. 2 **a** Dye solubilization behavior showing CMC in binary surfactant mixtures in aqueous solution at different mole fractions: *a* C_{12}TAB (α_{C12TAB}) with C_{12}TPPB and *b* C_{14}TAB (α_{C14TAB}) with C_{14}TPPB and *c* C_{16}TAB (α_{C16TAB}) with C_{16}TPPB, respectively, at 30 °C. The *inset figure* show the CMC value of the first surfactant in water at 30 °C. **b** Amount of Orange OT dye solubilized in binary surfactant mixture in aqueous solution at different mole fractions: *a* C_{12}TAB (α_{C12TAB}) with C_{12}TPPB and *b* C_{14}TAB (α_{C14TAB}) with C_{14}TPPB and *c* C_{16}TAB (α_{C16TAB}) with C_{16}TPPB, respectively, at 30 °C

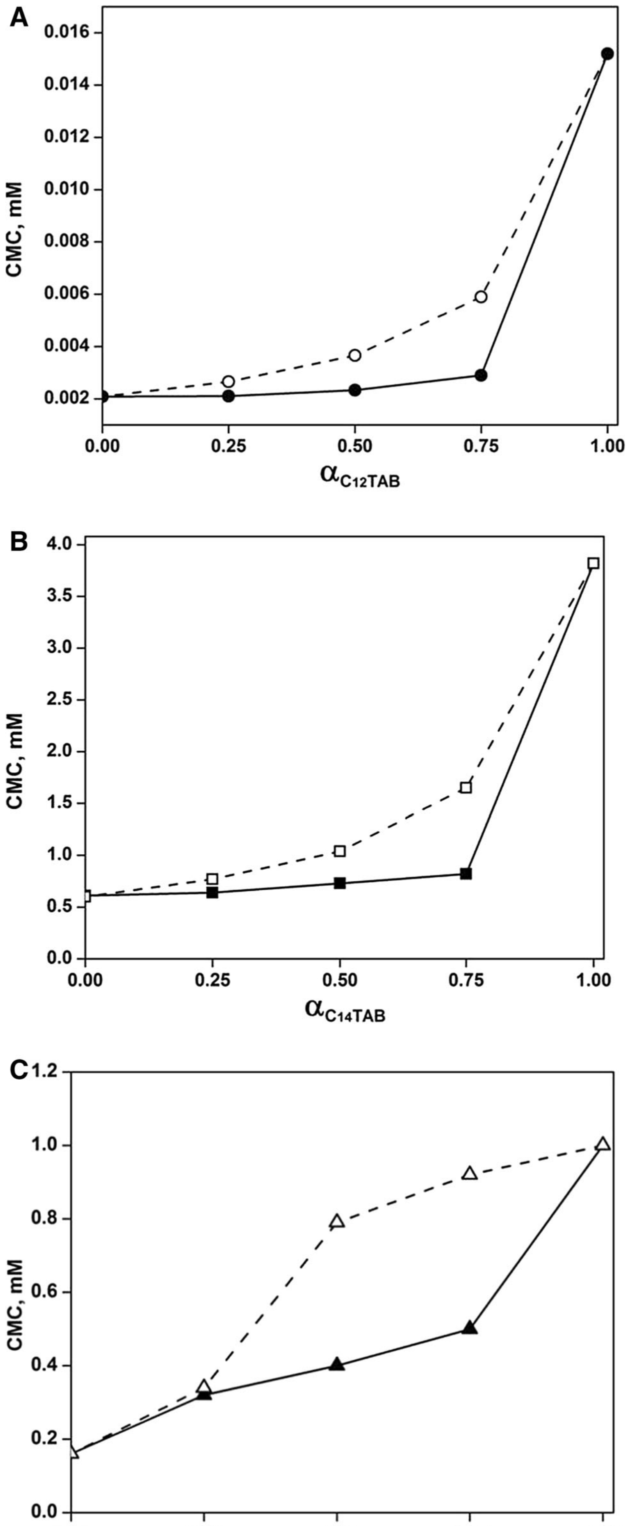

Fig. 3 Plot of CMC values (obtained from surface tension measurement) as a function of mole fraction of pure mixtures and their binary mixtures: **a** C_{12}TAB (α_{C12TAB}) with C_{12}TPPB and **b** C_{14}TAB (α_{C14TAB}) with C_{14}TPPB and **c** C_{16}TAB (α_{C16TAB}) with C_{16}TPPB at 30 °C. Experimental data (*solid line*) and ideal (*dotted line*)

repulsion, which favors the mixed micelle formation. A similar high degree of synergism was confirmed using Rosen's approach. The measured CMC values obtained for the pure and mixed components appeared closer to C_n-TPPB than C_nTAB, indicating a key role of the former in influencing the extent of interaction. The negative value of ΔG_M and ΔG_{ads} showed the micelle formation to be a spontaneous process and adsorption of surfactant at the air/solution interface to be energetically favorable, while a negative value of ΔG_{ex} ensured a higher order of stability for the mixed micelles. Considering these findings, we anticipate that such studies may prove beneficial in understanding the interfacial and micellar properties for well-characterized mixed micellar systems.

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