Chapter III

Self Aggregation of Cationic-Nonionic Surfactant Mixture in Aqueous Media: Tensiometric, Conductometric, Density, Light Scattering, Potentiometric and Fluorimetric Studies

Self aggregation of Tetradecyltrimethylammonium bromide (TTAB)-$[CH_3(CH_2)_{13}N^+(CH_3)_3Br^-]$ and Polyoxyethylene 23 lauryl ether (Brij-35) - $[CH_3\,(CH_2)_{11}(OCH_2CH_2)_{23}OH]$ binary surfactant mixture in aqueous medium was studied using tensiometric, conductometric, density, quasi elastic light scattering, potentiometric and fluorimetric measurements. The binary surfactant mixture was studied well above the Krafft temperature, which was evaluated by conductance measurements. Rubingh's nonideal solution theory predicted nonideal mixing and attractive interaction between the constituent surfactants in the mixed micelle. Moreover attractive interaction between the two surfactants in the mixed micelle is explained by assuming that water acts as a bridge between the hydrophilic polar groups of the surfactant molecules. The chain-chain interaction among the surfactant does not seem to be high in this case. Surface tension measurements indicate an existence of second state of aggregation for the mixed surfactant system, which is supported by the break in conductance-concentration of surfactant profile. Krafft temperature of TTAB decreases as the nonionic surfactant content increases in the mixed system. Quasielastic light scattering studies suggest an increase in hydrodynamic radius of micelle in the mixed surfactant system.

INTRODUCTION

Surfactant comprises a hydrophilic and a hydrophobic group. The different interactions of these two moieties with water is an important cause for surfactants to aggregate into micelles and other nanometer scale structures in aqueous solution.[1] Due to wide spread uses and application of surfactants as well as their micellar aggregates in chemical, biochemical, pharmaceutical and industrial fields, detailed investigation on the fundamentals of aggregation of existing conventional and newer amphiphiles are in progress.[2] The micelles composed of mixed surfactants occur in biological fluids and are very often used in industrial application, pharmaceutical and medicinal formulation for the purpose of solubilization, suspension and dispersion etc.[3,4] Extensive reports exist in literature on studies of different combination of mixed surfactant system viz. cationic-cationic,[5] nonionic-nonionic,[5,6] anionic-cationic,[7] anionic-nonionic[8,9] etc. Ionic-nonionic surfactant mixtures are important from fundamental as well as application point of view as they exhibit highly nonideal behavior on mixing and also their behavior can be complementary in the mixed micelle causing the cmc to decrease.[10] Cationic surfactants are useful as antifungal, antibacterial and antiseptic agents and have attracted recently more attention with reference to their interaction with DNA and lipids[11] whereas, the nonionic surfactants are useful as detergents, solubilizers and emulsifiers.[6]

In order to characterize the micelle formation of ionic-nonionic binary surfactant mixture, we are reporting detailed investigation of physicochemical properties of binary cationic-nonionic surfactant mixture (TTAB/Brij35). The physicochemical properties were characterized by adopting tensiometry, conductometry, fluorimetry, potentiometry and quasielastic light scattering measurements. Moreover, we have also discussed the evidence of existence of second state of surfactant aggregation for the mixed surfactant combination by employing tensiometric and fluorimetric techniques which has been further corroborated by conductance measurements in absence of any additive.

EXPERIMENTAL SECTION

Materials

Tetradecyltrimethylammonium bromide [$CH_3(CH_2)_{13}N^+(CH_3)_3Br^-$], M.W.336.4 (Lancaster, U.K.), TTAB was recrystallized thrice from dry acetone. Polyoxyethylene 23 lauryl ether (Brij-35) [CH_3 $(CH_2)_{11}$ $(OCH_2CH_2)_{23}$ OH] M.W.1199.8 (E. Merck, Germany) was used as received. The surface tension (γ) vs log C plot did not show any minimum. Double distilled water having specific conductivity 2-3 μScm^{-1}, pH=6.8 at 30°C was used throughout as the solvent for all measurements.

Methods

Krafft Temperature (T_k) Measurement

The Krafft temperature (T_k) of pure TTAB and binary TTAB/Brij 35 surfactant mixtures of different mole ratios has been determined by using electrical conductivity method.[12,13] The aqueous solution of surfactant (Total Concentration 5 mM, i.e. well above the cmc) were prepared by warming it at ~ 40 °C and was later placed in a refrigerator at ~5°C for at least 24 h, where the precipitation of hydrated surfactant crystal occurred. The temperature of the precipitated system was then raised gradually under constant stirring and the conductance (κ) was measured using a Welltronix, digital conductivity meter CM 100, having cell constant 1.00 cm^{-1}. The T_k was considered as the temperature where the conductance vs temperature profile showed an abrupt change in slope, as indicated by the arrows in the curve presented in Fig 1. This temperature was the same as that required to completely dissolve the hydrated solid surfactant and this can also be judged visually to be the point of complete clarification of the surfactant system. The reproducibility of T_k measurements on a single sample was within ± 0.1°C.

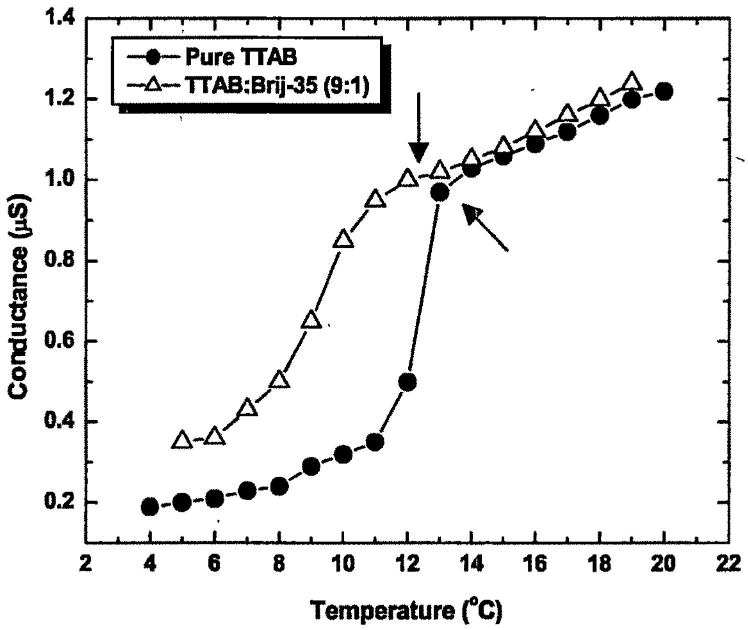

Figure 1. Representative plots of Conductance (C) vs Temperature (°C) for TTAB/Brij 35 mixed surfactant system. The arrow indicates Krafft Temperature.

Surface Tension Measurement

The critical micelle concentration (cmc) was determined by the Surface tension (γ) measurement using a du-Nouy ring tensiometer (S. C. Dey and Co. Kolkata, India) at 35°C. The temperatures were maintained within ±0.1°C by constantly circulating thermostated water through a jacketed vessel containing the solution. The concentration of solution was varied by aliquot addition of a stock surfactant solution of known concentration to a known volume of solvent in the vessel using a Hamilton microsyringe. For each set of experiments, the ring was cleaned by heating it in alcohol flame. The standard deviation of the mean in γ was ±0.5%.[9,14] The measured surface tension values were plotted as a function of the decadic logarithm of surfactant concentration. Representative plots of surface tension (γ) vs $\log_{10}$ Concentration of surfactant in solution ($\log_{10}C$) are shown in Figure 2. The reproducibility of the cmc was checked by duplicate runs and the error in the cmc was found to be less then ±1.0% (standard deviation of the mean) calculated from the experimental cmc data of at least two runs.

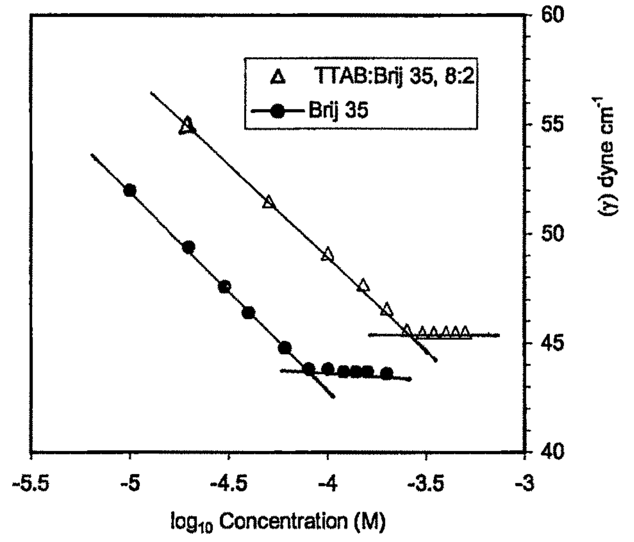

Figure 2. Representative plots of surface tension (γ) vs $\log_{10}C$ (concentration of surfactant, M) at 35 °C.

Conductance Measurements

The conductance measurements were done on a Welltronix, digital conductivity meter CM 100, having cell constant 1 cm^{-1}. A dip type cell of cell constant 1.01 cm^{-1} was used. The conductance of different solutions, which were obtained on aliquot addition of a known concentrated surfactant solution to a given volume of the thermostated solvent, was measured.[15] Representative conductance (k) vs concentration of surfactant (M) plots are shown in Figure 4.

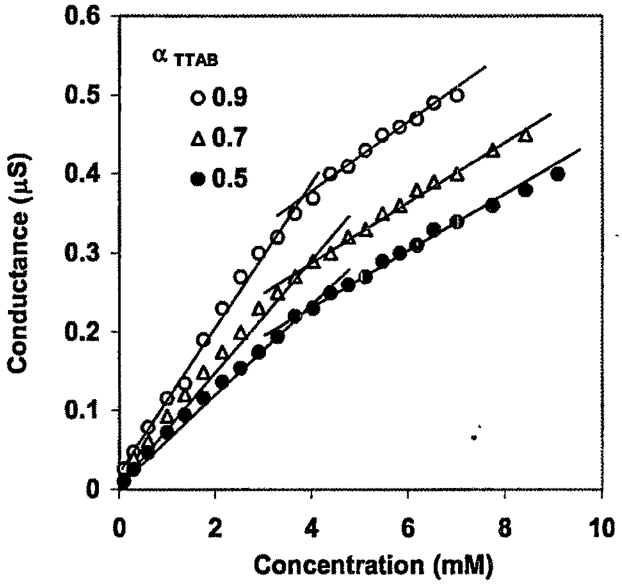

Figure 4. Representative plots of Conductance (C) vs Concentration of Surfactant (mM) at 35 °C.

Quasielastic Light Scattering (QELS)

QELS measurements were carried out for TTAB/Brij-35 mixed surfactant system (total concentration 25 mM) at five different scattering angles (50, 70, 90 110 and 130°) using a Malvern 4800 photon correlation spectroscopy system. The instrument is equipped with a 2 W argon ion laser (λ = 514.5 nm) with a vertically polarized light. All measurements were carried out at an output power of 250 mW and at 25 ±0.1°C. The surfactant solutions were filtered through 0.2µ Millipore Nylon filter directly in to the sample cell and sealed until use. The intensity correlation function was measured 5 times for each sample at each angle. The average decay rate was obtained from the measured autocorrelation function using the method of cumulants employing a quadratic fit[16] and the error in these repeated measurements was ≤ 5%.

RESULTS AND DISCUSSION

Krafft Temperature (T_k) of Pure Ionic and Binary Surfactant Mixture

The Krafft temperature can be defined as the melting point of hydrated surfactant. It is evident from Fig. 1 that, at low temperature, conductance increases slowly because the solubility of the ionic surfactant is quite limited. During a temperature transition stage, conductance increases sharply with increasing temperature, due to gradual dissolution of the surfactant until the Krafft Temperature. After T_k the conductance increases slowly due to the increase in ionic mobility with increasing temperature. The T_k of pure TTAB was found to be 13.2°C. The T_k of TTAB decreases with the increasing ratio of nonionic monomeric surfactant, as the cmc of mixed micelle is lower than that of pure TTAB (Figure 7). The T_k of TTAB decreased as system heterogeneity increases due to addition of Brij-35. This is due to a decrease in unimeric concentration of the precipitating surfactant caused by formation of mixed micelles[17,18].

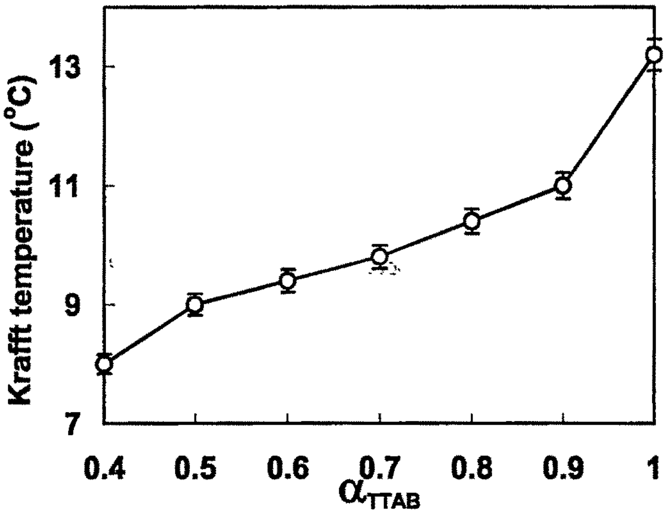

Figure 7. Variation of Krafft Temperature, T_k (°C) as a function of mole fraction of TTAB in TTAB/Brij 35 surfactant mixture.

As a result, the solution temperature must be lowered for precipitation to occur at equilibrium. As two surfactants are mixed above the cmc, dilution of least-soluble surfactant i.e. TTAB in micelle occurs, resulting in a shift in equilibrium towards micelle. Also as the nonionic surfactant is added, the absolute electrical potential on the micellar surface is reduced due to inversion of the Brij-35 between the charged head-group of the TTAB surfactant. Since the liquid phase is the binary surfactant mixture, the quantitative expression for the melting point depression can be written in the following form to calculate the enthalpy of fusion (ΔH_1^0)[19,20]

$$\Delta H_1^0 = \frac{-\ln \overline{x_2{}^m} RTT_1{}^o}{T_1^o - T} \qquad (2)$$

where $\overline{x_2{}^m}$ is the mole fraction of TTAB in mixed micelles. T_1^o and T are the T_k of TTAB and its binary mixtures, R is the gas constant. $\Delta H_1{}^0$ values thus computed for TTAB/Brij 35 surfactant mixture has been illustrated in Figure 8. The endothermic enthalpy of fusion of TTAB decreases as nonionic surfactant content increases in the system. The variation of the $\Delta H_1{}^0$ is linear with the concentration of X_{TTAB} in the solution. This indicates that 236.07 kJmol^{-1} of heat is required for the fusion of one mole of pure hypothetical TTAB micelle.

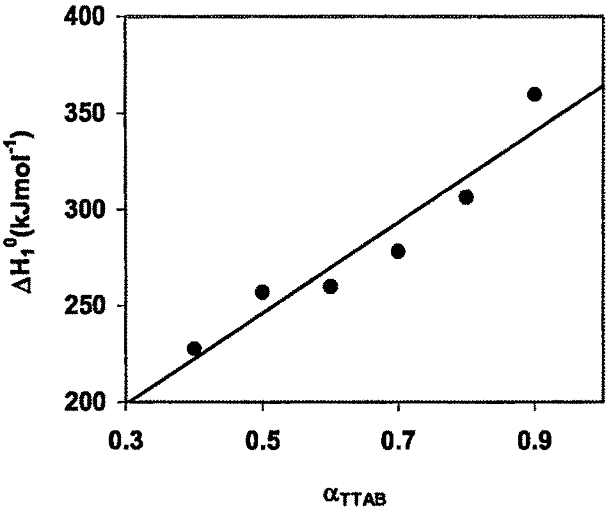

Figure 8. Plot of enthalpy of fusion (ΔH_l^0) vs mole fraction of TTAB in TTAB/Brij 35 surfactant mixture.

Surface Properties of Surfactant Mixtures

The cmc values of single as well as binary surfactant mixture (TTAB/Brij35) by surface tension, and conductance measurements are presented in Table 2. The cmc values of binary combinations fall between the cmc values of the constituent surfactants, though the cmc variation with mole fraction of TTAB is not linear.

TABLE 2 Critical Micelle Concentration (mM) of TTAB/Brij 35 Mixed Surfactant System at 35°C by Different Methods.

α_{TTAB}	CMC (mM)	
	ST	Conductance
0.0	0.08±0.001	-
0.3	-	4.50±0.09
0.4	0.100±0.001	-
0.5	0.125±0.0013	4.02±0.08
0.7	-	3.75±0.08
0.8	0.250±0.003	-
0.9	0.500±0.005	3.80±0.08
1.0	3.70±0.037	3.70±0.07

For pure TTAB, the surface tension, fluorescence (data not given), e.m.f. (data not given) and conductance gave the same value of cmc at 35°C (Table 2). There is no second cmc in this case. In case of Brij 35, we could not do the conductance and e.m.f. measurements, but surface tension and fluorescence methods gave the same cmc values. For 1:1, TTAB/Brij 35 system, surface tension and fluorescence (data not given) method gave same cmc values, but cmc value obtained by conductance is much higher. However, γ - $\log_{10}C$ plot does show a dip around the same value, where conductance shows a break (c.f. Figure 10a & 10b) This may be due to the second state of aggregation, which arises because of change of shape of a micelle which has also been observed by QELS measurements. However, by e.m.f measurements, we got a much different value of cmc for 1:1 surfactant mixture. At 9:1, TTAB/Brij 35 system, surface tension and fluorescence gave same value of cmc. The cmc values obtained by conductance and e.m.f. measurements did not tally. This indicates that, for pure ionic surfactants, all experimental methods are good enough for cmc determination. Whereas, emf and conductance methods are not sensitive enough to detect the break at very low concentration i.e for cmc determination of binary TTAB/Brij 35 surfactant mixture. We have also been able to obtain the so called second cmc for 8:2, TTAB/Brij-35 surfactant mixtures. It is evident from Table 2 that surface tension and fluorescence (data not given) measurements gave comparable results of cmc for mixed surfactant system. However conductance measurements gave a higher value of cmc and emf measurements resulted in cmc values intermediate to that obtained by conductance and surface tension measurements. This suggests that different methods are sensitive to different forms of micellar aggregates. This can be rationalized in terms of mass action model, according to which micellization is a stepwise process. Surface tension and fluorescence methods detect smaller micellar aggregates formed at lower concentration. However conductance method is capable to detect large micellar aggregates resulting due to sphere to rod transitions. The intermediate values of cmc obtained by emf measurements suggest that the ion selective electrode senses mixed micelles of intermediate sizes. This probably means that cmc determination depends upon the micelle size too, which is quite surprising. Overall, it can be inferred that surface tension and fluorescence methods give accurate estimate of micelle formation and hence cmc. However conductance measurements are comparatively less accurate. Whereas emf measurements, seem not to be suitable for determination of cmc of mixed surfactant system.

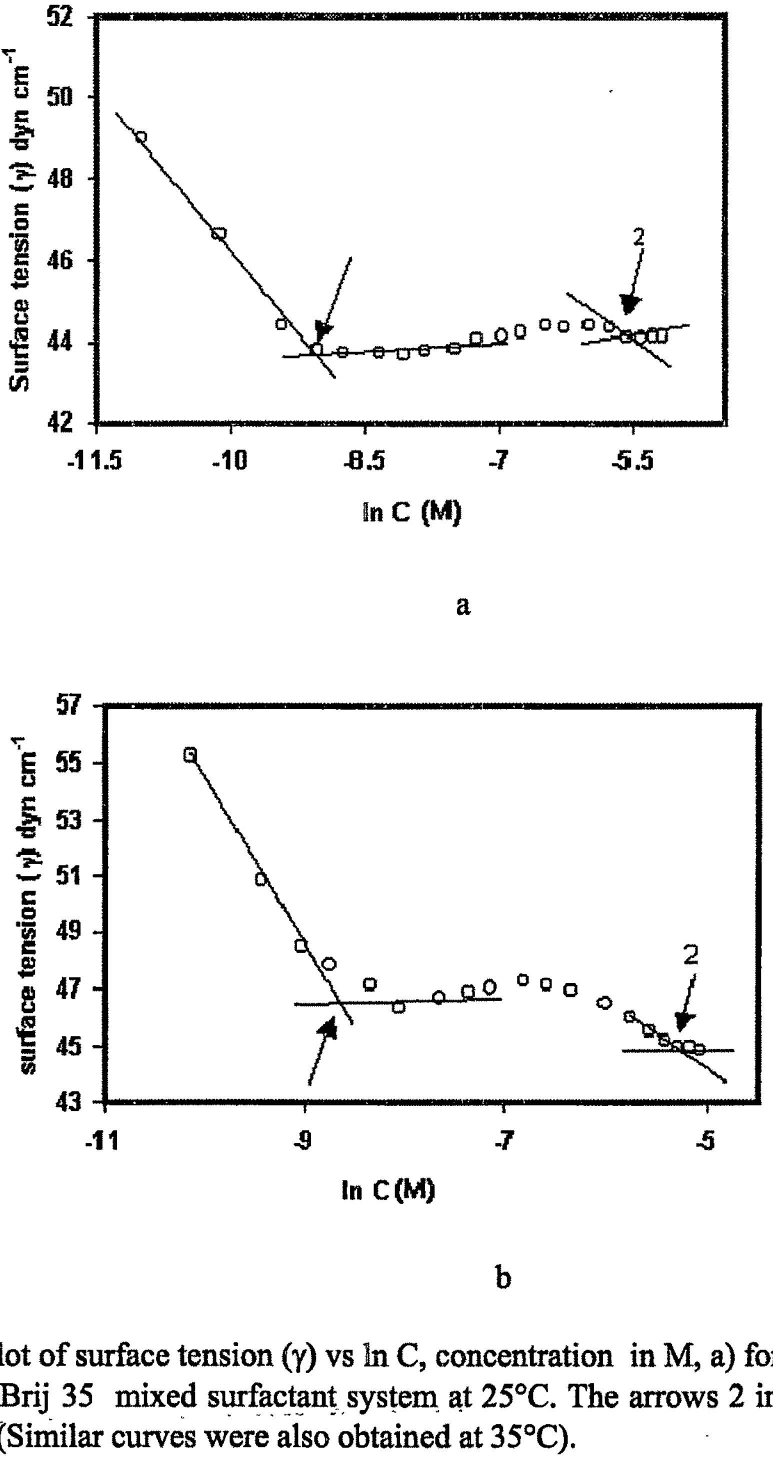

Figure 10. Plot of surface tension (γ) vs ln C, concentration in M, a) for 1:1, b) for 8:2, TTAB/Brij 35 mixed surfactant system at 25°C. The arrows 2 indicates the second cmc (Similar curves were also obtained at 35°C).

It is evident from Figure 10 that, in addition to the normal break point in γ - $\log_{10}$ C plot, there is another break in γ - log C plot for 1:1 and 8:2, TTAB/Brij-35 mixture. Different authors[21-23] have reported two different states of aggregates for nonionic as well as cationic surfactants. But in this article, we have reported the evidence for existence of second state of aggregation of 1:1 and 8:2, TTAB/Brij 35 mixed surfactant system. The first cmc corresponds to the normal spherical micellar aggregates formed by the association of surfactant monomers at a critical concentration. Whereas, the second state of aggregation represented by the second critical micelle concentration is due to structural transformations at surfactant concentration well above the critical micelle concentration. Such micellar transitions for pure cationic surfactants have been reported by different techniques earlier[23], however we have provided the evidence for second state of aggregation for a surfactant mixture, by tensiometric technique, because conductometric method is not very suitable for cmc determination, when dealing with systems of nonionics with very low cmcs (i.e Brij 35) with ionic surfactant (i.e TTAB).

It was suggested by Bernheim-Groswasser et al.[24] that, for micellar solution of cationic dimeric (gemini) and nonionic surfactants[25], the first cmc is due to the globular micelles, whereas the second cmc is because of coexistence of globular micelles with longer (semi flexible) linear micelles. i.e. the second state of aggregation results due to sphere to rod transition. This has been suggested by other workers[23,26,27] also to explain the second state of aggregation. However, we believe that for TTAB/Brij-35 mixed surfactant system, in addition to sphere to rod transition, an alternative mechanism is responsible for the second state of aggregation. The alternative phenomenon is the formation of two different kind of micelles by the constituent surfactants. One kind of micelle is the mixed micelle involving both TTAB and Brij-35 in one single micelle and other micelle are formed by individual surfactant (i.e. TTAB and Brij-35 micelles). The first break corresponds to the mixed micelle formed by TTAB and Brij-35 and the second break is due to the coexistence or separation of a mixed micelle in to micelle of individual constituent surfactants.

Surfactant-Surfactant Interaction

The cmc values for the mixed surfactant system (C_{12}) can be calculated theoretically using the Clint's equation,[28]

$$\frac{1}{c_{12}} = \frac{\alpha_1}{c_1} + \frac{1-\alpha_1}{c_2} \tag{8}$$

where the C_{12}, C_1 and C_2 are the cmc values of the mixture, surfactant 1 and surfactant 2 respectively. α_1 is the mole fraction of surfactant 1 and α_2 (i.e. $1-\alpha_1$) is the mole fraction of surfactant 2 respectively in solution. The cmc values obtained experimentally (cmc_{exp}) are plotted as a function of mole fraction of TTAB in Figure 11.

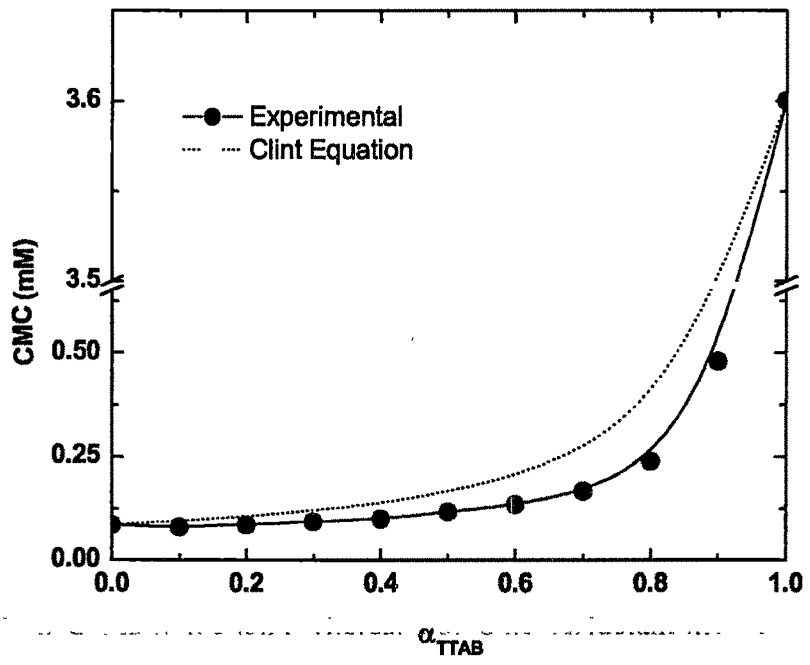

Figure 11. Variation of critical micelle concentration (mM) vs mole fraction of TTAB (α_{TTAB}) for the mixed surfactant system at 25°C.

It is clear from Figure 11 that, cmc$_{exp}$ values are lower than C_{12} values. This indicates that, there are interactions between the constituent surfactants in the mixed micelle, which results in nonideal behaviour. Hence in order to investigate the nature of interaction between the constituent surfactants in the mixed micelle, we calculated the interaction parameter β^m and B$_1$, using Rubingh as well as Meada's theory[29,30] respectively. The β^m values were calculated using the equations[31]

$$\frac{(X_1)^2 \ln\left(\alpha_1 C_{exp} / X_1 C_1\right)}{(1-X_1)^2 \ln\left[(1-\alpha_1) C_{12} / (1-X_1) C_2\right]} = 1 \tag{9}$$

$$\beta^m = \frac{\ln\left(\alpha_1 C_{exp} / X_1 C_1\right)}{(1-X_1)^2} \tag{10}$$

where X$_1$ is the mole fraction of surfactant 1 in the mixed surfactant micelle, C$_1$, C$_2$ and C$_{12}$ are the molar concentration in the solution phase of surfactant 1, 2 and their mixture, respectively. Whereas α_1 and α_2 (i.e 1-α_1) are stoichiometric mole fraction of surfactant 1 and 2 respectively. In case of micellar interactions, these are cmc values. The β^m values are presented in Table 3 and it is found that they are negative at all mole fractions of the mixed surfactant system suggesting that the interaction between the two surfactants is more attractive in the mixed micelle than the self interaction of two surfactants before mixing. Moreover, the β^m values become less negative as TTAB content in the mixed surfactant system increases. Similar behaviour has been observed for the interaction parameter calculated using Maeda's approach[30], which we discuss in the latter part of this paragraph. The β values obtained using Rubingh's method[29] are useful in understanding the interaction between the two surfactants. If long range electrical interactions are present in the system, β^m explains them very well. However Maeda[30] and Ruiz et al[32] have reported that both chain/chain and headgroup/headgroup interactions may operate in the mixed system. β^m values explain the headgroup/headgroup interactions, but it does not encompass the chain/chain interactions between the hydrocarbon segments of the constituent surfactant molecules, particularly when the chains are of dissimilar lengths. The lower cmc values of mixed system can be due to the decrease in ionic head group repulsions caused by the presence of nonionic surfactant molecules between the TTAB head groups. Maeda[30] suggested another parameter B_1, the chain-chain interaction parameter, that actually contributes to the stability of mixed micelle. The free energy of micellization (ΔG_m) as a function of ionic component in the mixed micelle (X_2) is given by,

$$\Delta G_m = RT(B_0 + B_1 X_2 + B_2 X_2^2) \tag{11}$$

$$\text{where } B_o = \ln C_2 \;\; (C_2 \text{ is the cmc of the nonionic surfactant}) \tag{12}$$

$$B_1 + B_2 = \ln\left(\frac{C_1}{C_2}\right) \;\; (C_1 \text{ is the cmc of the ionic surfactant}) \tag{13}$$

$$B_2 = -\beta^m \tag{14}$$

All quantities in the above equation are expressed on a unitary scale. The calculated values of B_1, B_2 and (ΔG_m) are reported in Table 3. It is evident that the ΔG_m values calculated from phase seperation model *($\Delta G_m = RT\ln Xcmc$, Xcmc* is cmc in mole fraction scale) and by Maeda's method[30] agree reasonably well (within ± 5% for most of the mole ratios of the mixed system). This indicates that the fraction of counter ion bound to the mixed micelle is probably negligible, because in that case the ΔG_m values would have been much different. This probably is the reason as to why a break point in the conductance-concentration plot is not observed at lower cmc obtained by the surface tension/fluorescence methods. The B_1 values are negative at lower mole fraction of TTAB in the mixed micelle and become positive at $\alpha_{TTAB} > 0.6$. The cationic surfactant has 14 carbon in its hydrocarbon chain, whereas nonionic surfactant has 12 carbons. Hence according to Maeda[30], as the chain lengths are different, there should be chain – chain interaction helping in the stability of the micelle. The interaction may also be explained by the fact that some water molecules may be shared by different head groups as well as by the hydrophobic chains. i.e water molecules may behave as some type of bridge between the molecules just below the water-micelle interface, and thereby the attractive interaction will ensue as we suggested earlier[33]. Mukerjee[34] also suggested the existence for attractive interaction between hydrocarbon/fluorocarbon surfactants in the mixed by what is termed as a "contact hydrophobic interaction". Such contact hydrophobic interaction also may be the reason for attractive interaction in the present hydrocarbon/hydrocarbon surfactant system though the interaction may not be as strong as in fluorocarbon/hydrocarbon system. However the B_1 values seem to be a function of composition of the system. The less negative values of β^m and positive B_1 values indicate that head group-head group repulsions are dominant at higher mole fraction of TTAB in the mixed micelle ultimately delaying mixed micelle formation.

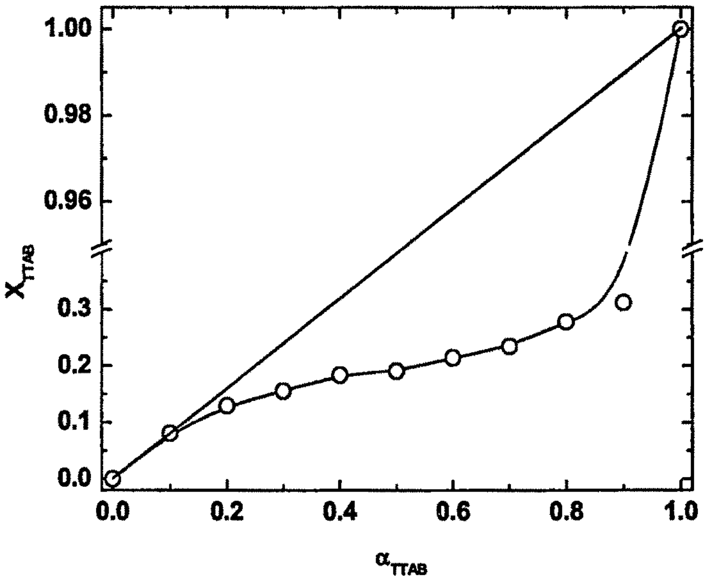

Figure 12. Plot of mole fraction of TTAB (X_{TTAB}) in the mixed micelle vs stoichiometric mole fraction of TTAB (α_{TTAB}) for the mixed surfactant system at 25°C.

Also, it is quite clear from Figure 12 as well as Table 3 that, the experimental mole fraction values of TTAB in the mixed micelle are lower than that of stoichiometric mole fraction values. This suggests less transfer of TTAB from the solution to the micellar phase and more dominance of Brij 35 in the mixed micelle.[35] Thus the negative β^m values are a result of reduction of electrostatic self repulsion between TTAB head group due to the presence of Brij 35.

Moreover, the excess free energy of mixing can be calculated from the activity coefficient (f) data as follows,

$$\Delta G_{ex} = RT\left[X_1 \ln(f_{TTAB}) + (1 - X_1)\ln(f_{Brij35})\right] \tag{15}$$

The calculated ΔG_{ex} values are all negative and are presented in Figure 13 . The negative excess free energy of mixing values suggest relatively more stable mixed micelle.

Quasielastic Light Scattering (QELS)

Figure 14 represents the average decay rates of electric field correlation functions (Γ) as a function of q^2 for 25mM TTAB/Brij-35 mixed surfactant system, where q is the scattering vector given by

$$q = \frac{4\pi n \sin(\theta/2)}{\lambda} \tag{16}$$

where n, θ and λ are refractive index of solvent, scattering angle (50 – 130°) and wave length of laser in vacuum respectively. For TTAB as well as TTAB/Brij-35 mixture at all mole ratios, measurements were carried out in presence of four different concentrations of NaCl. The diffusion coefficient (D_0) values were obtained from the slope of Γ vs q^2 plot. The corresponding equation being $\Gamma = D_o q^2$. The diffusion coefficient (D_o) for TTAB and Brij-35 mixed surfactant system, were evaluated by plotting diffusion coefficient as a function of concentration of NaCl and then extrapolating the same to zero concentration of salt.

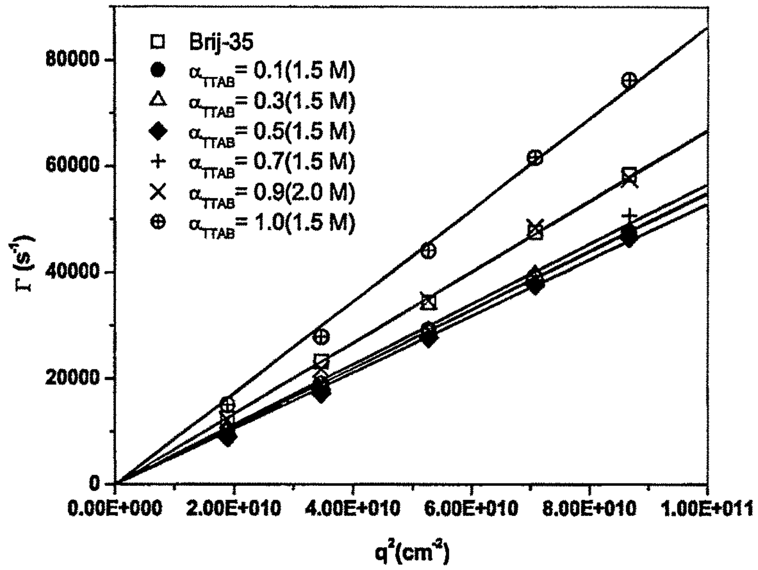

Figure 14. Representative plots average decay rate of intensity correlation function (Γ) as a function of q^2 for TTAB/Brij 35 mixed surfactant system (total surfactant concentration, 25 mM) at 25°C.

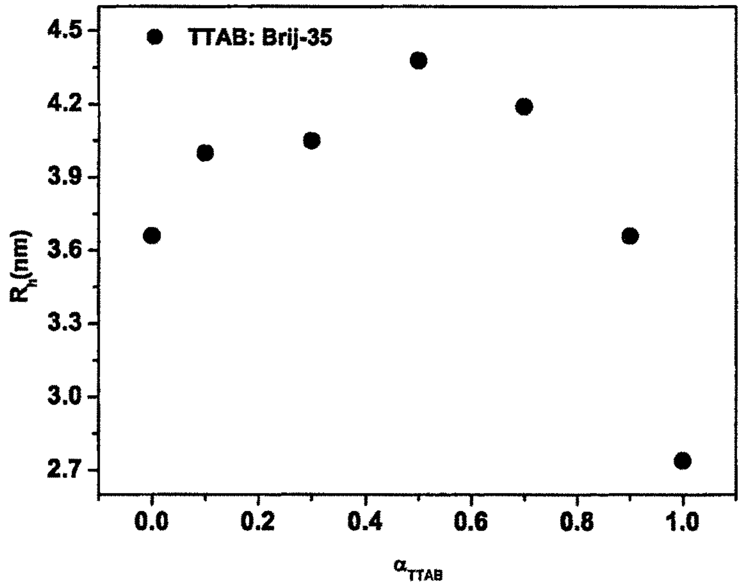

Figure 15. Hydrodynamic radius of micelle (R_h) of micelle as a function of mole fraction of TTAB for TTAB/Brij 35 mixed surfactant system at 25°C.

TABLE 1 Hydrodynamic Radius (R_h), for TTAB/Brij 35 Mixed Surfactant System.

α_{TTAB}	R_h (nm)
0.0	3.66 ±0.18
0.1	4.00 ±0.20
0.3	4.05 ±0.20
0.5	4.38 ±0.22
0.7	4.19 ±0.21
0.9	3.66 ±0.18
1.0	2.74 ±0.14

Translational diffusion coefficient values thus obtained (Table 1) were used to calculate the dissociated hydrodynamic radius of the micelle by applying the Stokes-Einstein equation[36]

$$R_h = \frac{k_B T}{6\pi\eta_0 D_o}$$

where k_B is the Boltzmann constant, T is the absolute temperature, and η_o is the solvent viscosity. The hydrodynamic radius of micelle *(R_h)* values are plotted as a function of mole fraction of TTAB in Figure 15. It is evident from Fig 15 that the R_h values for mixed system are higher than that of TTAB as well as Brij-35. This is because the head group-head group repulsions between the charged TTAB micelle are reduced due to the presence of Brij-35 in the mixed molecule. Hence micellar aggregation is facilitated and a mixed micelle having higher hydrodynamic radius compared to that of constituent surfactant is formed.

CONCLUSIONS

The self aggregation behaviour of binary TTAB/Brij 35, cationic-nonionic surfactant mixture in aqueous medium was studied by tensiometry, conductometry, density, quasi elastic light scattering and fluorimetry. The tensiometric results suggest an existence of second state of aggregation for the mixed surfactant system in 1:1 and 8:2, molar ratio, which is equivalent to the conductometric cmc obtained from the break in the conductance-concentration profile. Krafft temperature of TTAB decreases as the nonionic surfactant content increases in the mixed system, which indicates that Brij 35 increases the solubility of TTAB. Quasi-elastic light scattering studies suggest mixed micellar aggregates formed for this system have higher hydrodynamic radius than that of the aggregates formed by single surfactant. Rubingh and Maeda's theory was applied for analysis of this mixed surfactant system and both the approaches suggest attractive interactions between the constituent surfactants in the mixed micelle. Moreover attractive interactions between the constituent surfactants in the mixed micelle have been explained on the basis of "contact hydrophobic interactions" as well as by the presence of water bridge between the headgroups. Partial specific volume was measured employing density measurements and the hydration factor (δ) values thus obtained are higher in the mixed micelles compared to the individual pure components, suggesting that the mixed micelles are more hydrated, which is further substantiated by the higher values of hydrodynamic radius (R_h) compared to the dry micellar radius (R_O).

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