

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

K. Shivaji Sharma, Sandeep R. Patil, and Animesh K. Rakshit*

Department of Chemistry, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara 390 002, India

Karen Glenn, Maryjo Doiron, and Rama M. Palepu*,†

Department of Chemistry, St. Francis Xavier University, Nova Scotia, Antigonish, NS B2G 2W5, Canada

P. A. Hassan

Novel Materials and Structural Chemistry Division, Bhabha Atomic Research Center, Trombay, Mumbai 400 085, India

Received: April 20, 2004; In Final Form: June 19, 2004

Self-aggregation of tetradecyltrimethylammonium bromide (TTAB, $[\text{CH}_3(\text{CH}_2)_{13}\text{N}^+(\text{CH}_3)_3\text{Br}^-]$) and polyoxyethylene 23 lauryl ether (Brij-35, $[\text{CH}_3(\text{CH}_2)_{11}(\text{OCH}_2\text{CH}_2)_{23}\text{OH}]$) binary surfactant mixture in aqueous medium was studied using tensiometric, conductometric, density, quasielastic light scattering, potentiometric, and fluorometric 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. The partial specific volume of pure as well as binary surfactant mixtures was also evaluated, and it was inferred that the mixed micelles are more hydrated compared to individual components. The excess Gibbs free energy of mixing was evaluated, and it indicated relatively more stable mixed micelles for this binary combination. Surface tension measurements indicate an existence of a second state of aggregation for the mixed surfactant system, which is supported by the break in conductance–concentration of surfactant profile. The Krafft temperature of TTAB decreases as the nonionic surfactant content increases in the mixed system. Quasielastic light scattering studies suggest an increase in the hydrodynamic radius of the 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 widespread 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, dispersion, etc.^{3,4} Extensive reports exist in the 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

To characterize the micelle formation of ionic–nonionic binary surfactant mixture, we are reporting a detailed investigation of physicochemical properties of binary cationic–nonionic surfactant mixture (TTAB/Brij35). The physicochemical properties were characterized by adopting tensiometry, conductometry, fluorometry, 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 fluorometric techniques that have been further corroborated by conductance measurements in the absence of any additive.

* To whom correspondence should be addressed. E-mail: akrakshi@yahoo.co.in. Fax: +91 265 2795552.

† E-mail: rpalepu@stfx.ca.

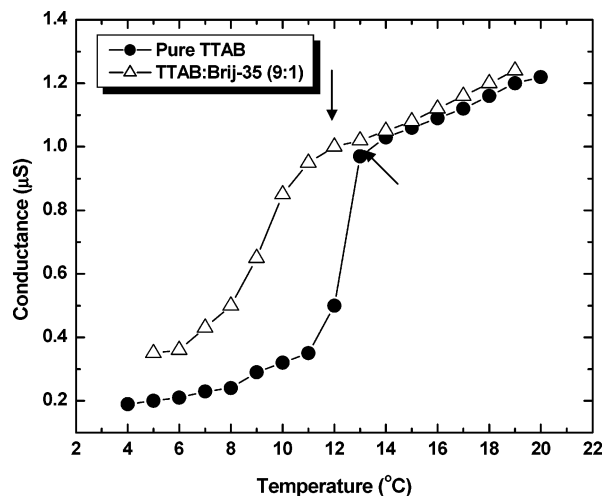


Figure 1. Representative plots of conductance (C) vs temperature ($^{\circ}\text{C}$) for TTAB/Brij 35 mixed surfactant system. The arrow indicates the Krafft temperature.

Experimental Section

Materials. Tetradecyltrimethylammonium bromide (TTAB, $[\text{CH}_3(\text{CH}_2)_{13}\text{N}^+(\text{CH}_3)_3 \text{Br}^-]$, MW 336.4, Lancaster, U.K.) was recrystallized thrice from dry acetone. Polyoxyethylene 23 lauryl ether (Brij-35, $[\text{CH}_3(\text{CH}_2)_{11}(\text{OCH}_2\text{CH}_2)_{23}\text{OH}]$, MW 1199.8, E. Merck) was used as received. The surface tension (γ) vs $\log C$ plot did not show any minimum. Cetyl pyridinium chloride (CPC) was purchased from Sigma and purified by repeated crystallization from acetone and used as quencher. Pyrene (Fluka) was recrystallized from cyclohexane. Sodium tetraphenylborate (NaBPh_4) (E. Merck, Germany) and Dioctyl phthalate (Plasticizer) (Suvidinath Laboratories) were used as received. Double distilled water having specific conductivity $2\text{--}3 \mu\text{S cm}^{-1}$, 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) was prepared by warming it at $\sim 40^{\circ}\text{C}$ and was later placed in a refrigerator at $\sim 5^{\circ}\text{C}$ 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} . 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 Figure 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 $\pm 0.1^{\circ}\text{C}$.

Surface Tension Measurement. The critical micelle concentration (cmc) was determined by the surface tension (γ) measurement using a duNoüy ring tensiometer (S. C. Dey and Co. Kolkata) at 35°C . The temperatures were maintained within $\pm 0.1^{\circ}\text{C}$ 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

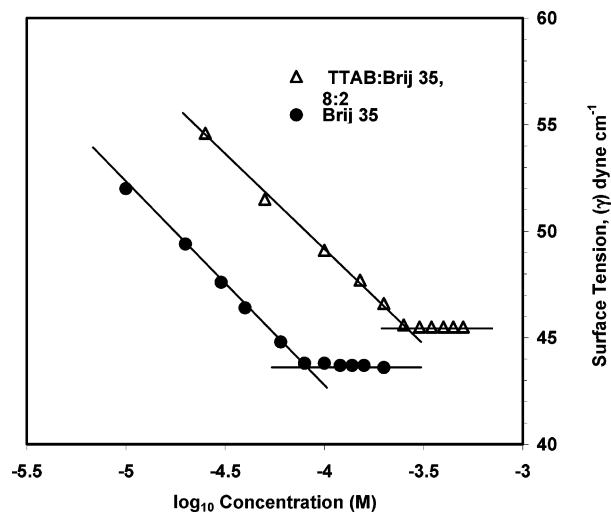


Figure 2. Representative plots of surface tension (γ) vs $\log C$ (concentration of surfactant, M) at 35°C .

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 $\pm 0.5\%$.^{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 $\log C$ 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 than $\pm 1.0\%$ (standard deviation of the mean) calculated from the experimental cmc data of at least two runs. The surface tension was determined both at Baroda and Antigonish (Fischer Tensiometer equipped with a 13 mm diameter Pt–Ir ring) and there was an excellent match of the cmc values.

Electrochemical Measurements. Potentiometric measurements were carried out using a cationic surfactant selective electrode, which was prepared as follows.

Membranes were made from low molecular weight poly(vinyl chloride) (PVC) mixed with a large quantity of plasticizer. PVC (0.8 g) and dioctyl phthalate (DOP, 1.2 g) were mixed in 10 mL of THF up to the complete dissolution of the PVC (solution A). DTABPh_4 was used to have BPh_4^- ion as the mobile anionic site in the membrane for TTA^+ detection, which was prepared by mixing equimolar aqueous solutions of two salts: dodecyltrimethylammonium bromide (DTAB) and sodium tetraphenylborate (NaBPh_4). The solution obtained was extracted three times in dichloromethane. After evaporation of solvent, the precipitate was recrystallized twice from an ether–methanol mixture. The DTABPh_4 so obtained was dissolved in THF to make a $10^{-2} \text{ mol L}^{-1}$ solution (solution B). Three milliliters of solution A was mixed with 0.2 mL of solution B, and the clear solution was spread on a clean and clear glass surface of a flat dish, which lost THF by evaporation at room temperature, forming the membrane in the form of thin film. The membrane was removed and cut into small pieces and fixed on the open end of a narrow glass tube with PVC–THF paste as glue. The membrane was then conditioned with the reference solution (very dilute solution of TTAB or TTAB/Brij 35 surfactant mixture) prior to electrochemical measurements. Aliquot addition of known concentration of surfactant solution to a fixed quantity of solvent (water) was done, and the corresponding emf values were recorded. Stable emf values ($\text{mV} \pm 1\%$) were recorded at regular interval of 3 min after each aliquot addition.

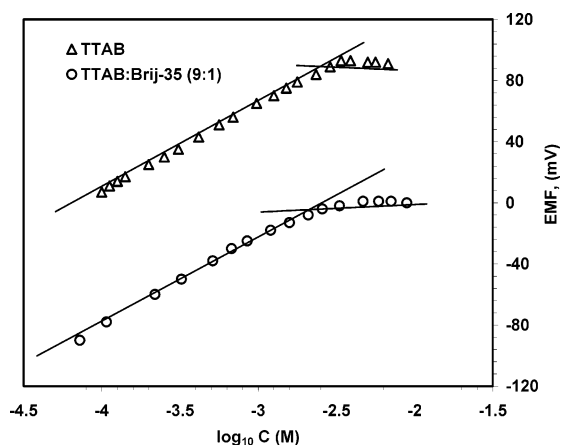


Figure 3. Representative plot of emf (mV) vs $\log C$ (concentration of surfactant, M) at 35 °C.

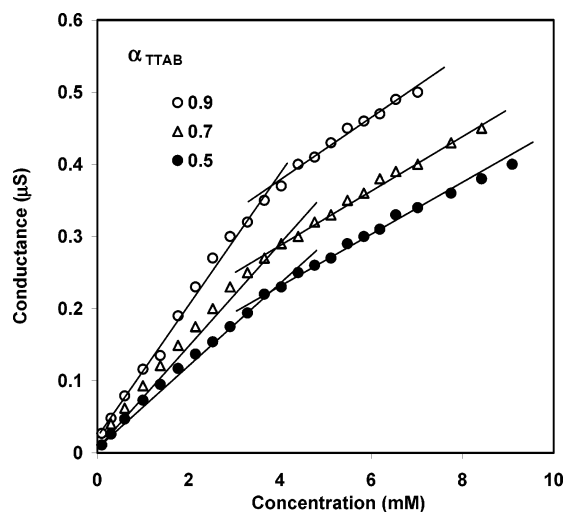


Figure 4. Representative plots of conductance (μS) vs concentration of surfactant (M) at 35 °C.

The emf values thus obtained were plotted as a function of decadic logarithm of surfactant concentration and the break in the emf– $\log C$ profile was considered as the critical micelle concentration (cmc) of the surfactant (Figure 3). Total duration to complete one set of experiment was ~ 3 h. The reproducibility of the emf measurements and hence cmc determinations was crosschecked by carrying out duplicate runs, and the cmc values were reproducible within $\pm 2\%$. The thermodynamic background of such electrode has been discussed in detail by Turmine et al.^{15a} The potential response of this membrane electrode for pure TTAB was equal to 59 mV per decade, indicating a reasonably good Nernstian behavior. However, the slope decreased continuously as the nonionic surfactant content increased in the mixed surfactant system, the least value being 32 mV. However, recently Siriex-Plenet et al.^{15b} have stated that the notion of a Nernstian behavior for a membrane electrode has no sense.

Conductance Measurements. The conductance measurements were done on a Welltronix, digital conductivity meter CM 100. 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.¹⁶ Representative conductance (k) vs concentration of surfactant (mM) plots are shown in Figure 4.

Fluorescence Measurements. The critical micelle concentration (cmc) and micellar aggregation number (N_{agg}) of single and mixed surfactant solutions were determined by steady-state

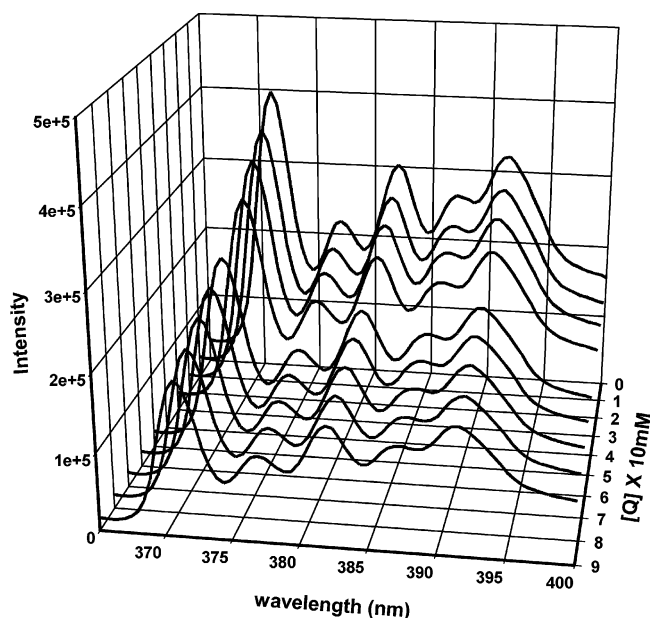


Figure 5. Representative fluorescence emission spectrum of pyrene in TTAB/Brij 35 mixed surfactant system.

fluorescence quenching measurements. Pyrene was used as a probe and cetylpyridinium chloride as quencher. The fluorescence emission spectra of pyrene monomers in the surfactant solution were determined with a FluroMax-3 JY Horiba fluorometer at excitation wavelength 335 nm and emission wavelength 385 nm. Each spectrum had one to five vibronic peaks from shorter to longer wavelengths (Figure 5). Excitation and emission band-passes were 1 and 0.5 nm, respectively. All fluorescence measurements were carried out at room temperature (~ 25 °C). Each scan is at a different quencher concentration (Figure 5), the lowest concentration being zero and highest being $0.8 \times 10^{-3} \text{ M}$.

An aliquot of the stock solution of pyrene in ethanol was transferred into a flask and the solvent was evaporated with nitrogen. The surfactant solution (50 mM) was added and pyrene concentration was maintained constant at 10^{-6} M . The quencher concentration was varied from (0 to $0.8 \times 10^{-3} \text{ M}$). The measured I_1/I_3 values were plotted as a function of the surfactant concentration and the break point was taken as the cmc (Figure 6).

The micellar aggregation number (N_{agg}) was deduced from the equation,^{17,18}

$$\ln I = \ln I_0 - \frac{(N_{\text{agg}}[Q])}{([S] - \text{cmc})} \quad (1)$$

where $[Q]$ and $[S]$ are the concentrations of quencher and total surfactant, respectively. I_0 and I are the fluorescence intensities in the absence and presence of quencher, respectively.

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 ($\lambda = 514.5 \text{ nm}$) 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 $0.2 \mu\text{m}$ Millipore Nylon filter directly into the sample cell, and the cells were sealed until use. The intensity correlation function was measured five times for each sample

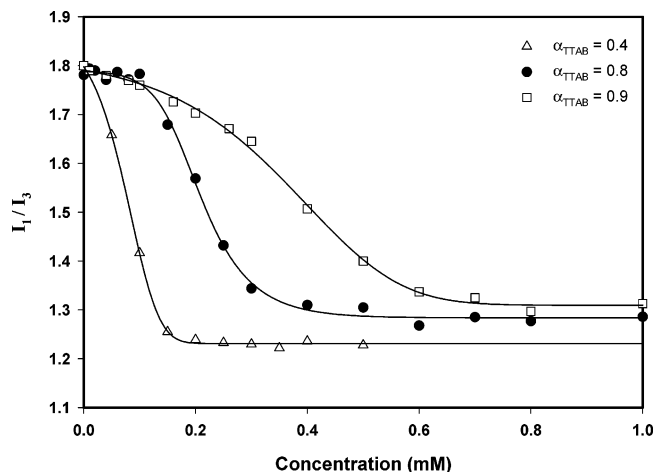


Figure 6. Representative illustration of variation of I_1/I_3 as a function of concentration of surfactant (mM) for TTAB/Brij 35 surfactant mixture at 25 °C.

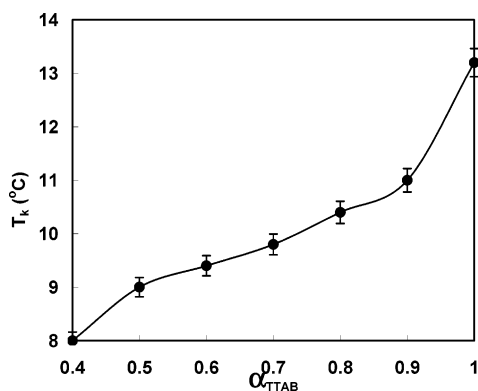


Figure 7. Variation of Krafft temperature, T_k (°C) as a function of mole fraction of TTAB in TTAB/Brij 35 surfactant mixture.

at each angle. The average decay rate was obtained from the measured autocorrelation function using the method of cumulants employing a quadratic fit¹⁹ and the error in these repeated measurements was $\leq 5\%$.

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 Figure 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 and the Brij 35 mixture 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.^{20,21} 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 the least-soluble surfactant, i.e., TTAB, in micelles occurs, resulting in a shift in equilibrium toward the micelle. Also, as the nonionic surfactant is added, the absolute electrical

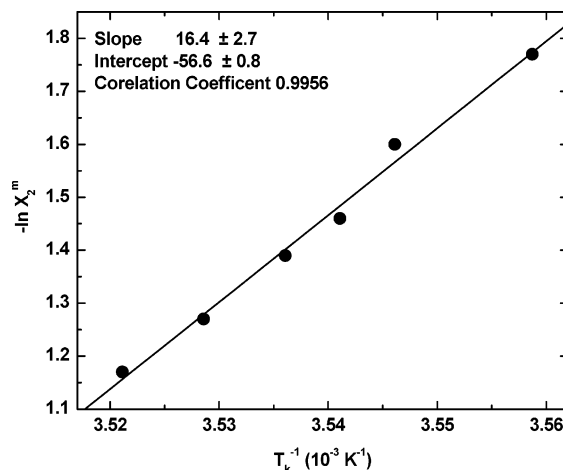


Figure 8. Plot of T_k^{-1} against $-\ln X_2^m$ for TTAB/Brij 35 surfactant mixture.

potential on the micellar surface is reduced due to presence of the Brij 35 between the charged headgroups of the TTAB surfactant. Because the liquid phase is the binary surfactant mixture, and the Krafft temperature is interpreted as the melting temperature of the hydrated solid surfactant,^{22,23} it is found that the following relation holds well (Figure 8),

$$-\ln X_2^m = \frac{\Delta H_1^0}{RT_k} + C \quad (2)$$

where ΔH_1^0 is the enthalpy of fusion of hypothetical pure TTAB hydrated micelle.^{22,23} The calculated ΔH_1^0 is 137 kJ mol⁻¹, X_2^m is the mole fraction of TTAB in mixed micelles, and R is the gas constant.

Partial Specific Volumes. Partial specific volumes of pure and binary mixtures of TTAB with Brij35 were calculated employing the following equation²⁴

$$v = \frac{1}{\rho_w} \left[1 - \frac{d\rho}{dc} \right] \quad (3)$$

where c is the concentration in g cm⁻³ and ρ and ρ_w are the densities of the sample and the water, respectively. The density measurements were carried out with an Anton Parr DMA 5000 density meter. The change in density as a function of concentration of TTAB at different mole fraction in the binary surfactant mixture is illustrated in Figure 9. The measurement has an accuracy of 5×10^{-6} g cm⁻³ and calibrated with dry air and degassed distilled water at 25 °C. The temperature was controlled to ± 0.001 °C.

The unhydrated radius (R_0) of the micelle or mixed micelles was estimated as follows

(a) The average molar mass (M_w) of the mixed micelles was obtained by employing the following equation,

$$M_w = N_{\text{agg}} [X_1 M_1 + (1 - X_1) M_2] \quad (4)$$

where N_{agg} is the aggregation number of the mixed micelle, X_1 is the mole fraction of TTAB in the mixed micelle obtained from Rubingh's method, and M_1 and M_2 are molar masses of TTAB and Brij35, respectively.

(b) Employing the average molar mass of the micelle, the dry micellar volume, V_0 , can be obtained by the relationship^{25,26}

$$V_0 = \frac{v M_w}{N_A} \quad (5)$$

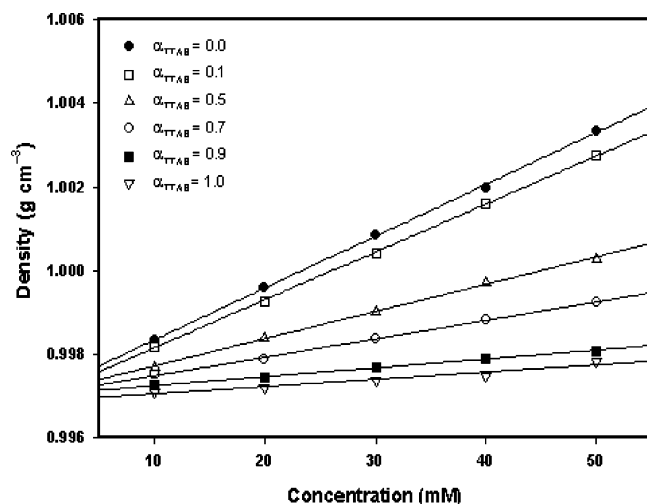


Figure 9. Variation of density (g cm^{-3}) as a function of concentration of surfactant (mM) at different mole ratios for TTAB.

TABLE 1: Hydrodynamic Radius (R_h), Translational Diffusion Coefficient (D_0), Dry Micellar Radius (R_0), Hydration Factor (δ), and Area (a_0) for TTAB/Brij 35 Mixed Surfactant System

α_{TTAB}	$10^7 D_0$ (cm^2/s)	R_h (nm)	R_0 (nm)	δ	a_0 (\AA^2)
0.0	6.70 ± 0.34	3.66 ± 0.18	2.58	1.50	232
0.1	6.12 ± 0.31	4.00 ± 0.20	2.46	3.32	230
0.3	6.05 ± 0.30	4.05 ± 0.20	2.38	3.73	222
0.5	5.59 ± 0.28	4.38 ± 0.22	2.50	3.12	207
0.7	5.85 ± 0.29	4.19 ± 0.21	2.42	3.49	204
0.9	6.70 ± 0.34	3.66 ± 0.18	2.54	1.62	180
1.0	8.95 ± 0.45	2.74 ± 0.14	1.88	1.94	89

(c) The dry micellar radius (R_0) is then obtained assuming a spherical geometry for the micelle, i.e.

$$V_0 = \frac{4}{3}\pi R_0^3 \quad (6)$$

(d) The values so obtained were employed to estimate the hydration factor δ from the hydrodynamic diameter (d_h) (obtained from dynamic light scattering studies) and the dry micellar diameter (d_0), using the following relationship²⁷

$$\delta = \left[\left(\frac{d_h}{d_0} \right)^3 - 1 \right] \nu \rho_w \quad (7)$$

The value of δ is expressed in grams of water associated with 1 g of dry micellar surfactant or mixed micellar surfactant (Table 1).

Partial specific volumes of the mixed micelle vary very slightly as a function of α_{TTAB} in the present study. The partial specific volume is a thermodynamic parameter sensitive to hydrophobic and hydrophilic interactions involving solute and solvent; therefore information obtained from partial specific volume about micellar hydration is thermodynamic and not hydrodynamic in nature. It is apparent from our present study that the thermodynamic contributions to micellar hydration of the mixed micelles are very similar in nature.

Micellar hydration factor δ was determined using the eq 7. It is assumed that the micellar hydration is the difference between the hydrodynamic and the dehydrated micellar volumes, and the values are listed in Table 1. The values of δ are higher in the mixed micelles compared to the individual pure components. This result suggests that the mixed micelles are more hydrated. This is further substantiated by the higher values of hydrodynamic radius (R_h) compared to the dry micellar radius

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

α_{TTAB}	CMC (mM)			
	fluorescence ^a	ST	EMF	conductance
0.0	0.085 ± 0.004	0.080 ± 0.001		
0.1	0.080 ± 0.004		1.51 ± 0.03 (32.5) ^b	
0.3	0.093 ± 0.005		1.70 ± 0.03 (40.0)	4.50 ± 0.09
0.4	0.100 ± 0.005	0.100 ± 0.001		
0.5	0.117 ± 0.006	0.125 ± 0.001	1.82 ± 0.04 (41.7)	4.02 ± 0.08
0.7	0.167 ± 0.008		2.82 ± 0.06 (44.4)	3.75 ± 0.08
0.8	0.240 ± 0.012	0.250 ± 0.003		
0.9	0.480 ± 0.024	0.500 ± 0.005	3.23 ± 0.07 (56.0)	3.80 ± 0.08
1.0	3.60 ± 0.18	3.70 ± 0.04	3.70 ± 0.07 (59.0)	3.70 ± 0.07

^a Fluorescence studies are at 25 °C. ^b Values in the parentheses are the slope of $\log C$ vs EMF.

(R_0). The decrease in radius of the dry micelle compared to that of dry pure Brij 35 micelle, can be attributed to a decrease in micellar hydration.

The micellar dehydration of the POE segments of the Brij 35 can also be inferred from the surface area per headgroup a_0 . The values of a_0 presented in Table 1 were estimated from the dry radius and aggregation number by assuming spherical geometry. This parameter is considered to be important and plays a decisive role in the geometrical or packing properties of the micelles and controls the magnitude of steric repulsions between the heads.²⁷ The surface area per headgroup in the mixed micelles decreases regularly with an increase in the TTAB mole fraction in the mixed systems. This suggests that the presence of TTAB in the mixed micelles promotes less hydration of the headgroups.

The incorporation of water in nonionic micelles can be via two different mechanisms: (a) the binding of water to the ether groups through hydrogen bonding thereby contributing to the hydration and (b) the osmotic flux and mechanical entrapment of water within the mesh of the hydrated POE chains in the outer shells of the micelles. In the presence of increasing TTAB mole fraction in the mixed micellar system one can assume the slight dehydration and contraction of the hydrophilic chains and an increase in the water content in the outer shells of the micelle. The second effect is reflected in the R_h and the first one in R_0 . Charlton and Doherty²⁸ observed similar effects for TX 100 micelles in the presence of electrolytes.

Surface Properties of Surfactant Mixtures. The cmc values of single as well as binary surfactant mixture (TTAB/Brij35) by surface tension, conductance, potentiometric, and fluorescence 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.

For pure TTAB, the surface tension, fluorescence, emf, and conductance gave the same value of cmc at 35 °C (Table 2). There was no second cmc in this case. In case of Brij 35, we could not do the conductance and emf measurements, but surface tension and fluorescence methods gave the same cmc values. For the 1:1 TTAB/Brij 35 system, surface tension and fluorescence methods gave the same cmc values, but the cmc value obtained by conductance was much higher. However, the $\gamma - \log C$ plot did show a dip around the same value, where conductance showed a break (cf. Figure 10a,b). 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 emf measurements, we got a much different value of the cmc for the 1:1 surfactant mixture.

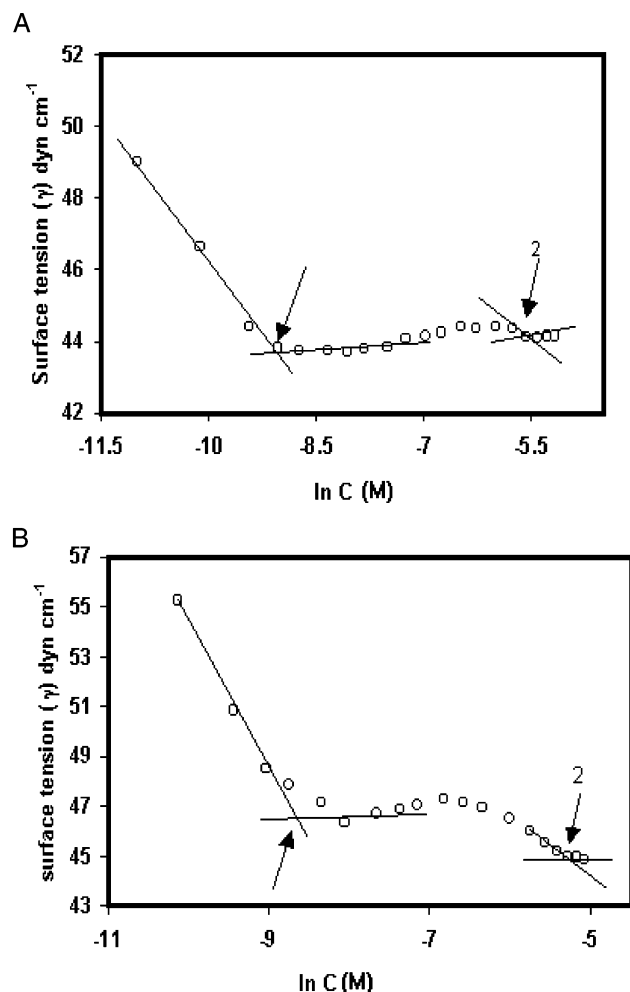


Figure 10. Plot of surface tension (γ) vs $\ln C$, concentration in M, (A) for 1:1 and (B) for 8:2 TTAB/Brij 35 mixed surfactant systems at 25 °C. Arrows 2 indicate the second cmc (Similar curves were also obtained at 35 °C).

For the 9:1 TTAB/Brij 35 system, surface tension and fluorescence gave the same value of the cmc. The cmc values obtained by conductance and emf 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 the binary TTAB/Brij 35 surfactant mixtures. We have also been able to obtain the so-called second cmc for 8:2 TTAB/Brij-35 surfactant mixture. It is evident from Table 2 that surface tension and fluorescence measurements gave comparable results of cmc for mixed surfactant systems. 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 the mass action model, according to which micellization is a stepwise process. Surface tension and fluorescence methods detect smaller micellar aggregates formed at lower concentrations. However, the conductance method is capable of detecting 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 on the micelle size too, which is quite surprising.

Overall, it can be inferred that surface tension and fluorescence methods give an 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.

It is evident from Figure 10 that, in addition to the normal break point in the $\gamma - \log C$ plot, there is another break in the $\gamma - \log C$ plot for 1:1 and 8:2 TTAB/Brij-35 mixtures. Different authors^{29–31} 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 systems. 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 concentrations well above the critical micelle concentration. Such micellar transitions for pure cationic surfactants have been reported by different techniques earlier;³¹ however, we have provided evidence for a second state of aggregation for a surfactant mixture, by the tensiometric technique, because the 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.³² that, for a micellar solution of cationic dimeric (gemini) and nonionic surfactants,³³ 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^{31,34,35} also to explain the second state of aggregation. However, we believe that for TTAB/Brij-35 mixed surfactant systems, in addition to sphere to rod transitions, an alternative mechanism is responsible for the second state of aggregation. The alternative phenomenon is the formation of two different kinds 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 the other micelle is formed by individual surfactant micelles (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 into micelles of individual constituent surfactants.

Surfactant–Surfactant Interaction. The cmc values for the mixed surfactant system (C_{12}) can be calculated theoretically using Clint's equation,³⁶

$$\frac{1}{C_{12}} = \frac{\alpha_1}{C_1} + \frac{1 - \alpha_1}{C_2} \quad (8)$$

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. 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 that result in nonideal behavior. Hence, 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,^{37,38} respectively.

TABLE 3: Various Physicochemical Parameters for the TTAB/Brij 35 Mixed Surfactant System by Fluorescence Measurements at 25 °C

α_{TTAB}	CMC (mM)	X_{TTAB}	$\beta^m = -B_2$	γ_1	γ_2	B_0	B_1	ΔG_{mic} PS model (kJ/mol)	ΔG_{mic} Maeda (J/mol)	N_{agg}
0.0	0.085	0.000						-33.2		36 ± 2
0.1	0.080	0.105	-4.8	0.02	0.95	-13.39	1.06	-33.3	-33.2	33 ± 2
0.2	0.086	0.130	-4.4	0.04	0.93	-13.39	0.61	-33.2	-33.2	—
0.3	0.093	0.153	-4.2	0.05	0.91	-13.39	0.40	-33.0	-33.1	32 ± 2
0.4	0.100	0.173	-4.0	0.06	0.89	-13.39	0.22	-32.8	-33.0	—
0.5	0.117	0.198	-3.9	0.08	0.86	-13.39	0.14	-32.4	-32.9	38 ± 2
0.6	0.135	0.226	-3.9	0.10	0.82	-13.39	0.10	-32.0	-32.7	—
0.7	0.167	0.253	-3.7	0.13	0.79	-13.39	0.07	-31.5	-32.3	36 ± 2
0.8	0.240	0.278	-3.2	0.19	0.78	-13.39	0.57	-30.6	-31.6	—
0.9	0.480	0.312	-2.0	0.38	0.82	-13.39	1.72	-28.9	-33.2	45 ± 2
1.0	3.60	1.000						-23.9		50 ± 3

The β^m values were calculated using the equations³⁹

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

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

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 concentrations in the solution phase of surfactant 1 and 2 and their mixture, respectively, and α_1 and α_2 (i.e., $1 - \alpha_1$) are stoichiometric mole fractions of surfactants 1 and 2, respectively. In the 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 the TTAB content in the mixed surfactant system increases. A similar behavior has been observed for the interaction parameter calculated using Maeda's approach,³⁸ which we discuss in the latter part of this paragraph. The β^m values obtained using Rubingh's method³⁷ 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, Maeda³⁸ and Ruiz et al.⁴⁰ 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 the mixed system can be due to the decrease in ionic headgroup repulsions caused by the presence of nonionic surfactant molecules between the TTAB headgroups. Maeda³⁸ 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_i) is given by

$$\Delta G_m = RT(B_0 + B_1 X_i + B_2 X_i^2) \quad (11)$$

where

$$B_0 = \ln C_2 \quad (C_2 \text{ is the cmc of the nonionic surfactant}) \quad (12)$$

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

$$B_2 = -\beta^m \quad (14)$$

All quantities in the above equations 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 the phase separation model ($\Delta G_m = RT \ln X_{\text{cmc}}$, X_{cmc} is cmc in mole fraction scale) and by Maeda's method³⁸ agree reasonably well (within $\pm 5\%$ for most of the mole ratios of the mixed system). This indicates that the fraction of counterion bound to the mixed micelle is probably negligible, because in that case the ΔG_m values would have been much different. This probably is why a break point in the conductance–concentration plot is not observed at the 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 $\alpha_{\text{TTAB}} > 0.6$. The cationic surfactant has 14 carbons in its hydrocarbon chain, whereas the nonionic surfactant has 12 carbons. Hence, according to Maeda,³⁸ as the chain lengths are different, there should be chain–chain interactions helping in the stability of the micelle. The interactions may also be explained by the fact that some water molecules may be shared by different headgroups 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.⁴¹ Mukerjee⁴² also suggested the existence of an attractive interaction between hydrocarbon/fluorocarbon surfactants in the

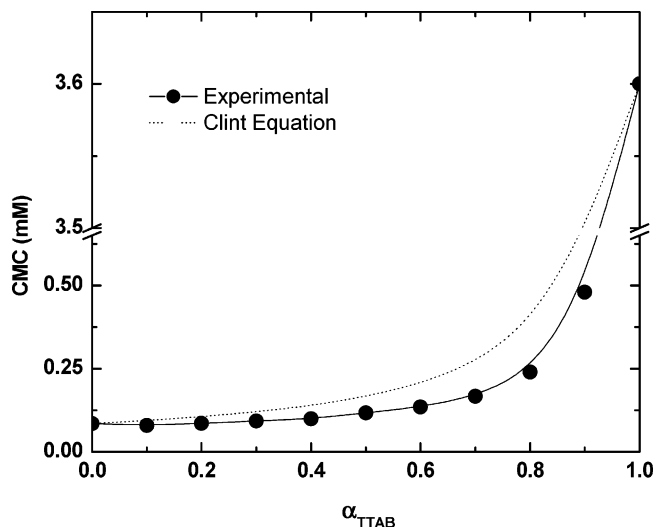


Figure 11. Variation of critical micelle concentration (mM) vs mole fraction of TTAB (α_{TTAB}) for the mixed surfactant system at 25 °C.

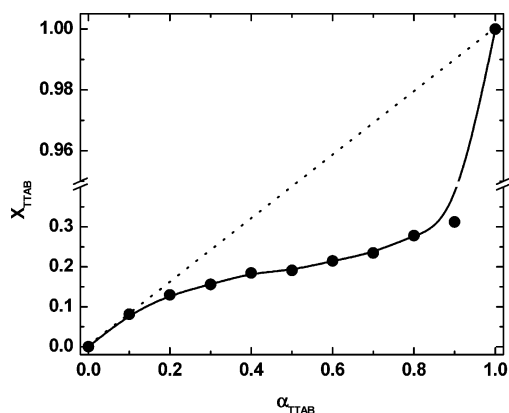


Figure 12. Plot of mole fraction of TTAB (X_{TTAB}) in the mixed micelle vs stoichiometric mole fraction of TTAB (α_{TTAB}) for the mixed surfactant system at 25 °C.

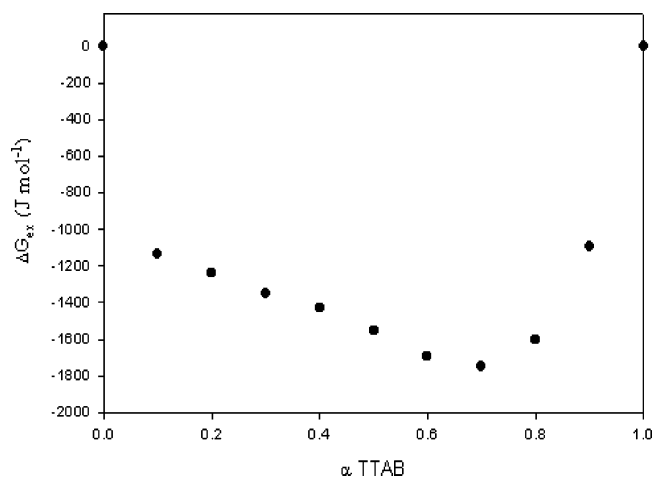


Figure 13. Excess free energy of mixing (ΔG_{ex}) as a function of mole fraction of TTAB for TTAB/Brij 35 mixed surfactant system at 25 °C.

mixed micelle by what is termed a “contact hydrophobic interaction”. Such a contact hydrophobic interaction also may be the reason for the attractive interaction in the present hydrocarbon/hydrocarbon surfactant system though the interaction may not be as strong as in the 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 headgroup–headgroup repulsions are dominant at higher mole fractions of TTAB in the mixed micelle, ultimately delaying mixed micelle formation. 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.⁴³ Thus the negative β^{m} values are a result of reduction of electrostatic self-repulsion between TTAB headgroups 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,

$$\Delta G_{\text{ex}} = RT[X_1 \ln(f_1) + (1 - X_1) \ln(f_2)] \quad (15)$$

where 1 and 2 are TTAB and Brij 35, respectively. 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

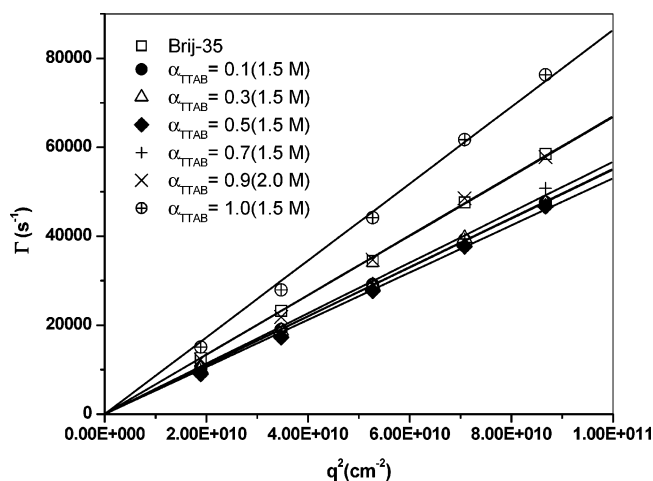


Figure 14. Representative plots of average decay rate of intensity correlation function (Γ) as a function of q^2 for TTAB/Brij 35 mixed surfactant system (total surfactant concentration, 25 mM) at 25 °C values in the bracket are concentrations of NaCl.

(Γ) as a function of q^2 for the 25 mM TTAB/Brij-35 mixed surfactant system, where q is the scattering vector given by

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

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

Translational diffusion coefficient values thus obtained (Table 1) were used to calculate the dissociated hydrodynamic radius of the micelle by applying the Stokes–Einstein equation⁴⁴

$$R_h = \frac{k_B T}{6\pi\eta_0 D_0} \quad (17)$$

where k_B is the Boltzmann constant, T is the absolute temperature, and η_0 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 Figure 15 that the R_h values for mixed systems are higher than that of TTAB as well as Brij-35. This is because the headgroup–headgroup 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 a higher hydrodynamic radius compared to that of constituent surfactant is formed.

Conclusions

The self-aggregation behavior of binary TTAB/Brij 35, cationic–nonionic surfactant mixture in aqueous medium was studied by tensiometry, conductometry, density, quasielastic light scattering and fluorometry. The tensiometric results suggest the existence of a second state of aggregation for the mixed surfactant systems in 1:1 and 8:2 molar ratios, which is reflected by the conductometric cmc obtained from the break in the

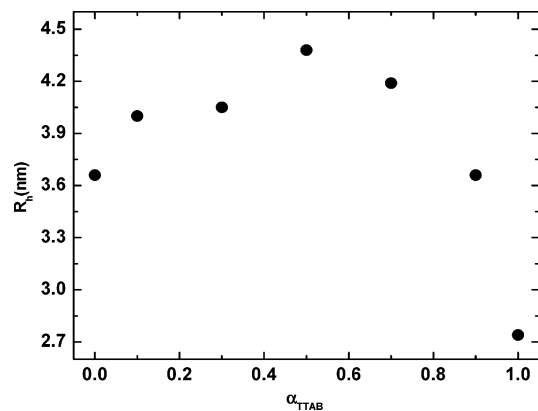


Figure 15. Hydrodynamic radius of micelle (R_h) of micelle as a function of mole fraction of TTAB for TTAB/Brij 35 mixed surfactant system at 25 °C.

conductance–concentration profile. The 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. Quasielastic light scattering studies suggest mixed micellar aggregates formed for this system have hydrodynamic radii higher than those of the aggregates formed by a 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 a water bridge between the headgroups. The partial specific volume was measured by 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 the hydrodynamic radius (R_h) compared to those of the dry micellar radius (R_0).

Acknowledgment. Inter University Consortium for DAE Facilities, Bhabha Atomic Research Centre (BARC), Mumbai, India, is acknowledged for financial support (IUC/CRS/M-70/2000/346). R.M.P. is grateful to NSERC for generous support in the form of an operating grant. K.G. and M.D. acknowledges the USRA from NSERC (2003).

References and Notes

- (1) Dawey, T. W.; Ducker, W. A.; Hayman, A. R. *Langmuir* **2000**, *16*, 2430.
- (2) Lawrence, C. A. In *Cationic Surfactants*; Jurgerman, E., Ed.; Marcel Dekker: New York, 1979; p 491.
- (3) Jana, P. K.; Moulik, S. P. *J. Phys. Chem.* **1991**, *95*, 9525.
- (4) Moulik, S. P.; Haque, M. E.; Jana, P. K.; Das, A. R. *J. Phys. Chem.* **1996**, *100*, 701.
- (5) Haque, M. E.; Das, A. R.; Rakshit, A. K.; Moulik, S. P. *Langmuir* **1996**, *12*, 4084.
- (6) Sulthana, S. B.; Rao, P. V. C.; Bhat, S. G. T.; Nakano, T. Y.; Sugihara, G.; Rakshit, A. K. *Langmuir* **2000**, *16*, 980.
- (7) Elkadi, N.; Martins, F.; Clausse, D.; Schulz, P. C. *Colloid Polym. Sci.* **2003**, *281*, 353.
- (8) Castaldi, M. L.; Ortona, O.; Paduano, L.; Vitagliano, V. *Langmuir* **1998**, *14*, 5994.
- (9) Sulthana, S. B.; Rao, P. V. C.; Bhat, S. G. T.; Rakshit, A. K. *J. Phys. Chem.* **1998**, *102*, 9653.
- (10) Shiloach, A.; Blankschtein, D. *Langmuir* **1998**, *14*, 7166.
- (11) Moulik, S.; Dutta, P.; Chatteraj, D. K.; Moulik, S. P. *Colloids Surf.* **1998**, *11*, 1.
- (12) Zana, R.; Benraou, M.; Rueff, R. *Langmuir* **1991**, *7*, 1072.
- (13) Song, L. D.; Rosen, M. J. *Langmuir* **1996**, *12*, 1149.
- (14) Sharma, K. S.; Rodgers, C.; Palepu, R. M.; Rakshit, A. K. *J. Colloid Interface Sci.* **2003**, *262*, 482.
- (15) (a) Turmine, M.; Mayaffre, A.; Letellier, P. *J. Colloid Interface Sci.* **2003**, *264*, 7. (b) Sirieix-Plenet, J.; Turmine, M.; Letellier, P. *Talanta* **2003**, *60*, 1071.
- (16) Patil, S. R.; Mukaiyama, T.; Raskhit, A. K. *J. Disp. Sci. Technol.* **2003**, *24*, 559.
- (17) Turro, N. J.; Yekta, A. *J. Am. Chem. Soc.* **1978**, *100*, 5981.
- (18) Abe, M.; Ochiyama, H.; Yamaguchi, T.; Suzuki, T.; Ogino, K.; Scamehorn, J. F.; Christian, S. D. *Langmuir* **1992**, *8*, 2147.
- (19) Hassan, P. A.; Raghavan, S. R.; Kaler, E. W. *Langmuir* **2002**, *18*, 2543.
- (20) Scamehorn, J. F.; Harwell, J. H. In *Mixed Surfactant Systems*; Ogino, K., Abe, M., Eds.; Marcel Dekker: New York, 1993; p 283.
- (21) Scamehorn, J. F. In *Phenomena in Mixed Surfactant Systems*; Scamehorn, J. F., Ed.; ACS Symposium Series, No. 311; American Chemical Society: Washington, DC, 1986; p 1.
- (22) Tsujii, K.; Saito, N.; Takeuchi, T. *J. Phys. Chem.* **1980**, *84*, 2287.
- (23) Tsujii, K.; Saito, N.; Takeuchi, T. *J. Phys. Chem.* **1982**, *86*, 1437.
- (24) Schott, H. J. *Colloid Interface Sci.* **1995**, *173*, 265.
- (25) Paradies, H. H. *J. Phys. Chem.* **1980**, *84*, 599.
- (26) Birdi, K. S. *Prog. Colloid Polym. Sci.* **1985**, *70*, 23.
- (27) Briganti, G.; Puvvada, S.; Blankschtein, D. *J. Phys. Chem.* **1991**, *95*, 8989.
- (28) Charlton, I. D.; Doherty, A. P. *J. Phys. Chem. B* **2000**, *104*, 8327.
- (29) Mu, J.-H.; Li, G.-Z.; Zhang, W.-C.; Wang, Z.-W. *Colloids Surf. A* **2001**, *194*, 1.
- (30) Prasad, M.; Moulik, S. P.; MacDonald, A.; Palepu, R. *J. Phys. Chem. B* **2004**, *108*, 355.
- (31) Gonzalez, P. A.; Czapkiewicz, J. L.; Castilo, J. L. D.; Rodriguez, J. R. *Colloids Surf. A* **2001**, *193*, 129.
- (32) Bernheim-Groswasser, A.; Zana, R.; Talmon, Y. *J. Phys. Chem. B* **2000**, *104*, 4005.
- (33) Bernheim-Groswasser, A.; Wachtel, E.; Talmon, Y. *Langmuir* **2000**, *16*, 4131.
- (34) Treiner, C.; Makayassi, A. *Langmuir* **1992**, *8*, 794.
- (35) Makayassi, A.; Buru, R.; Treiner, C. *Langmuir* **1994**, *10*, 1359.
- (36) Clint, J. H. *Surfactant Aggregation*; Chapman and Hall: New York, 1992.
- (37) Rubingh, D. N. In *Solution Chemistry of Surfactants*; Mittal, K. L., Ed.; Plenum Press: New York, 1979; Vol. 3, p 337.
- (38) Maeda, H. J. *Colloid Interface Sci.* **1995**, *172*, 98.
- (39) Rosen, M. J. *Surfactants and Interfacial Phenomena*, 2nd ed.; John-Wiley: New York, 1989.
- (40) Ruiz, C. C.; Aguiar, J. J. *Mol. Phys.* **1999**, *97*, 1095.
- (41) Rodgers, M. P.; Rodgers, C. C.; Rakshit, A. K.; Palepu, R. M. *Colloid Polym. Sci.* **2003**, *281*, 800.
- (42) Mukerjee, P. *Colloids Surf. A* **1994**, *84*, 1.
- (43) DasBurman, A.; Dey, T.; Mukherjee, B.; Das, A. R. *Langmuir* **2000**, *16*, 10020.
- (44) Hassan, P. A.; Yakhmi, J. V. *Langmuir* **2000**, *16*, 7187.