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

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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, 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.

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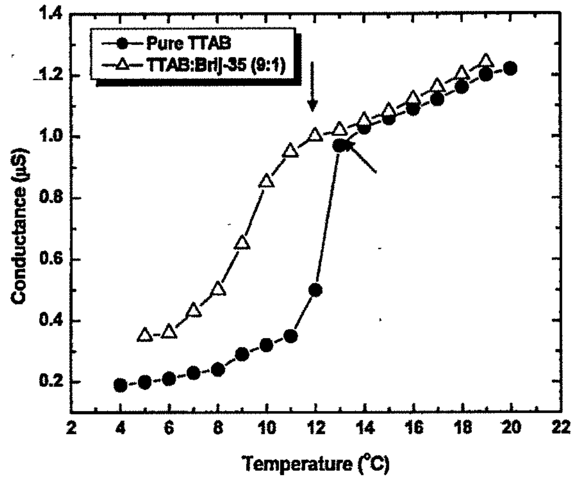

Figure 1. Representative plots of conductance (*C*) vs temperature (°C) for TTAB/Brij 35 mixed surfactant system. The arrow indicates the Krafft temperature.

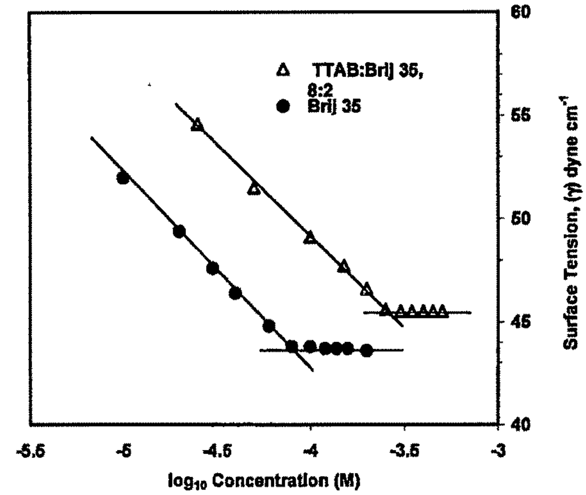

Figure 2. Representative plots of surface tension (γ) vs log *C* (concentration of surfactant, M) at 35 °C.

Experimental Section

Materials. Tetradecyltrimethylammonium bromide (TTAB, $[CH_3(CH_2)_{13}N^+(CH_3)_3\ Br^-]$, MW 336.4, Lancaster, U.K.) was recrystallized thrice from dry acetone. Polyoxyethylene 23 lauryl ether (Brij-35, $[CH_3(CH_2)_{11}(OCH_2CH_2)_{23}OH]$, 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 2−3 μS 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 ~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}. 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 ±0.1 °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 ±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 concentration of surfactant in solution (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 ±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 Tensiomat 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} 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 (mV ±1%) were recorded at regular interval of 3 min after each aliquot addition.

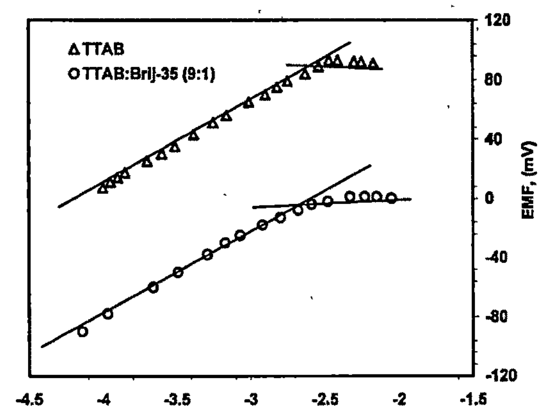

Figure 3. Representative plot of emf (mV) vs log C (concentration of surfactant, M) at 35 °C.

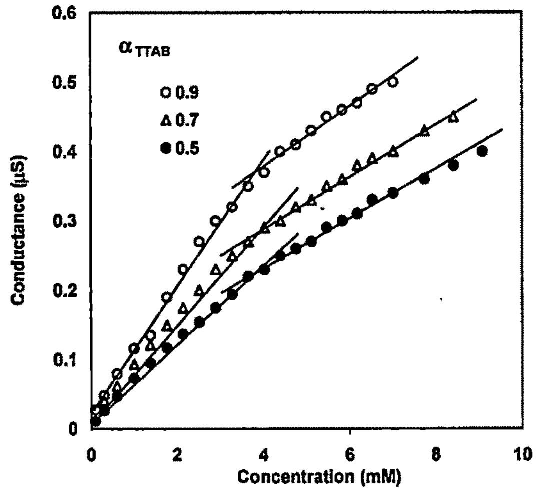

Figure 4. Representative plots of conductance (μS) vs concentration of surfactant (M) at 35 °C.

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 ±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 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 × 10^{-3} M.

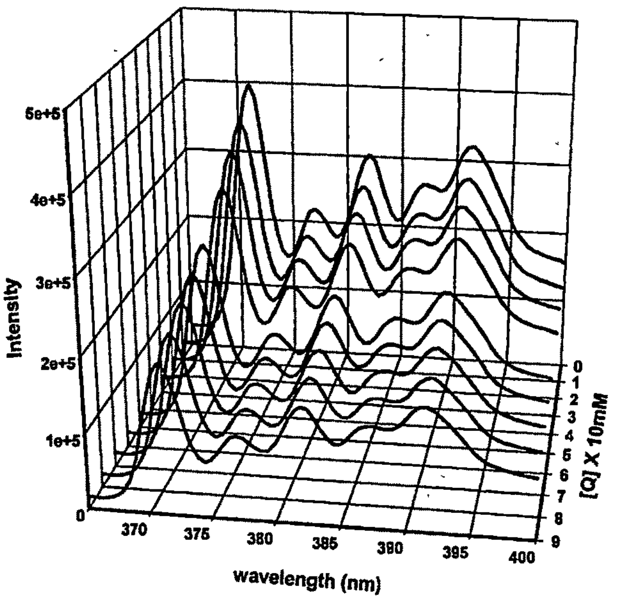

Figure 5. Representative fluorescence emission spectrum of pyrene in TTAB/Brij 35 mixed surfactant system.

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 × 10^{-3} 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]

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

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 (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 0.2 μm 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

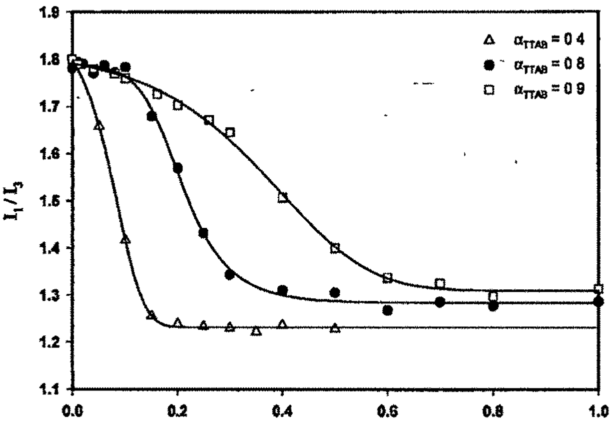

Figure 6. Representative illustration of variation of I_1/I_3 as a function of concentration of surfactant (mM) for TTAB/Brij 35 surfactant mixture at 25 °C.

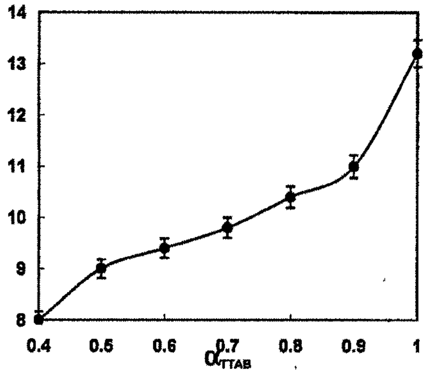

Figure 7. Variation of Krafft temperature, T_k (°C) as a function of mole fraction of TTAB in TTAB/Brij 35 surfactant mixture.

at each angle. The average decay rate was obtained from the measured autocorrelation function using the method of cumulants employing a quadratic fit[19] 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 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 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),

$$-\ln X_2^{\mathrm{m}} = \frac{\Delta H_1^{0}}{RT_{\mathrm{k}}} + C \tag{2}$$

where $\Delta H_1°$ is the enthalpy of fusion of hypothetical pure TTAB hydrated micelle.[22,23] The calculated $\Delta H_1°$ is 137 kJ mol^{-1}, X_2^{m} is the mole fraction of TTAB in mixed micelles, and R is the gas constant.

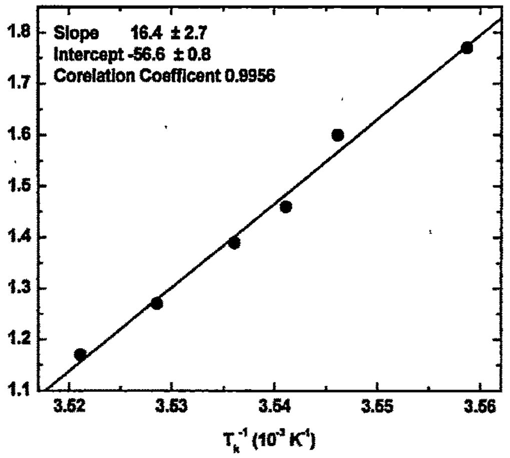

Figure 8. Plot of T_k^{-1} against $-\ln X_B$ for TTAB/Brij 35 surfactant mixture.

Partial Specific Volumes. Partial specific volumes of pure and binary mixtures of TTAB with Brij35 were calculated employing the following equation[24]

$$v = \frac{1}{\rho_{\mathrm{w}}}\left[1 - \frac{\mathrm{d}\rho}{\mathrm{d}c}\right] \tag{3}$$

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,

$$M_w = N_{\mathrm{agg}}[X_1M_1 + (1 - X_1)\,M_2] \tag{4}$$

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]

$$V_0 = \frac{vM_{\mathrm{w}}}{N_{\mathrm{A}}} \tag{5}$$

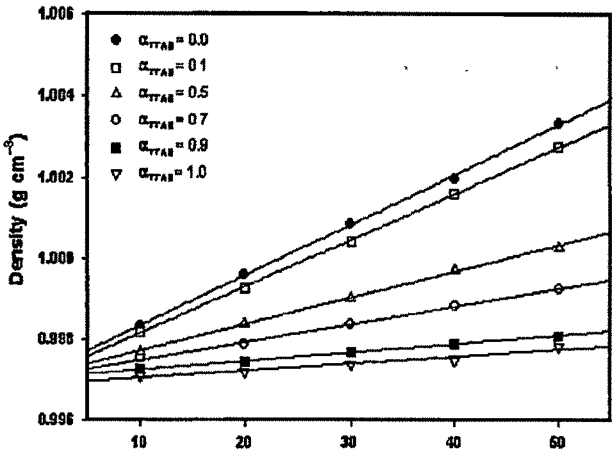

Figure 9. Variation of density (g cm^{-3}) as a function of concentration of surfactant (mM) at different mole ratios for TTAB.

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

α_{TTAB}	10^7D_0 (cm^2/s)	R_h (nm)	R_0 (nm)	δ	a_0 (Å^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.

$$V_0 = {}^4/_3\pi R_0^{\,3} \tag{6}$$

(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 relationship[27]

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

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 (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.

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

	CMC (mM)			
α_{TTAB}	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.

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 Doherty[28] 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 γ − 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.

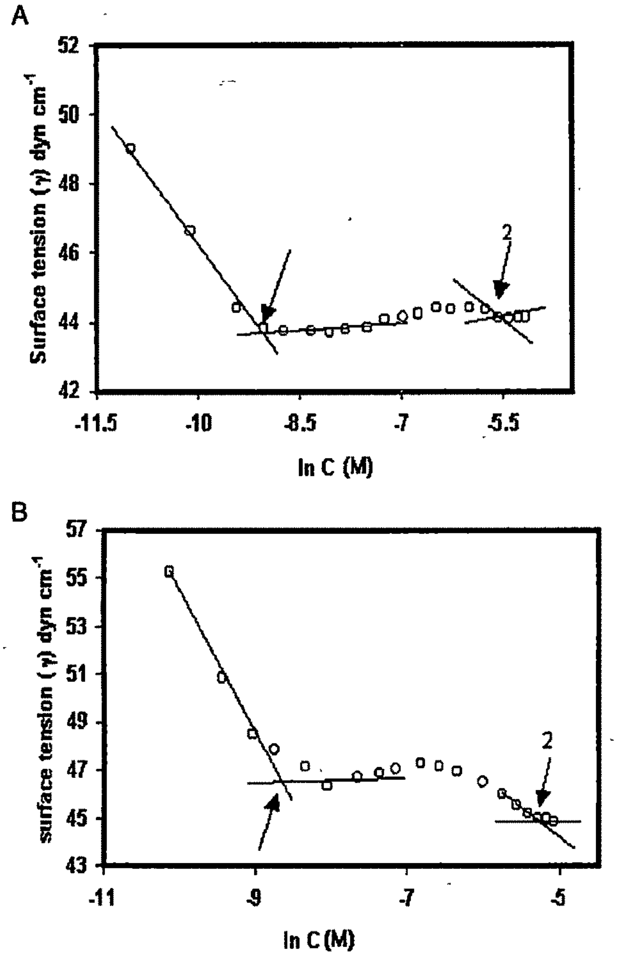

Figure 10. Plot of surface tension (γ) vs ln C, concentration in M, (A) for 1:1 and (B) for 8:2 TTAB/Brij 35 mixed surfactant systems at 25 °C. Arrows 2 indicate the second cmc (Similar curves were also obtained at 35 °C).

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]

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

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 ($\mathrm{cmc_{exp}}$) are plotted as a function of mole fraction of TTAB in Figure 11. It is clear from Figure 11 that $\mathrm{cmc_{exp}}$ 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 equations[39]

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

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

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 method[37] 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[38] 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. Maeda[38] 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

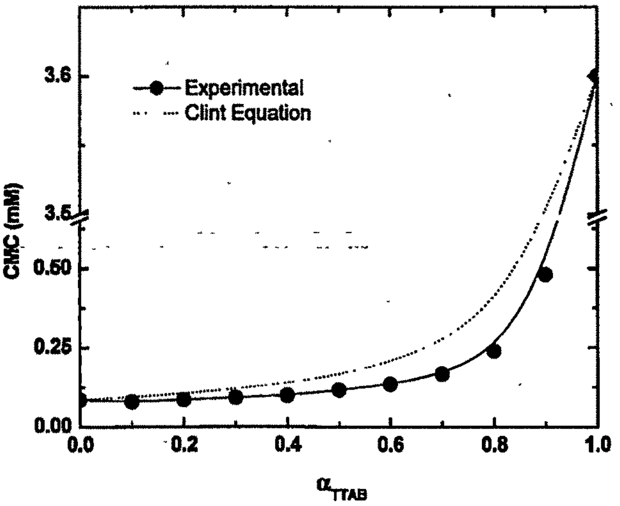

Figure 11. Variation of critical micelle concentration (mM) vs mole fraction of TTAB (α_{TTAB}) for the mixed surfactant system at 25 °C.

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

where

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

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

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

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 ($\Delta G_m = RT \ln X$cmc, Xcmc is cmc in mole fraction scale) and by Maeda's method[38] agree reasonably well (within ±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 $\alpha_{TTAB} > 0.6$. 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] Mukerjee[42] also suggested the existence of an attractive interaction between hydrocarbon/fluorocarbon surfactants in the

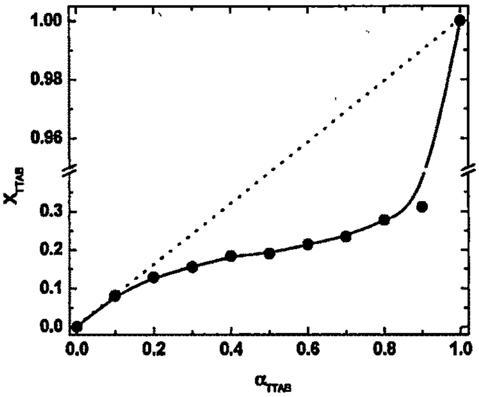

Figure 12. Plot of mole fraction of TTAB (X_{TTAB}) in the mixed micelle vs stoichiometric mole fraction of TTAB (α_{TTAB}) for the mixed surfactant system at 25 °C.

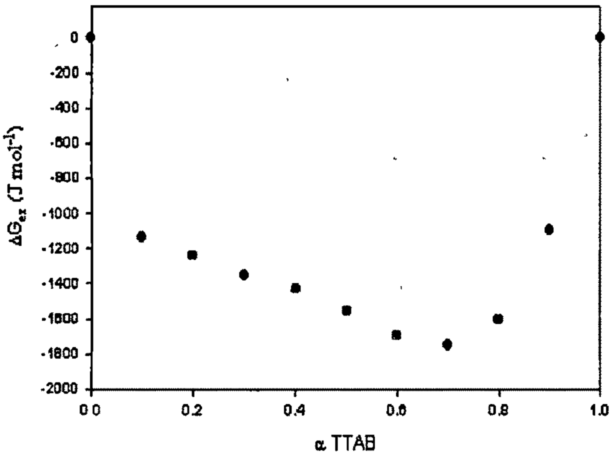

Figure 13. Excess free energy of mixing (ΔG_{ex}) as a function of mole fraction of TTAB for TTAB/Brij 35 mixed surfactant system at 25 °C.

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,

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

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

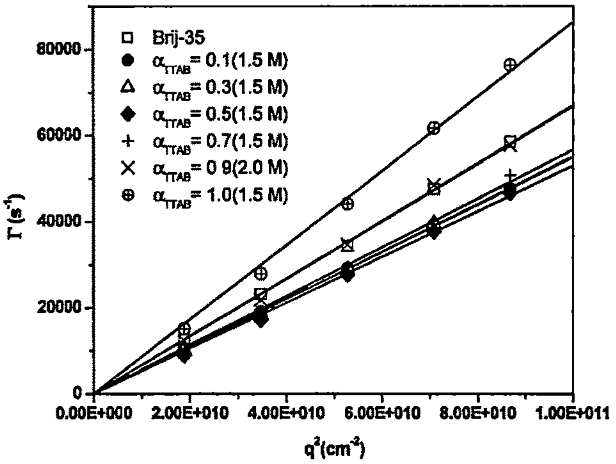

Figure 14. Representative plots of average decay rate of intensity correlation function (Γ) as a function of q^2 for TTAB/Brij 35 mixed surfactant system (total surfactant concentration, 25 mM) at 25 °C values in the bracket are concentrations of NaCl.

(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

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

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 equation[44]

$$R_h = \frac{k_B T}{6\pi\eta_0 D_0} \tag{17}$$

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

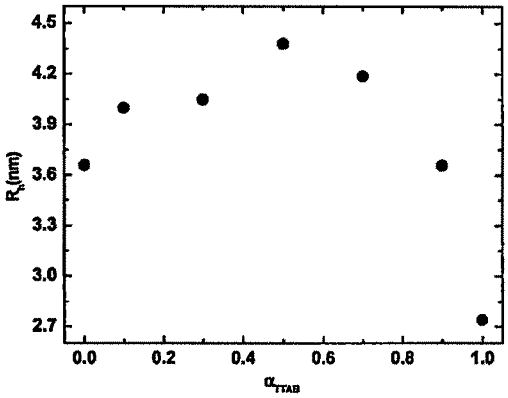

Figure 15. Hydrodynamic radius of micelle (R_h) of micelle as a function of mole fraction of TTAB for TTAB/Brij 35 mixed surfactant system at 25 °C.

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_O).

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Studies of mixed surfactant solutions of cationic dimeric (gemini) surfactant with nonionic surfactant $C_{12}E_6$ in aqueous medium

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Abstract

The interaction between the alkanediyl-α,ω-type cationic gemini surfactant, $[(C_{16}H_{33}N^+(CH_3)_2(CH_2)_4N^+(CH_3)_2C_{16}H_{33})2Br^-]$, 16–4–16 and the conventional nonionic surfactant $[CH_3(CH_2)_{10}CH_2(OCH_2CH_2)_6OH]$, $C_{12}E_6$ in aqueous medium has been investigated. The critical micelle concentrations of different mixtures have been measured by surface tension using a du Nouy tensiometer in aqueous solution at different temperatures (303, 308, and 313 K). Maximum surface excess ($\Gamma_{\max}$) and minimum area per molecule ($A_{\min}$) were evaluated from a surface tension vs $\log_{10} C$ (C is concentration) plot. The cmc value of the mixture was used to compute β^m, the interaction parameter. The β^σ, the interaction parameter at the monolayer air–water interface, was also calculated. We observed synergism in 16–4–16/$C_{12}E_6$ system at all concentration ratios. The micelle aggregation number (N_{agg}) has been measured using a steady state fluorescence quenching method at a total surfactant concentration ~2 mM at 25 °C. The micropolarity and the binding constant (K_{sv}) of mixed systems were determined from the ratio of intensity of peaks (I_1/I_3) of the pyrene fluorescence emission spectrum. The micellar interiors were found to be reasonably polar. We also found, using Maeda's concept, that the chain–chain interactions are very important in this system.

Keywords: Gemini surfactant; Nonionic surfactant; Mixed micellization; Synergism; Micelle aggregation number; β-Parameter

1. Introduction

Gemini or dimeric surfactants, consisting of two hydrophobic chains and two hydrophilic groups covalently attached through a spacer, are attracting considerable interest in both academic and industrial research. Since geminis were first synthesized and studied for their superior performance as catalysts in organic reactions [1], a considerable number of investigations on their unusual physicochemical properties, such as low cmc values (10 to 100 times lower than corresponding conventional surfactants) [2], greater efficiency in decreasing the surface tension of water (C_{20} values) [2,3], better wetting [4], unusual micellar structure [5], better solubilizing power [6], low Kraft point [2,6–8], better viscoelasticity, gelification, and shear thickening [6] and enhanced properties for lowering the oil–water interfacial tension [7] have been reported. Cationic gemini dimeric surfactants are also capable of various biological activity [9,10] and have an effect on photosynthesis [10]. An arginine-based dimeric surfactant displayed a broad range of antimicrobial activity [11]. These dimeric surfactants are expected to be commercially used in the near future, probably as specialist surfactants [12] in the fields of soil remediation, enhanced oil recovery, drug entrapment and release, etc. [4]. These surfactants are currently extensively investigated for their possible use in formulations mixing them with ionic [13], nonionic [13–15], Zwitterionic [15], and sugar-based surfactants [16].

The micellization behavior of alkanediyl-α,ω-bisalkyldimethylammonium bromide type dimeric surfactants has been the most investigated [7,17–25]. They are often referred to as *m*–*s*–*m* surfactants, where *m* and *s* are the numbers of carbon atoms of alkyl and alkanediyl groups, respectively [26]. Mixtures of surfactant solutions form mixed micellar aggregates that exhibit characteristic properties superior to those of the individual components, and synergism can often be observed. In most practical application such as cosmetic products, mixing an ionic surfactant with another surfactant is common. An important mixed

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system is that including cationic gemini surfactants with conventional nonionic surfactants. This paper aims to investigate molecular interaction in the mixed micellization of the cationic gemini surfactant 1,4-butanediyl-α,ω-bis-hexadecyldimethylammoniumbromide [$(C_{16}H_{33}N^+(CH_3)_2$-$(CH_2)_4N^+(CH_3)_2C_{16}H_{33})2Br^-$], referred to as 16–4–16, and the conventional ethoxylated nonionic surfactant $C_{12}E_6$, hexaoxyethylene *n*-dodecyl ether, [$CH_3(CH_2)_{10}CH_2(OCH_2$-$CH_2)_6OH$]. The mixtures are characterized by their critical micelle concentrations (cmc) at different temperatures (303, 308, and 313 K) and the micelle aggregation number (N_{agg}) determined by the steady state fluorescence quenching technique at a total surfactant concentration of about 2 mM at 25 °C. The surface excesses (Γ_{max}) and the minimum area per molecule (A_{min}) were also evaluated from surface tension plots. The nature and strength of the interactions between the surfactant mixtures were obtained by calculating the values of their β parameters. The interaction parameter for the mixed monolayer formation at the aqueous solution/air interface, β^σ was also calculated. We also obtained the micropolarity and binding constant for 16–4–16/$C_{12}E_6$ mixed systems. We computed the chain–chain interaction in the mixed micelle as well.

2. Experimental

2.1. Materials

Hexaoxyethylene *n*-dodecyl ether, $C_{12}E_6$ [$CH_3(CH_2)_{11}$-$(OCH_2CH_2)_6OH$, molar mass = 450.68, Lion corporation, Tokyo, Japan] was used without further purification. Cationic dimeric (gemini) surfactant, 1,4-butanediyl-α, ω-bishexadecyldimethylammonium bromide [$(C_{16}H_{33}N^+$-$(CH_3)_2(CH_2)_4N^+(CH_3)_2C_{16}H_{33})2Br^-$], referred as 16–4–16, was a gift sample from Professor S. Bhattacharya, IISc, Banglore, India and used as obtained. The synthesis and purification of this surfactant have been described earlier by Bhattacharya et al. [20,21]. The surface tension vs concentration plot did not show any minimum, proving the high purity of samples, which is also confirmed by ^1H NMR measurement. Cetylpyridinium chloride (Loba Chemi, Baroda, India) was recrystallized twice from benzene. Pyrene (Fluka, Germany) was recrystallized from cyclohexane. Triple-distilled water having specific conductivity 2–3 µS cm^{-1}, pH 6.8 at 303 K was used throughout as the solvent for all measurements.

2.2. Surface tension measurements

The surface tension (γ) was measured by the ring method using a du Nouy tensiometer (S.C. Dey & Co., Kolkata, India) at temperatures of 303, 308, and 313 K. The temperatures (±0.1 °C) were maintained by circulating thermostated water through a jacketed vessel containing the solution. The concentration of solution was varied by adding aliquots of stock solution of known concentration to the known volume of solution in the vessel using a Hamilton microsyringe. The ring was cleaned by heating it in alcohol flame. The measured surface tension values were plotted as a function of logarithm of surfactant concentration and the critical micelle concentration (cmc) was estimated from the break point in the resulting curve [27]. Representative plots of surface tension (γ) vs logarithm of surfactant concentration ($\log_{10} C$) are shown in Fig. 1. The reproducibility of the surface tension (γ) vs concentration curve was checked by duplicate runs. The reproducibility (standard deviation of the mean) in the cmc was found to be ±0.1%, calculated from the experimental cmc data from at least two runs.

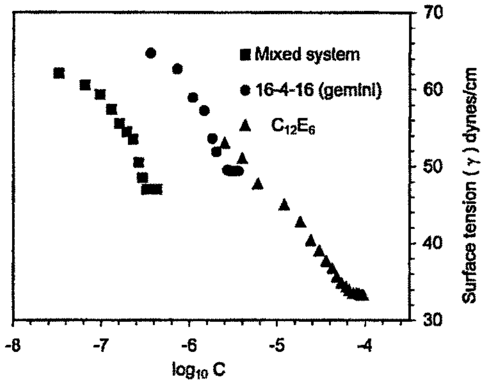

Fig. 1. Representative plots of surface tension vs $\log_{10} C$ for (■) mixed 16–4–16:$C_{12}E_6$ (5:5), (●) pure 16–4–16, (▲) pure $C_{12}E_6$ at 30 °C.

2.3. Fluorescence measurements

The micellar aggregation numbers (N_{agg}) of single and mixed surfactant solutions were determined by steady state fluorescence quenching measurements. Pyrene was used as a probe and cetylpyridinium chloride as a quencher. The fluorescent emission spectra of pyrene monomers in the surfactant solution were determined with a fluorescent spectrophotometer (Hitachi F-4010) at the excitation wavelength 335 nm and emission wavelength 385 nm. Each spectrum had one to five vibronic peaks from shorter to longer wavelengths (Fig. 2). All fluorescence measurements were carried out at room temperature (~25 ± 0.1 °C).

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 (2 mM) was added and pyrene concentration was kept constant at 10^{-6} M. The quencher concentration was varied from 0 to 8 × 10^{-5} M.

The micellar aggregation number (N_{agg}) was deduced from the equation [28,29]

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

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

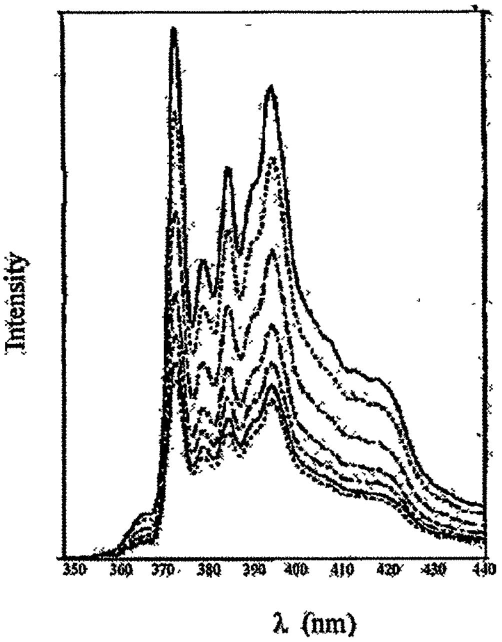

Fig. 2. Representative fluorescence (emission) spectra of 10^{-5} M pyrene in aqueous micellar solution of 16–4–16:$C_{12}E_6$ (5:5) at different quencher concentrations (maximum intensity indicates no quencher and minimum intensity indicates maximum amount of quencher).

values can also be used to calculate the Stern–Volmer binding constant, K_{sv}, using the relation [30]

$$\frac{I_0}{I} = 1 + K_{sv}[Q], \tag{2}$$

where K_{sv} is a product of k_q, the bimolecular quenching constant, and τ, the lifetime of the fluorescent molecule. The ratio of intensity of the first (I_1) and third (I_3) vibronic peaks, i.e., I_1/I_3, of the pyrene fluorescence emission spectrum in the presence of surfactants is considered to be the index of micropolarity of the system; i.e., it gives an idea of the microenvironment in the micelle. A low value of this ratio (<1) is generally taken as the pyrene having nonpolar surroundings, whereas a higher value (>1) is taken as the pyrene having polar surroundings [31].

3. Results and discussion

3.1. *Surface properties of surfactant mixtures*

The intramicellar interactions in the surfactant mixture are studied at the critical micelle concentration, where their effect on mixed micelle formation can be measured [32]. The critical micelle concentrations (cmc) of pure and mixed surfactant systems were determined from the break points of the surface tension vs concentration curves at different temperatures. Surface tension is a fast, convenient, and nondestructive means of determining cmc [33]. The cmc data are presented in Table 1. The cmc values of pure $C_{12}E_6$ at a given temperature are in good agreement with the reported values in the literature [34–36]. However, the cmc values for 16–4–16 that we determined are 10 times lower than the literature value determined by fluorescence technique [20] by Bhattacharya et al. However, Zana et al. [37] recently mentioned that the fluorescence technique is not a good method for determining cmc—at least in the case of gemini surfactants—and suggested that surface tension is a more suitable method for cmc determination. Tsubone et al. [39] synthesized anionic gemini surfactants and also determined their cmcs in μM. The cmc values of conventional nonionic $C_{12}E_6$ as well as dimeric 16–4–16 were found to decrease with increased temperature. This phenomenon is generally seen for nonionic surfactants [38]. With an increase in the temperature, the dehydration of hydrophilic groups of $C_{12}E_6$ takes place, which results in an increase in hydrophobic interaction and consequently a cmc decrease. The decrease in the cmc for 16–4–16 with increasing temperature may be due to enhancement of the degree of ionization, which causes a modification of the magnitude of electrostatic repulsion, as well as due to destruction of water structures surrounding alkyl chains. The cmc values of 16–4–16/$C_{12}E_6$ mixed systems, as well as those of the pure surfactants, were evaluated by surface tension (γ) measurement only. From Table 1, it can be seen that in the mixed surfactant systems at any mole ratio the cmc value is lower than either pure 16–4–16 or $C_{12}E_6$ surfactant, indicating synergetic behavior (Fig. 1). The cmc values of mixed systems were found to decrease with increasing temperature. The decrease in cmc value indicates that these surfactant molecules in mixed system significantly alter the micellization process. The cmc values of dimeric surfactant are much smaller than those of the corresponding monomeric surfactant, because two alkyl chains at a time are transferred from water to the micelle pseudophase.

Table 1
Critical micelle concentration values for 16–4–16:$C_{12}E_6$ mixed surfactant systems in aqueous medium at different temperatures

$N_{16\text{–}4\text{–}16}$	Critical micelle concentration (μM)		
	303 K	308 K	313 K
0.0	71.0[a]	62.0	51.0
0.1	0.81	0.60	0.54
0.3	0.93	0.58	0.44
0.5	0.33	0.26	0.25
0.7	0.56	0.52	0.34
0.9	0.36	0.29	0.18
1.0	2.72	2.19	1.82

[a] Refs. [34–36].

The surface excess (Γ_{max} (mol cm^{-2})) is an effective measure of the adsorption at the air/water interface. The concentration of the surfactant is always more at the surface than that in the bulk. The surface excess (Γ_{max}) and minimum area per molecule (A_{min}) values were calculated by the Gibbs adsorption equation [40],

$$\Gamma_{max}\,(\mathrm{mol\,cm^{-2}}) = \left(\frac{-1}{nRT}\right)\left(\frac{d\gamma}{d\ln C}\right), \tag{3}$$

Table 2
Surface excess concentration (Γ_{max}) and minimum area per molecule (A_{min}) of 16–4–16:$C_{12}E_6$ mixed surfactant systems in aqueous medium at different temperatures

$N_{16\text{–}4\text{–}16}$	$\Gamma \times 10^{10}$ (mol cm^{-2})			A_{min} (nm^2)		
	303 K	308 K	313 K	303 K	308 K	313 K
0.0	2.48	2.71	2.86	0.67	0.61	0.58
0.1	0.50	1.19	0.68	3.31	1.39	2.43
0.3	0.69	1.44	0.91	2.40	1.15	1.82
0.5	1.79	0.79	0.32	0.93	2.09	5.18
0.7	1.05	1.03	1.02	1.58	1.61	1.62
0.9	1.90	0.83	1.25	0.87	1.99	1.33
1.0	1.36	0.86	1.25	1.22	1.93	1.33

Table 3
Interaction parameter values for 16–4–16:$C_{12}E_6$ mixed surfactant systems in aqueous medium at surface tension 55 dyn/cm (β^{σ}) and at cmc (β^{m})

$N_{16\text{–}4\text{–}16}$	β^{σ}			β^{m}		
	303 K	308 K	313 K	303 K	308 K	313 K
0.1	−18.1(0.46)[a]	−12.8(0.46)	−9.2(0.47)	−13.3(0.53)	−13.9(0.54)	−13.5(0.54)
0.3	−16.6(0.49)	−10.6(0.51)	−13.0(0.51)	−10.7(0.59)	−11.9(0.59)	−12.3(0.59)
0.5	−19.3(0.51)	−14.1(0.53)	−18.8(0.53)	−14.3(0.60)	−14.5(0.60)	−13.7(0.60)
0.7	−13.1(0.55)	−10.9(0.57)	−11.8(0.57)	−11.5(0.65)	−11.4(0.65)	−12.5(0.64)
0.9	−12.4(0.59)	−17.5(0.58)	−8.4(0.67)	−14.9(0.66)	−13.0(0.60)	−12.4(0.60)

[a] In the parenthesis the value of X (ionic) is given.

$$A_{min}\ (\text{nm}^2) = \frac{10^{14}}{N\Gamma_{max}}, \tag{4}$$

where $d\gamma/d\ln C$ is the maximum slope in each case and R, T, C, and N are the gas constant, absolute temperature, concentration, and Avogadro number, respectively. The slope of the tangent at the given concentration of the γ vs $\log C$ plot has been used to calculate Γ by using curve fitting to a polynomial equation of the form $y = ax^2 + bx + c$ in Microsoft Excel. The R^2 (regression coefficient) value of the fit lies between 0.9652 and 0.9997. The value of n for the Gibbs equation is the number of species whose concentration at the interface varies with the surfactant bulk phase concentration and was taken as 3 [7]. From Table 2 it was found that the surface excess concentration of 16–4–16 is less than that of pure $C_{12}E_6$, which was expected. The minimum area per molecule of pure 16–4–16 is higher than pure nonionic $C_{12}E_6$, as the 16–4–16 is bigger in molecular size. By small angle neutron scattering (SANS) studies it was found that the volume of 16–m–16 (m = 0–12) type surfactant is >1000 Å^3 [20]. So it is obvious that 16–4–16 has a higher minimum area per molecule than the nonionic. The minimum area per molecule is higher in mixed surfactant systems than for either of the pure surfactants, except in a few cases (Table 2). The magnitude of A_{min} is low, suggesting that the air/water interface is close-packed and therefore the orientation of the surfactant molecule at the interface is almost perpendicular to the interface.

3.2. *Surfactant–surfactant interaction*

The nature and the strength of the interaction between two surfactant molecules in the mixed micelle were determined by calculating the values of their β parameter by Rubingh's approach [41]. This can be generally obtained from the surface tension (γ)–concentration plots of aqueous solution of the individual surfactant and their mixtures. The interaction parameter for the mixed monolayer at the air/water interface as well as in the mixed micelle (β^{σ} or β^{m}) was calculated by [38]

$$\frac{(X_1)\ln(\alpha_1 C_{12}/X_1 C_1)}{(1 - X_1)\ln[(1 - \alpha_1)C_{12}/(1 - X_1)C_2]} = 1, \tag{5}$$

$$\beta = \frac{\ln(\alpha_1 C_{12}/X_1 C_1)}{(1 - X_1)^2}, \tag{6}$$

where X_1 is the mole fraction of surfactant 1 in the total mixed surfactant at monolayer or micelle and C_1, C_2, and C_{12} are the molar concentrations in the solution phases of surfactant 1 and 2 and their mixture, respectively. In case of micellar interaction these are cmc values. α is the mole fraction of surfactant 1. The β values are β^{σ} or β^{m} for monolayer or micelle, respectively. Equation (5) is solved iteratively for X_1, which is then substituted into Eq. (6) to calculate β. The β^{σ} or β^{m} values for these mixed system are listed in Table 3. As seen from the tabulated data both β^{σ} or β^{m} values are negative, showing attractive interaction (synergism) between these surfactant molecules. The β^{σ} values change with overall surface tension and hence they were computed at particular surface tension values of the solution (55 dyn cm^{-1}). The existence of synergism in mixtures containing two surfactants has been shown to depend not only on the strength of interaction between them but also on the relevant properties of the individual surfactant components of the mixtures [42]. The nonionic surfactants of the poly(ethylene oxide) class have a large number of oxygen atoms with unpaired electrons. These will have a tendency to react coulombically with the cationic gemini surfactant. The activity coefficients were calculated using the relation [38]

$$\ln(f_1) = \beta^m (1 - X_1)^2, \tag{7}$$

$$\ln(f_2) = \beta^m (X_1)^2, \tag{8}$$

where X_1 is the mole fraction of surfactant 1 in the micelle and f_1 and f_2 are the activity coefficients of surfactants 1 and 2, respectively, in the mixed micelle. The activity coefficient values (f_1 and f_2) of 16–4–16/$C_{12}E_6$ mixed surfactant systems in aqueous medium at different temperatures were computed and activity coefficients for nonionic surfactant (f_2) were found to be very low, whereas f_1 values were reasonably high, though both were much less than unity, indicating nonideal behavior and attractive interaction between the surfactants in the micelle (data are not given). The activity coefficient values of 16–4–16 are high in both the mixed systems and f_2 values of $C_{12}E_6$ are low, indicating negative deviation from ideality and an attractive interaction. It is also interesting to note that the X values in the mixed micelles and in mixed monolayers are almost (though not exactly) the same, with a slightly higher value in the micellar state. The temperature does not seem to have any effect on the composition of either the micelle or the surfactants at the air–water interface. The β^m values so obtained are useful in understanding the interaction between the two surfactants. If long-range electrical interaction is present in the system, it has been found that β^m explains that interaction very well. However, Maeda [43] and Ruiz et al. [44] have stated that both chain–chain and head group–head group interactions are present in a mixed system. According to Maeda, the β^m value obtained by the use of regular solution theory encompasses the head group–head group interaction but not the hydrocarbon chain–chain interactions, particularly when the chains are of dissimilar lengths. Maeda [43] explained that a mixed ionic–nonionic surfactant system often has a cmc much lower than the cmcs of the pure components. This can be attributed to the decrease in the ionic head group repulsion caused by the presence of nonionic surfactant molecules between the head groups. The author suggested that besides the regular solution interaction parameter, there could be another parameter (B_1) that actually contributes to the stability of the mixed micelle. The free energy of micellization (ΔG_m) as a function of ionic component in the mixed micelle (X_2) is given by

$$\Delta G_m = RT\left(B_0 + B_1 X_2 + B_2 X_2^2\right), \tag{9}$$

where

$$B_0 = \ln C_1 \quad (C_1 \text{ is the cmc of the nonionic surfactant}), \tag{10}$$

$$B_1 + B_2 = \ln\left(\frac{C_2}{C_1}\right) \quad (C_2 \text{ is the cmc of the ionic surfactant}), \tag{11}$$

$$B_2 = -\beta^m. \tag{12}$$

Table 4
B_0, B_1, and B_2 values for 16–4–16:$C_{12}E_6$ mixed surfactant systems

$N_{16\text{–}4\text{–}16}$	B_0 (avg)	B_1	B_2
0.9	−13.7	−18.2	14.9
0.7		−14.8	11.5
0.5		−17.6	14.3
0.3		−14.0	10.7
0.1		−16.6	13.3

All quantities in the above equations are expressed on a unitary scale. The calculated results of B_1 and B_2 are given in Table 4. Hence ΔG_m can be calculated. It is interesting to note that the ΔG_m values calculated from the phase separation model ($\Delta G_m = RT\ln(\text{cmc})$, cmc in mole fraction scale) and by Maeda's method agree reasonably well (within ±3%). This indicates that the degree of counterion binding of the mixed micelles is probably negligible. The B_1 values are highly negative in the present case, indicating that the chain–chain interaction plays a major role in the stability of the mixed micelle. The gemini surfactant has two chains of 16 carbons, whereas nonionics have only one of 12 carbons. Hence, according to Maeda, as the chain lengths are very different, there should be chain–chain interaction helping to stabilize the micelle. However, the B_1 values seem to be a function of the composition of a system as well the head groups.

3.3. *Micellar aggregation numbers (N_{agg}) in cationic gemini/nonionic surfactant mixtures*

The fluorescence method is a convenient method for determining the micelle aggregation numbers (N_{agg}) [44]. We determined N_{agg} by the steady state fluorescence quenching method at different mole ratios of the binary 16–4–16/$C_{12}E_6$ mixtures. The N_{agg} of pure and mixed surfactants are presented in Fig. 3. It is evident that the N_{agg} values of the mixed surfactant system are larger than 16–4–16 but lower than $C_{12}E_6$ single surfactant at all mole ratios. Such behav-

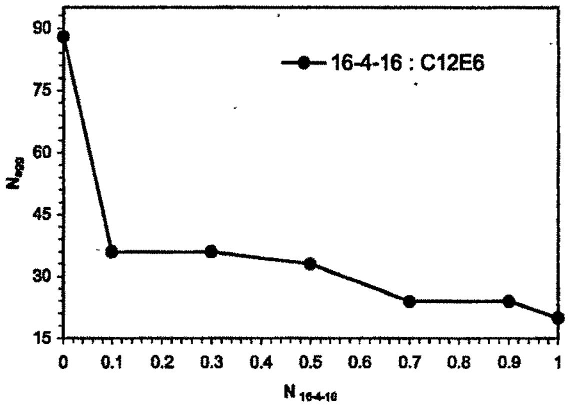

Fig. 3. Variation of the aggregation number (N_{agg}) for 16–4–16:$C_{12}E_6$ with the mole fraction of ionic surfactant in mixed surfactant systems. The solid lines are guides for the eyes.

ior was expected. However, by SANS studies [20], it was not possible to obtain the aggregation number of 16–4–16 gemini surfactant. The decrease of N_{agg} is obviously associated with the increased average repulsive interaction between head groups with increasing 16–4–16, as nonionic surfactant molecules are progressively replaced by cationic dimeric surfactants. As a consequence, the average optimal surface area per hydrophilic group increases. The smallest aggregation number corresponds to the highest surface charge density, i.e., pure cationic gemini 16–4–16 surfactant. The size of the mixed micelles in the solution is mainly determined by the repulsions between head groups due to steric origin for oxyethylene head groups and of electrostatic origin for quaternary ammonium head groups and also by the packing parameters of the surfactants making up the mixture.

3.4. Microenvironment

The ratio of intensity of first (I_1) and third (I_3) vibronic peaks, I_1/I_3, in a monomeric pyrene fluorescence emission spectrum is known to be sensitive to local polarity around the probe [31]. Figure 2 represents an illustration of intensity against wavelength (emission) to yield I_1/I_3. The I_1/I_3 values (>1) suggest a polar environment around pyrene. I_1/I_3 and K_{sv} (Eq. (2)) are presented in Table 5. K_{sv} is the ratio of the bimolecular quenching constant to the unimolecular decay constant. Also, K_{sv} is the product of k_q, the rate constant of the quenching process, and τ, the actual lifetime of the probe in the absence of bimolecular quenching [30]. Thus from the values of K_{sv}, we can assume that quenching is efficient; also, the lifetime of pyrene in $C_{12}E_6$ in most mole ratios of the mixed micelle is higher if we assume that k_q for systems are of similar magnitude.

The apparent dielectric constant (D) of the medium (in this case the pyrene environment inside the micelle) can be estimated [43] by employing the relation

$$I_1/I_3 = 1.00461 + 0.01253D. \qquad (13)$$

In our present study we have computed the apparent dielectric constant of the pure micelles as well as the mixed micelles from the experimental I_1/I_3 data. For pure $C_{12}E_6$ the apparent dielectric constants were found to be 13.20, whereas that of $C_{12}E_8$ was 16.0 [43]. The observed results are reasonable, as the more oxyethylene groups in the system, the higher the dielectric constant. According to Turro [45], the dielectric constant inside the mixed micelle can be computed from the relation

$$D_{12} = \sum X_i D_i. \qquad (14)$$

In Table 5 the experimentally determined and calculated apparent dielectric constants are presented for the system. It is obvious that the experimental values are somewhat different from the calculated values. However, we believe that this difference is expected because the surfactants are having attractive interactions inside the micelle.

4. Conclusions

The interfacial and micellar behavior in a mixture of cationic dimeric and nonionic surfactant systems were studied. We observed that, in general, the attractive interaction in the mixed micelle is lower than that in the mixed monolayer at the air/water interface. However, the values are negative, which indicates that the surfactants interact reasonably well in both micellar and monolayer states. The cmc value in mixed surfactant systems at any mole ratio is less than those of either pure 16–4–16 or $C_{12}E_6$, which indicates synergistic behavior. Aggregation number values of the mixed surfactant system are larger than for 16–4–16 but lower than for $C_{12}E_6$ single surfactant at all mole ratios. The micropolarity of the mixed system is almost the same but the binding constant decreases with increasing mole fraction of 16–4–16. The chain–chain interactions seem to be very important for the stability of mixed micelles.

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Table 5

Micropolarity (I_1/I_3) binding constant (K_{sv}) and apparent dielectric constant (D) for 16–4–16:$C_{12}E_6$ mixed surfactant systems

$N_{16\text{–}4\text{–}16}$	X at micelle	I_1/I_3	K_{sv} ($\times 10^5$)	Expt. D^a	Calc. D^b
1.0	–	1.46	0.73	36.3	36.4
0.9	0.66	1.43	1.12	34.0	28.5
0.7	0.65	1.40	1.71	31.6	28.2
0.5	0.60	1.39	2.26	30.8	27.1
0.3	0.59	1.35	3.56	27.6	26.9
0.1	0.53	1.26	6.85	20.4	25.5
0.0	–	1.17	9.69	13.2	13.2

[a] Calculated from Eq. (13).

[b] Calculated from Eq. (14).

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Investigation of the Properties of Decaoxyethylene *n*-Dodecyl Ether, $C_{12}E_{10}$, in the Aqueous Sugar-rich Region

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ABSTRACT: Interfacial, thermodynamic, and morphological properties of decaoxyethylene *n*-dodecylether [$CH_3(CH_2)_{11}(OCH_2CH_2)_{10}OH$] ($C_{12}E_{10}$) in aqueous solution were analyzed by tensiometric, viscometric, proton nuclear magnetic resonance (NMR), and small-angle neutron scattering (SANS) techniques. Dynamic and structural aspects at different temperatures in the absence and presence of sugars at different concentrations were measured. Critical micelle concentrations (CMC) were determined by surface tension measurements in the presence of ribose, glucose, and sucrose. The heat capacity ($\Delta C_{p\,m}$), transfer enthalpy ($\Delta H_{m\,tr}$), transfer heat capacities ($\Delta C_{p\,m\,tr}$), micellization constant (K_m), Setchenow constant (K_S^N), and partition coefficient (q) were determined and discussed as an extension of the usual thermodynamic quantities of micellization and adsorption at the air–water interface. An enthalpy–entropy compensation effect was observed with an isostructural temperature (T_c) of about 310 K for both micellization and interfacial adsorption. SANS measurements were taken to elucidate structural information, viz., aggregation number (N_{agg}), shape, size, and number density (N_m) on $C_{12}E_{10}$ micelles in D_2O at different concentrations of sugars (0.05, 0.02, 0.3, and 0.5 M) and temperatures (30, 45, and 60°C). Intrinsic viscosity gave the hydrated micellar volume (V_h), volume of the hydrocarbon core (V_c), and volume of the palisade layer of the oxyethylene (OE) unit (V_{OE}). SANS, as well as rheological data, supported the formation of nonspherical micelles with or without sugars. By SANS, we also observed that at the studied temperature intervals, oblate ellipsoid micelles changed into prolate ellipsoids and the number density of micelles decreased with an increase in temperature both in the presence and in the absence of sugars and also on increasing the concentration of sugars. Proton NMR showed a change in chemical shift of the OE group of micelles above the CMC. We also studied the phase separation of $C_{12}E_{10}$ by sugars in cloud point measurements.

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KEY WORDS: Aggregation number, cloud point, critical micelle concentration, nonionic surfactant, small-angle neutron scattering, viscosity

Surfactant molecules self-assemble into finite-sized aggregates called micelles in aqueous solution. These are significant for their numerous uses, including solubilization, dispersion, emulsification, catalysis, and technological, biological, and pharmaceutical applications. Such aggregates are formed in various shapes, e.g., globular, ellipsoidal, cylindrical, and disk-shaped (1). The morphology of micelles depends on the chemical structure of the surfactant monomer (2) and on solution conditions such as concentration, temperature, co-surfactant, and ionic strength (3,4). Control of the morphology of these types of aggregates by the addition of external additives or by the proper choice of surfactant mixture has become increasingly important in recent years, both from a theoretical and from an experimental point of view.

To achieve a deep understanding of the physicochemical properties of micelles, their dynamic and morphological properties must be observed simultaneously (5). No single technique is capable of yielding both types of information unambiguously; thus, there is a need to combine both types of studies to gather this information. The aggregational and surface properties of surfactants in solution are very sensitive and are influenced or tuned to the desired range and application by altering the solvent polarity and type, temperature, pressure, pH, and presence of various foreign substances

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Abbreviations: $\partial\Sigma/\partial\Omega$, cross-section per unit volume; γ, surface tension; σ, Traube's constant; π_{CMC}, surface pressure at the CMC; $\Delta C_{p\,m}$, heat capacities of micelle formation; $\Delta C_{p\,m\,tr}$, transfer heat capacities of micellization; $\Delta G^{\#}_{vis}$, activation of micelle formation; ΔG°_{m}, Gibbs free energy of micellization; ΔG°_{ad}, Gibbs free energy of adsorption; $\Delta H^{\#}_{vis}$, activation enthalpy; ΔH°_{m}, standard enthalpy of micellization; ΔH°_{ad}, standard enthalpy of adsorption; $\Delta H_{m\,tr}$, transfer enthalpies of micellization; Γ_{max}, maximum surface excess; ρ_p, scattering length density of the particle; $|\eta|$, intrinsic viscosity; η_r, relative viscosity; $\Delta S^{\#}_{vis}$, activation entropy; ΔS°_{m}, standard entropy of micellization; ρ_s, scattering length density of the solvent; ΔS°_{ad}, standard entropy of adsorption; a, semimajor axis; A_{agg}, aggregation number; A_{CMC}, area per molecule at the CMC; A_{min}, limiting area per molecule; $b = c$, semiminor axis; C, concentration of surfactant; $C_{12}E_{10}$, decaoxyethylene *n*-dodecylether; CMC, critical micelle concentration; CP, cloud point; CTAB, cetyltrimethylammonium bromide; d, density of the *n*-alkane at different temperatures; K_m, micellization constant; k_s^N, Setchenow constant; m', molarity of the additive; M, molecular weight of the solvent; M_c, molecular weight of the *n*-alkane at different temperatures; M_m, micellar molecular weight; N_A, Avogadro's number; N_{agg}, aggregation number; N_m, number density of micelles; NMR, nuclear magnetic resonance; OE, oxyethylene; PSD, position-sensitive detector; q, partition coefficient; Q, scattering vector; R, hard-sphere diameter of the additives; SANS, small-angle neutron scattering; SDS, sodium dodecyl sulfate; T_c, isostructural temperature; v, volume of a single surfactant monomer at a given temperature; V, volume of alkyl chain lengths in a single $C_{12}E_n$ molecule; V_c, volume of the hydrocarbon core; V_h, hydrated micellar volume; V_m, micellar volume; V_{OE}, volume of the palisade layer of the OE unit; X_{CMC}, CMC expressed as a mole fraction.

(co-solvent) (6–13). The nature of the co-solvent determines the direction in which changes in the critical micelle concentration (CMC) of the surfactants occur. The co-solvents may be distributed between an aqueous and a micellar phase and may accumulate both in the palisade layer and inside the micelle hydrophobic core, thus favoring the stability of the system. Electrolytes generally decrease the CMC (14), whereas nonelectrolytes may increase or decrease the CMC (15–17), and some organic co-solvents, when present in greater amounts, even cause disappearance of the micelles (14).

The effect of sugars, *viz.*, glucose (18–21), fructose (18,21), and sucrose (10,12,21,22), on the micellization process has been studied. However, some aspects warrant further investigation. Blandamer *et al.* (19) found that, by adding glucose, fructose, and arabinose to the micellar catalyzed reaction of 2,4-dinitrochlorobenzene with hydroxide ions, the first-order rate constant increased, indicating an enhancement of the catalytic action of cetyltrimethylammonium bromide (CTAB). However, they mentioned that attempts to measure the effect of sugars on the CMC of CTAB proved unsuccessful.

Most of the publications referenced above address the possible effect of sugars on ionic surfactants, whereas few describe the effect on nonionic surfactants (10,12,22,23). However, no comprehensive thermodynamic and morphological study of decaoxyethylene *n*-dodecylether nonionic surfactant, $C_{12}E_{10}$, in the presence of sugars has been identified. Sugars were chosen because they are the stuff of life for most organisms (24) and are nonionic. Consequently, whatever effects are observed would be mainly chemical in nature and not electrochemical. Alkyl polyoxyethylene-type nonionic surfactants were chosen because they are widely used in detergency, cosmetics, fabric softening; emulsion formulations such as shampoos, conditioners, and paints, pharmaceutical dosages, and drug delivery systems, and their use will continue in the future owing to their higher solubility at low temperatures. Moreover, the additive effect was expected to cause low CMC values, which would reduce the total amount of surfactant, thereby lowering the cost and toxicity.

Interfacial, thermodynamic, small-angle neutron scattering (SANS), viscosity, cloud point, and ^1H nuclear magnetic resonance (NMR) properties of a $C_{12}E_{10}$-water-sugar ternary system were studied to help in understand the interaction of nonionic additives with nonionic surfactants.

EXPERIMENTAL PROCEDURES

Materials. $C_{12}E_{10}$ was a commercially available product (Sigma, St. Louis, MO) and was used without further purification. Owing to polydispersity in the number of oxyethylene (OE) units, it was not a pure sample, as was mentioned by Dorsey *et al.* (25). However the surface tension–concentration plots at a given temperature did not show any minimum. D-Ribose ($C_5H_{10}O_5$), D-glucose ($C_6H_{12}O_6$), and sucrose ($C_{12}H_{22}O_{11}$) (Merck, Darmstadt, Germany) were dried *in vacuo* before use. For analysis of the physicochemical properties, all solutions were prepared by using triple-distilled deionized water showing electric conductance of 2–3 μS cm^{-1} at 303 K. For the SANS study, 99.4% D_2O (Heavy Water Division, BARC, Mumbai, India) was used, and for ^1H NMR, 99.8% D_2O (Merck) was used. D_2O was used instead of water when preparing solutions for the SANS experiments to provide a very good contrast between the micelles and the solvent.

Surface tension measurements. Surface tension (γ) was measured with a du Noüy ring tensiometer (S.C. Dey and Co., Kolkata, India) at different temperatures (308, 313, 318, and 323 K) and in sugar solutions of various concentrations (wt/vol), *viz.*, 0.25, 0.5, 0.75 and 1.0%. Temperatures were kept constant (±0.1 K) by circulating thermostated water through a jacketed vessel containing the solution. Other conditions were the same as reported in our recent papers (26,27). Representative plots of γ vs $\log_{10}C$ isotherms are shown in Figure 1.

SANS measurements. SANS is well-known as an ideal technique for studying micellar morphology (28,29), and this also has been demonstrated for surfactant micelles in the presence of various additives (30–35). SANS experiments were performed on the SANS spectrometer at the Dhruva reactor, Trombay, Mumbai, India (36). The spectrometer used a BeO filter as a monochromator beam and had a resolution ($\Delta Q/Q$) of about 15% at $Q = 0.05$ Å^{-1}. The scattered neutrons were detected in an angular range of 0.5–15° with a linear position-sensitive detector (PSD). The accessible wave vector transfer, Q ($= 4\pi \sin \theta/\lambda$, where 2θ is the scattering angle and λ is the wavelength of the incident neutrons), in the spectrometer was 0.02 to 0.32 Å^{-1}. The wavelength of neutrons used for these experiments was usually between 4 and 10 Å. The PSD allowed simultaneous recording of the data over the full Q range. Each solution was held in a 1.0-cm-pathlength

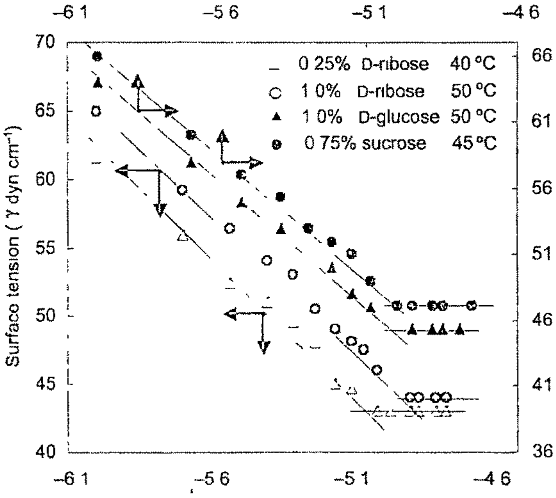

FIG. 1. Representative plots of surface tension (γ) vs $\log_{10}C$ (molarity) in the presence of sugars.

ultraviolet-grade quartz cell with a tight-fitting Teflon stopper that was sealed with Parafilm. The spectra were recorded at 30, 45, and 60°C (±0.2°) while keeping the quartz cell between metal heaters. The sample-to-detector distance was 1.8 m for all runs. The intensities were normalized to an absolute cross-section unit. Thus, plots of a cross-section per unit volume ($\partial\Sigma/\partial\Omega$) vs. scattering vector (Q) were obtained. The experimental points were fitted using a nonlinear least squares method. Both the semi-major axis (a) and semiminor axis ($b = c$) were fitting parameters. The volumes of the monomeric surfactants, calculated from the density and molecular weight of the corresponding hydrocarbon and then by dividing the molar volume of the hydrocarbon by Avogadro's number (N_A), were 381.4, 388.2, and 395.3 Å^3/molecule at 30, 45, and 60°C, respectively. The aggregation number (N_{agg}) for the micelle was related to the micellar volume (V_m) by the equation, $N_{agg} = V_m/v$ (37), where $V_m = 4/3\pi ab^2$ and v is the volume of a single surfactant monomer at a given temperature. From the calculated values of N_{agg}, the number density of micelles N_m is calculated by the following equation:

$$N_m/\text{cm}^{-3} = \frac{(C - \text{CMC}) \times 10^3 N_A}{N_{agg}} \qquad [1]$$

where C is the concentration of surfactant in mol L^{-1}. It was assumed that the micelle had an inner core consisting of a hydrophobic part and an outer shell that contained ether and the water of hydration. Intermiceller interference effects were neglected, and the measured distributions were analyzed in terms of the form factor of an ellipsoid.

Data treatment. SANS data were corrected for background, empty cell-scattering, and sample transmission factors. The corrected intensities were normalized to absolute cross-section units; thus, the coherent differential scattering cross-section per unit volume, $\partial\Sigma/\partial\Omega$, vs. Q was obtained. The absolute calibration had an estimated uncertainty of 5%. Experimental data points were fitted using a nonlinear least squares routine as described next. Comparisons between the experimentally obtained and theoretically calculated cross-sections are shown in Figures 3–6.

SANS data analysis. For a system composed of monodispersed, uniform, ellipsoidal colloidal particles, the coherent differential scattering cross-section per unit volume ($\partial\Sigma/\partial\Omega$) is given by

$$\partial\Sigma/\partial\Omega = n\,(\rho_p - \rho_s)^2\, V^2\, P(Q) S(Q) \qquad [2]$$

where n denotes the number density of particles, ρ_p and ρ_s are, respectively, the scattering length densities of the particle and the solvent, and V is the volume of the particle. $P(Q)$ is the intraparticle-structure factor and is established by the shape and size of the particle. $S(Q)$ is the interparticle-structure factor, which depends on the spatial arrangement of particles and is thereby sensitive to interparticle interactions. For dilute solutions, interparticle interference effects were negligible. Measurements were taken at low concentration such that $S(Q) \sim 1$ and $P(Q)$ were calculated for ellipsoidal micelles. The dimensions of the micelles, aggregation number, and number density of micelles were determined from the analysis. The semimajor axis (a) and semiminor axis ($b = c$) were the parameters used in analyzing the SANS data. We found that the experimental SANS intensity best matched the values obtained using an ellipsoidal model. In all the measurements, the concentration of $C_{12}E_{10}$ (50 mM) was held constant, and the concentration of sugars (0.05, 0.1, 0.2, 0.3 M) and the temperature (30, 45, and 60°C) were varied. Further experimental details and theoretical expressions for data treatment were identical to those described previously (38).

Viscosity measurement. The viscosity of the surfactant solution was affected by the interaction of both the hydrophobic core and the hydrophilic outer shell of the micelle with water. It measured the solute–solvent interaction and the shape and size of the micelle. The latter were affected by temperature changes. Thus, the viscosity of the $C_{12}E_{10}$ (50 mM) surfactant solution was determined in the absence and presence of sugars and at the same temperatures as for the SANS measurements. The flow time of the surfactant solution and water was measured using an Ubbelohde suspended-level viscometer. The density of the surfactant solution was determined with a pyncnometer. Density and viscosity measurements were carried out in a thermostated water bath (±0.1°C). Samples were carefully filtered before injection into the viscometer. Three consecutive flow times agreeing within ± 0.02 s were taken and the mean flow time was considered. The intrinsic viscosity, $|\eta|$, was calculated using the relation,

$$|\eta| = \lim_{C \to 0} (\eta_r - 1)/C \qquad [3]$$

where the limit to zero concentration indicates that intermolecular interactions were absent and η_r indicates the relative viscosity of the surfactant solution. Some researchers (39,40) have taken $|\eta|$ to be equal to $(\eta_r - 1)/C$ without the condition of limiting the concentration. In this article, $|\eta|$ was calculated without taking the zero concentration limit into account as in our previous work (27).

Cloud point (CP). Phase separation of the surfactant solution was studied by determining the CP of $C_{12}E_{10}$ (1% wt/vol) in the presence of an increasing amount of sugar, as described previously (11). The CP was an average of the temperature at which clouding appeared and then disappeared. These temperatures did not differ by greater than ±0.2°C.

NMR measurement. ^{1}H NMR measurements of $C_{12}E_{10}$-sugars (1:1 wt/vol) were carried out at room temperature (25°C ± 0.5) with a Bruker Advance 300 spectrophotometer (Bruker, Karlsruhe, Germany) operating at 300 MHz.

RESULTS AND DISCUSSION

Thermodynamics of micellization and interfacial adsorption of $C_{12}E_{10}$. Interaction with sugars. Surface tension is a fast, nondestructive, and dependable means of determining the CMC (41). The CMC values of $C_{12}E_{10}$ in the presence of sugars at different temperatures are presented in Table 1. At a particular temperature, the CMC value without any additive was in good agreement with values in the literature (9,10,14,42). The CMC values of $C_{12}E_{10}$ were found to decrease with an increase in temperature in the absence of sugars, consistent with observations in a previous work (8). The presence of sugars had almost the same effect, i.e., there was a decrease in the CMC at a lower temperature. From the experimental results, it seems two antagonistic effects of structure making and structure breaking were happening simultaneously in the system in the presence of sugars. Sugars are water-structure makers and, owing to their larger number of hydroxyl groups, sucrose is a better structure maker than ribose or glucose. In the case of OE micelles, the head group will be strongly hydrated. In the presence of sugars, the sugars may interact with the surfactants or simply replace some of the water molecules of the hydrated OE groups, affecting the repulsive interaction between the head groups. Under such conditions, the CMC of $C_{12}E_{10}$ increases when the sugar concentration is increased. In the presence of sugars, the CMC increased with an increase in temperature in all cases studied. This was observed earlier in the presence of different additives (9,10,42). For a nonionic surfactant without any additive, the CMC decreased with an increase in temperature owing to the dehydration of the hydrophilic moiety of the surfactant molecule caused by a breaking of the water structure. In the presence of an additive, however, the reverse was seen, indicating that these molecules significantly altered the micellization process. As shown in Table 1, increasing the number of OH groups in the sugars decreased the CMC values, particularly at higher temperatures. Sugars form intermolecular hydrogen bonds with the solvent water molecules and thereby promote the water structure, which is also promoted by the hydrophobic parts of the surfactant molecule through hydrophobic interaction. In the presence of additives, the water structure is broken as the temperature increases, but aqueous-sugar structures are formed. Consequently, there is overall structure formation and the CMC increases.

TABLE 1
Critical Micelle Concentration (CMC) of Decaoxyethylene *n*-Dodecyl Ether ($C_{12}E_{10}$) in the Presence of Sugars at Different Temperatures[a]

Concentration of sugar (%)	CMC (μM)			
	308 K	313 K	318 K	323 K
D-Ribose				
0.00	11.8 ± 0.12	10.0 ± 0.10	8.9 ± 0.09	7.1 ± 0.07
0.25	7.4 ± 0.08	8.3 ± 0.08	8.9 ± 0.09	9.3 ± 0.09
0.50	7.5 ± 0.08	8.1 ± 0.08	9.1 ± 0.09	10.2 ± 0.10
0.75	7.9 ± 0.08	8.7 ± 0.09	9.3 ± 0.09	10.0 ± 0.10
1.00	7.9 ± 0.08	8.9 ± 0.09	9.6 ± 0.10	10.9 ± 0.11
D-Glucose				
0.25	7.1 ± 0.07	8.1 ± 0.08	8.9 ± 0.09	9.1 ± 0.09
0.50	7.3 ± 0.07	8.3 ± 0.08	8.5 ± 0.09	9.0 ± 0.09
0.75	7.6 ± 0.08	8.7 ± 0.09	9.5 ± 0.10	10.0 ± 0.10
1.00	8.1 ± 0.08	8.9 ± 0.09	9.8 ± 0.10	10.0 ± 0.10
Sucrose				
0.25	6.7 ± 0.07	7.1 ± 0.07	8.1 ± 0.08	8.9 ± 0.09
0.50	7.1 ± 0.07	7.9 ± 0.08	8.1 ± 0.08	8.9 ± 0.09
0.75	7.2 ± 0.07	8.1 ± 0.08	8.9 ± 0.10	9.5 ± 0.10
1.00	7.9 ± 0.08	8.1 ± 0.08	8.9 ± 0.10	9.3 ± 0.09

[a]Values represent mean ± SD, $n = 3$

The Gibbs free energy of micellization (ΔG°_m) for a nonionic surfactant is directly proportional to the $\ln X_{CMC}$ (CMC on a mole fraction scale) at constant temperature by the relation (4) $\Delta G^\circ_m = RT\ln X_{CMC}$. The initial standard state is hypothetical, where the surfactant molecules are in mole fraction units and behaving as though they are at infinite dilution, and the final state is the micelle itself. In Table 2 the ΔG°_m, ΔH°_m, and ΔS°_m at the standard state in mole fraction units at 45°C are reported in the presence of various amount of sugars. In the absence of additives, the free energy of micellization becomes more negative with an increase in temperature. That is, the formation of micelles becomes relatively more spontaneous at higher temperatures. Even in the presence of sugars, the variation is similar, although the CMC increases with temperature. The reason for such an observation has been given previously (10).

The standard enthalpy of micellization (ΔH°_m) and the standard entropy of micellization (ΔS°_m) were computed from the reasonably linear ΔG°_m vs. T plots, the slope being ΔS°_m. The ΔH°_m was then computed by using Equation 4:

$$\Delta H^\circ_m = \Delta G^\circ_m + T\Delta S^\circ_m \qquad [4]$$

The process of micellization was endothermic, although it became exothermic in the presence of sugars. The exothermicity may be due to additive–surfactant attractive interaction (4), which results in the stability of the system. The exothermic and endothermic characteristics of micellization are specific to the surfactant, the additive, and the temperature of micellization, although they were independent of temperature in the present system. The entropy of micellization (ΔS°_m) was positive, indicating that the micellization process was somewhat entropy-dominated in the absence of sugars. However, it should be noted that the micellization process was exothermic in these systems, therefore, the formation of micelles was very much favored in the presence of sugars. Rosen (8) stated that the presence of hydrated OE groups of the surfactant introduces structure in the liquid phase, and that the removal of the surfactant *via* micellization results in an increase in the overall randomness and hence an increase in entropy. Micelle formation also frees water molecules due to the absence of hydrophobic interaction and release of the so-called "iceberg" water.

A linear correlation between ΔH°_m and ΔS°_m was observed in all these systems (Fig. 2). Such a relationship was suggested by Lumry and Rajender (43). The slope of the line, i.e., the compensation temperature (T_c), was found to be 318 K in aqueous medium, higher than the expected 270 to 294 K (43). The small variations observed here and in an earlier work (15) may be due to the difference in the bulk structural property of the solution compared with water. However, deviations from such a linear relationship are well known. As mentioned by Krug *et al.* (44), error in the data

TABLE 2
Thermodynamic and Transfer Heat Parameters of Micellization of $C_{12}E_{10}$ Aqueous Solution in the Presence of Sugars at 45°C[a]

Concentration of sugar (%)	$-\Delta G^\circ_m$ (kJ mol^{-1})	ΔH°_m (kJ mol^{-1})	ΔS°_m (J mol^{-1} K^{-1})	$\Delta C_{p\,m}$ (J mol^{-1} K^{-1})	$-\Delta H_{m\,tr}$ (kJ mol^{-1})	$\Delta C_{p\,m\,tr}$ (J mol^{-1} K^{-1})
D-Ribose						
0.00	40.4	20.95	196	–0.120	—	—
0.25	41.4	–12.6	90.4	–0.003	33.6	0.117
0.50	41.3	–16.8	77.0	–0.001	37.8	0.119
0.75	41.3	–12.8	89.6	–0.003	33.8	0.117
1.00	41.2	–17.2	75.2	–0.006	38.2	0.114
D-Glucose						
0.25	41.4	–14.0	86.4	–0.005	35.0	0.115
0.50	41.5	–10.9	96.0	–0.001	31.9	0.119
0.75	41.2	–15.0	82.6	–0.002	36.0	0.118
1.00	41.1	–11.9	92.2	–0.005	32.9	0.115
Sucrose						
0.25	41.6	–16.5	78.8	–0.002	37.5	0.118
0.50	41.6	–15.6	81.6	–0.012	36.6	0.108
0.75	41.4	–10.6	97.2	–0.001	31.6	0.119
1.00	41.4	–9.5	100.2	–0.002	30.5	0.118

[a] The error in the data is <2%. Abbreviations: ΔG°_m, Gibbs free energy of micellization; ΔH°_m, standard enthalpy of micellization; ΔS°_m, standard entropy of micellization; $\Delta C_{p\,m}$, heat capacities of micelle formation; $\Delta H_{m\,tr}$, transfer enthalpies of micellization; $\Delta C_{p\,m\,tr}$, transfer heat capacities of micelle formation; for other abbreviation see Table 1.

may also lead to compensation. This type of relationship was discussed in an earlier publication (45).

The heat capacities for micelle formation ($\Delta C_{p\,m}$) were also evaluated from the plot of ΔH_m vs. T, the slope being $\Delta C_{p\,m}$ (Table 2). The variation in heat capacities with concentration of the additives did not show regularity in any of the assessments. The transfer enthalpies ($\Delta H_{m\,tr}$) and transfer heat capacities ($\Delta C_{p\,m\,tr}$) of micelles from water to the aqueous solution were obtained using the relation

$$\Delta H_{m\,tr} = \Delta H_m(\text{aq. additive}) - \Delta H_m(\text{aq.}) \quad [5]$$

$$\Delta C_{p\,m\,tr} = \Delta C_{p\,m}(\text{aq. additive}) - \Delta C_{p\,m}(\text{aq.}) \quad [6]$$

The transfer enthalpies of micelles were found to be negative (Table 2). Negative transfer enthalpies also were reported for the transfer of NaCl and amino acids from water to an aqueous urea solution (14,46). This shows that the transfer of hydrophilic (OE) groups from water to the

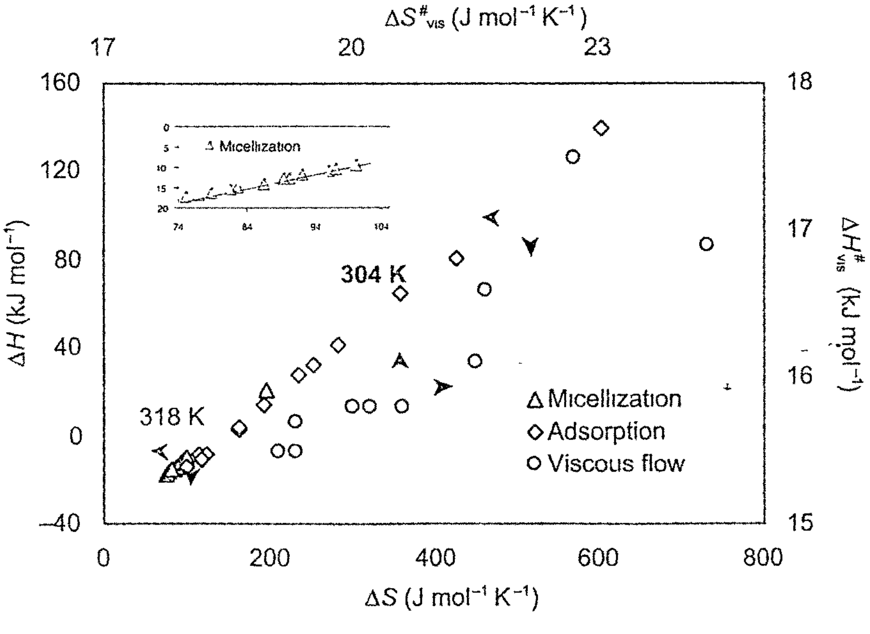

FIG. 2. Enthalpy–entropy compensation plot for all systems together

aqueous-sugar solution was exothermic, whereas that of the hydrophobic group was endothermic. The strong OE–sugar interaction was the predominant cause. The transfer heat capacities of micellization $\Delta C_{p\,m\,tr}$ for the transfer of micelles from water to the additive-containing solution were positive, suggesting increased hydration of the micelles attributable to increased hydrogen bonding between OE and the sugars present in the solution. The $\Delta C_{p\,m\,tr}$ values remained more or less constant over all systems, suggesting no obvious structural transition.

Sulthana *et al* (9) showed that for dilute solutions of polar additives in an aqueous surfactant solution at CMC, the following general form of the classical Setchenow equation was well obeyed:

$$\log \mathrm{CMC}_w/\mathrm{CMC}_{w+A} = K_M m' \qquad [7]$$

where CMC_w and CMC_{w+A} are the CMC values of a surfactant in the absence and in the presence of additives, K_M is a micellization constant, and m' is the molarity of the additive In a dilute solution with respect to a polar additive, the constant K_M takes the form

$$K_M = \tfrac{1}{2}[k_s^N + qM/2.303\times 1000] \qquad [8]$$

where k_s^N is the Setchenow constant or salting-out constant, q is the ideal partition coefficient of the solute between the micelle and water, and M is the molecular weight of the solvent. The salting-out constant is calculated by the empirical relationship

$$k_s^N = 0.637 - 0.014n(\mathrm{CH_2}) - 0.146R \qquad [9]$$

where $n(\mathrm{CH_2})$ is the number of methylene groups in the linear hydrocarbon chain and R is the hard-sphere diameter of the additives calculated from van der Waals volumes. The R values for D-ribose, D-glucose, and sucrose were calculated as 6.06, 6.56, and 8.04 Å^3, respectively (47).

The k_s^N values calculated for all three additives were negative, indicating a salting-in effect in the aqueous surfactant solution The K_M values obtained at all ratios of sugars are given in Table 3 The ideal partition coefficient, q, obtained using the K_M and k_s^N values tended toward zero for all systems. Such a q value suggests that the additives did not penetrate the micelle, i.e , the additives were not partitioned between the micelle and the solvent. Therefore, the variation in the CMC with the addition of these solutes can be entirely ascribed to the effect of these additives on the bulk solvent properties The solvent molecules induced a shift in the equilibrium between the micelles and the surfactant monomers in favor of the latter by their interaction with both the surfactant monomers and the solvent molecules. Since these additives did not penetrate, they can probably be assumed to have located themselves at the micelle–solvent interface. In other words, a large amount of the additive was present in the solvent, which was in contact with the hydrophilic group of the micelle. These results were supported by NMR and SANS data, as discussed later

TABLE 3
Micellization Constant, K_m (L mol^{-1}), for $\mathrm{C_{12}E_{10}}$ in the Presence of Sugars at Different Temperatures[a]

Sugar	308 K	313 K	318 K	323 K
D-Ribose	−0.64	−0.73	−0.65	−1.18
D-Glucose	−1.36	1.03	−1.25	−1.21
Sucrose	−3.04	−2.53	−2.26	−1.19

[a]The error in the data is <2% For other abbreviation see Table 1

The air–water interface of a surfactant solution is well populated by the adsorbed molecules. The maximum surface excess (Γ_{max}) is an effective measure of adsorption at the air–water interface and was calculated by the Gibbs adsorption equation (8). Γ_{max} was calculated from limiting area per molecule (A_{min}) values (26). The slope of the tangent at the given concentration of the γ vs $\log C$ plot (i e., $d\gamma/d\log C$) was used to calculate Γ_{max} by fitting a curve to a polynomial of the form, $y = ax^2 + bx + c$ in Microsoft Excel. The regression coefficient (R^2) value for the fit was between 0.9673 and 0.9996. The Γ_{max} increased with an increase in temperature (Table 4). This resulted from a decrease in the hydration of the ethoxy segment of the nonionic surfactant as the temperature increased, hence, the tendency to locate at the air–water interface was higher The magnitude of A_{min} was much lower than 1.5 nm^2 (data not given), suggesting that the air–water interface was closely packed and the orientation of the surfactant molecule was almost perpendicular to the surface.

The effectiveness of a surface-active molecule was measured by surface pressure (π_{CMC}) at the CMC, i.e , $\pi_{CMC} = \gamma_0 - \gamma_{CMC}$, where γ_0 and γ_{CMC} are the surface tension of pure water and the surface tension of the surfactant solution at CMC, respectively. The value of the free energy of adsorption at the air–water interface (ΔG°_{ad}) was calculated using the relation (8,9)

$$\Delta G^\circ_{ad} = RT\ln \mathrm{CMC} - N\pi_{CMC}A_{min} \qquad [10]$$

Table 5 presents the thermodynamic parameters of adsorption, i.e , ΔG°_{ad}, ΔH°_{ad}, and ΔS°_{ad}, of $\mathrm{C_{12}E_{10}}$ in the presence of sugars at the air–water interface at 45°C. The ΔG°_{ad} values were negative throughout, indicating that the adsorption of the surfactant at the air–water interface took place spontaneously in the presence or absence of sugars. The standard entropy (ΔS°_{ad}) and enthalpy (ΔH°_{ad}) of adsorption were obtained from the slope of the $\Delta G^\circ_{ad} - T$ plot. As expected, ΔG°_{ad} values were more negative than their corresponding ΔG°_m, indicating that when a micelle was formed, work had to be done to transfer the excess surfactant molecules present in the monomeric form at the surface to the micellar stage through the aqueous medium Under this condition, the interface was saturated with monomeric surfactant molecules

ΔG°_{ad} became more negative with an increase in temperature (data not shown) in either the presence or absence of additives, suggesting that the adsorption at higher temperatures was more facile ΔH°_{ad} in a pure aqueous solution was positive, as was ΔH°_m. However, in the presence of sugars,

TABLE 4

Maximum Surface Excess (Γ_{max}) and Traube's Constant ($\times 10^{-7}$) of $C_{12}E_{10}$ in the Presence of Sugars at Different Temperatures[a]

	$\Gamma_{max} \times 10^{10}$ (mol cm^{-2})											
Concentration of sugar (%)	D-Ribose				D-Glucose				Sucrose			
	308 K	313 K	318 K	323 K	308 K	313 K	318 K	323 K	308 K	313 K	318 K	323K
0.00	2.3	2.4	3.3	3.6	—	—	—	—	—	—	—	—
	(5.5)	(68.6)	(125)	(19.0)								
0.25	3.9	4.1	3.7	3.6	2.2	2.2	2.6	4.3	4.2	5.5	2.5	2.8
	(7.3)	(10.1)	(6.7)	(10.5)	(7.3)	(1.8)	(3.9)	(3.4)	(4.2)	(5.9)	(7.5)	(5.6)
0.50	2.6	2.5	1.8	1.6	2.9	2.3	2.6	2.3	2.8	3.0	2.6	2.8
	(21)	(8.9)	(57.8)	(25.7)	(11.7)	(3.3)	(9.1)	(5.2)	(8.2)	(8.3)	(12.9)	(12.2)
0.75	2.7	2.7	4.4	2.4	2.5	2.5	3.6	3.2	3.6	4.2	2.9	2.3
	(14.8)	(9.0)	(5.3)	(16.4)	(15.4)	(4.6)	(10.0)	(6.9)	(4.3)	(4.3)	(12.9)	(10.1)
1.00	2.8	2.8	4.3	4.1	2.4	3.1	2.1	2.4	2.8	2.3	3.3	3.6
	(7.6)	(5.2)	(3.9)	(4.6)	(24.9)	(10.1)	(13.4)	(17.0)	(7.7)	(7.7)	(8.1)	(6.7)

[a]Values in parentheses are Traube's constant ($\times 10^{-7}$) The error in the data is <2% For other abbreviation see Table 1

the results did not follow a regular trend. This suggests that these additives interacted with the hydrophilic group of the surfactant, which was exothermic, as was shown earlier for NaCl by Jha and Ahluwalia (46). The $\Delta S°_{ad}$ in a pure aqueous solution and in the presense of sugar additives was positive. This may be ascribed to a larger freedom of motion of the hydrocarbon chain at the interface and also to the mixing of surfactant monomers with additive molecules A linear correlation between $\Delta H°_{ad}$ and $\Delta S°_{ad}$ was observed in all systems having a T_c of 304 K (Fig. 2). However, one must remain conscious of the limitations of this observation, as has just been discussed.

Weiner and Zografi (48) suggest that

$$\Delta G°_{ad} = -RT \ln \sigma \qquad [11]$$

where σ is known as Traube's constant (6) and is defined by the relation

$$\sigma = (\partial \pi / \partial C)_{C \to 0} = -(\partial \gamma / \partial C)_{C \to 0} \qquad [12]$$

This means σ is the rate of change of the surface pressure per unit of concentration change at an infinite dilution. The σ values are given in Table 4. One can note that the σ of the pure $C_{12}E_{10}$ given in Table 4 is similar to the data of Ueno *et al* (49) thereby suggesting that the adsorption data were reasonable When the effect of different sugars on σ was computed, little difference in σ values was observed as a function of sugars. probably because the sugar concentrations were not very high

SANS studies of $C_{12}E_{10}$. Effect of sugars and temperature on the $C_{12}E_{10}$ micellar structure The experimental and theoretically fitted results of SANS for $C_{12}E_{10}$ micellar solutions are shown in Figures 3–6, and the estimated structural parameters, i e., aggregation number (N_{agg}), semimajor (a) axis semiminor ($b = c$) axis, axial ratio (a/b), and number density of micelles (N_m) are given in Table 6 One can see that the effect of temperature on size parameters was significant

TABLE 5

Thermodynamics of Adsorption and Structural Effect of Sugars on Micellization and Adsorption Parameters of $C_{12}E_{10}$ Aqueous Solutions at 45°C[a]

Concentration of sugar (%)	$-\Delta G°_{ad}$ (kJ mol^{-1})	$\Delta H°_{ad}$ (kJ mol^{-1})	$\Delta S°_{ad}$ (J mol^{-1} K^{-1})	$\Delta G°_m - \Delta G°_{ad}$ (kJ mol^{-1})	$\Delta H°_m - \Delta H°_{ad}$ (kJ mol^{-1})	$T(\Delta S°_m - \Delta S°_{ad})$ (kJ mol^{-1})
D-Ribose						
0.00	54.5	81.0	426	14.1	−60.0	−73.1
0.25	46.9	27.5	234	5.5	−40.1	−45.7
0.50	52.5	139.3	603	11.2	−156.1	−167.3
0.75	46.3	14.8	192	5.0	−27.6	−32.6
1.00	45.5	−13.7	100	4.3	−3.5	−7.9
D-Glucose						
0.25	45.5	−8.9	115	4.1	−5.1	−9.1
0.50	47.7	−8.6	123	6.2	−2.3	−8.6
0.75	48.0	−11.1	116	6.8	−3.9	−10.6
1.00	48.7	2.8	162	7.6	−14.7	−22.3
Sucrose						
0.25	47.2	32.6	251	5.6	−49.1	−54.7
0.50	48.6	41.1	283	7.0	−56.7	−64.0
0.75	48.6	65.2	358	7.2	−75.8	−83.0
1.00	47.4	3.8	161	6.0	−13.3	−19.2

[a]The error in the data is <2% Abbreviations $\Delta G°_{ad}$, Gibbs free energy of adsorption, $\Delta H°_{ad}$, standard enthalpy of adsorption, $\Delta S°_{ad}$, standard entropy of adsorption, for other abbreviations, see Tables 1 and 2

TABLE 6
Micellar Parameters of 50 mM $C_{12}E_{10}$ at Different Temperatures and in the Presence of Sugars[a]

Micellar system	Semimajor axis a (Å)	Semiminor axis $b = c$ (Å)	Axial ratio a/b	Aggregation number N_{agg}	Micellar density N_m (cm^{-3} × 10^{16})
$C_{12}E_{10}$ (°C)					
30	41.5 ± 2.1	26.8 ± 1.3	1.5 ± 0.08	327 ± 16	9.2 ± 0.46
45	72.2 ± 3.6	26.6 ± 1.3	2.7 ± 0.14	551 ± 28	5.5 ± 0.28
60	101.1 ± 5.1	28.9 ± 1.4	3.5 ± 0.18	895 ± 45	3.4 ± 0.17
$C_{12}E_{10}$ + 0.3 M D-glucose (°C)					
30	44.5 ± 2.2	26.2 ± 1.3	1.7 ± 0.09	336 ± 17	8.9 ± 0.45
45	80.5 ± 4.0	26.9 ± 1.3	3.0 ± 0.15	629 ± 31	4.8 ± 0.24
60	122.9 ± 6.1	28.6 ± 1.4	4.3 ± 0.22	1066 ± 53	2.8 ± 0.14
$C_{12}E_{10}$ + D-glucose (M) at 30°C					
0.05	31.1 ± 1.6	26.6 ± 1.3	1.2 ± 0.06	242 ± 12	12.4 ± 0.62
0.2	37.9 ± 1.9	26.4 ± 1.3	1.4 ± 0.07	290 ± 15	10.4 ± 0.52
0.3	44.5 ± 2.2	26.2 ± 1.3	1.7 ± 0.09	336 ± 17	8.9 ± 0.45
0.5	48.7 ± 2.4	25.2 ± 1.3	1.9 ± 0.10	340 ± 17	8.9 ± 0.45
$C_{12}E_{10}$ + 0.3 M sugar at 30°C					
D-Ribose	41.7 ± 2.1	25.2 ± 1.3	1.7 ± 0.09	291 ± 15	10.3 ± 0.52
D-Glucose	44.5 ± 2.2	26.2 ± 1.3	1.7 ± 0.09	336 ± 17	8.9 ± 0.45
Sucrose	43.1 ± 2.2	24.6 ± 1.2	1.8 ± 0.09	287 ± 14	10.5 ± 0.53

[a]For other abbreviation see Table 1

Conversely, temperature was nearly independent of the addition of sugars. Table 6 shows that, on increasing the temperature from 30 to 60°C, the semiminor axis remained almost constant (~26 Å), whereas the semimajor axis increased by 2.5-fold and N_{agg} increased by threefold. This indicated a twofold lateral association at 45°C and a threefold association at 60°C. The micelles were ellipsoid at 30°C, however, they likely aggregated laterally and became rodlike with double and triple aggregation numbers. The N_{agg} were high (8); however, there may have been some voids in the micelle structure. Higher temperatures may have caused more voids. Hence, the arrangement of the molecules in the micelle was not compact but rather loose, with consequent voids. The formation of micelles in the presence of sugars was therefore reasonably complex. In the presence of D-glucose at different temperatures, both the axial ratio and the N_{agg} were different from those of pure $C_{12}E_{10}$, indicating that sugar molecules interfered with micelle formation, probably by being at the micelle–water interface.

The axial ratio and N_{agg} increased when the concentration of D-glucose was increased. At the same concentration (0.3 M), N_{agg} was not significantly affected by any additive and was the same as for pure $C_{12}E_{10}$, whereas the axial ratio remained more or less constant. The micellar growth in both size and N_{agg} also was observed by Kumar *et al.* (31). They observed the effect of quaternary ammonium bromide, R_4NBr, on sodium dodecyl sulfate (SDS) micelles and found that the N_{agg} of 0.3 M of SDS in 0.3 M of C_4H_9NBr gave 340, with an axial ratio of 6.06. Robson and Dennis (33) investigated the geometry of the nonionic surfactant Triton X-100 by intrinsic viscosity and by SANS studies and showed that Triton X-100 formed both oblate and prolate ellipsoid micelles. We also found oblate ellipsoid micelles at 30°C, which become prolate ellipsoids (or rods) at 60°C. Recently, Pal *et al.* (50) analyzed the effect of hydrotropes on CTAB micelles by using SANS and viscosity measurements, and observed N_{agg} values >500 with axial ratios of >7. The authors concluded that the micellar shape changed from spherical to ellipsoidal depending on the additive.

As illustrated in Figures 3 and 4, no correlation peaks were observed in the low (up to 0.025) Q region, but absolute intensities were increased by *ca.* 1.5 times at high temperatures, showing the absence of spatial correlation among the nearest neighbors. A rise in temperature resulted in the dehydration of both the core and corona of the aggregates, thereby systematically elongating the semimajor axis (a), increasing the aggregation number, and even decreasing the N_m of the micelles. A look at column six in Table 6 reveals that the elongation along the major axis of the aggregates systematically increased the N_{agg} and decreased the N_m at elevated temperatures, both in the presence and in the absence of sugars. The increase in N_{agg} suggests that more surfactant molecules had been added into the space created by the expulsion of water, probably from both the core and corona portions of the micelles. The increase in size of the micelles should decrease the number density of aggregates in a unit volume (N_m), which was also observed.

CP. CP is the manifestation of solvation/desolvation phenomena in a nonionic surfactant solution. The desolvation of the hydrophilic group of the surfactant leads to the formation of clouding. All three sugars studied decreased the CP of $C_{12}E_{10}$ (Fig. 7). As already mentioned, sugars can form a structured solvent, and sucrose is probably a better structure maker than ribose and glucose because it has more hydroxyl groups. This suggests that, in its presence, there are fewer water molecules surrounding the micelles and, consequently, it is easier for the micelles to approach each other. The CP of $C_{12}E_{10}$

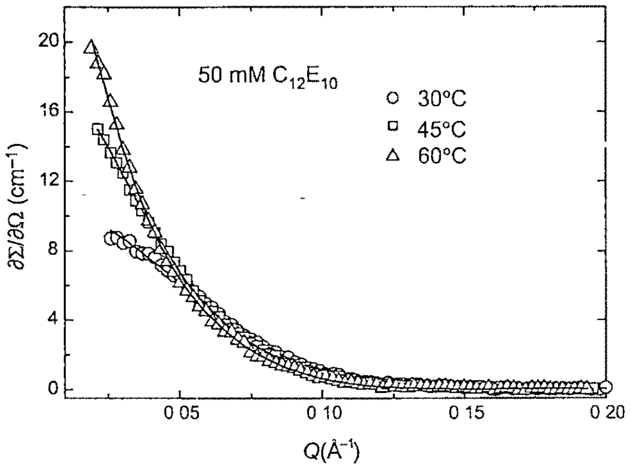

FIG. 3. Small-angle neutron scattering (SANS) distribution for 50 mM of decaoxyethylene *n*-dodecyl ether ($C_{12}E_{10}$) at different temperatures. Solid lines are theoretical fits, symbols are experimental values.

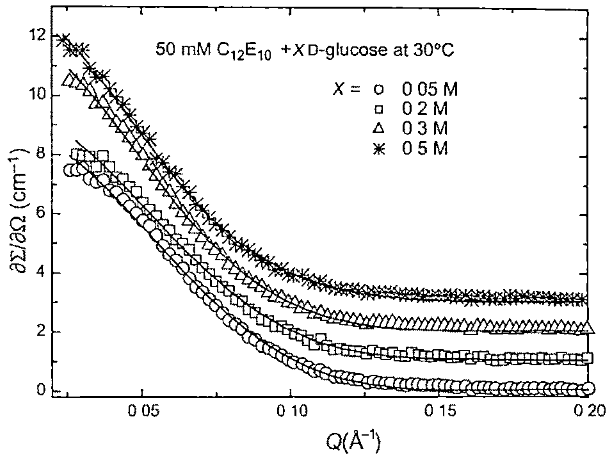

FIG. 5. SANS distribution for 50 mM of $C_{12}E_{10}$ in the presence of D-glucose at different concentrations at 30°C. Solid lines are theoretical fits, symbols are experimental values. Distributions were shifted by 0, 1, 2, 3 units in a vertical direction, respectively. For abbreviations see Figure 3.

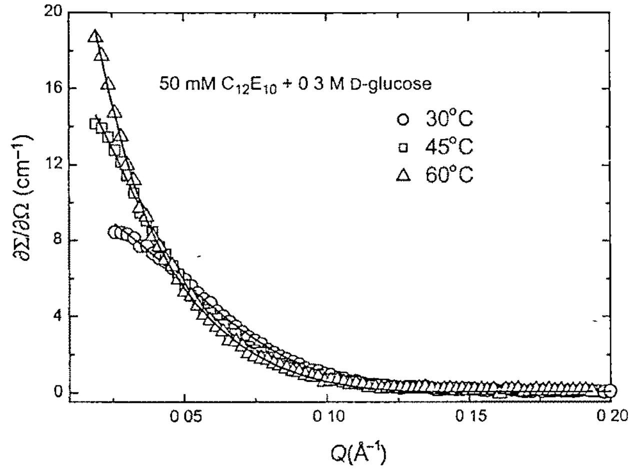

FIG. 4. SANS distribution for 50 mM of $C_{12}E_{10}$ in the presence of 0.3 M of D-glucose at different temperatures. Solid lines are theoretical fits, symbols are experimental values. For abbreviations see Figure 3.

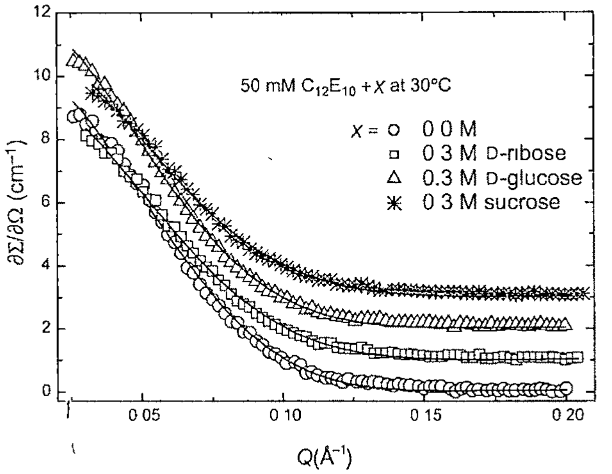

FIG. 6. SANS distribution for 50 mM of $C_{12}E_{10}$ in the presence of D-ribose, D-glucose, and sucrose at 30°C. Solid lines are theoretical fits, symbols are experimental values. Distributions were shifted by 0, 1, 2, 3 units in a vertical direction, respectively. For abbreviations see Figure 3.

(1% wt/vol) is 88°C (11). We did not study the system by using SANS or viscosity measurements around this temperature.

Viscosity. The intrinsic viscosity |η| decreased with an increase in temperature, indicating pronounced micellar dehydration (Table 7). That the viscosity of a liquid decreases with a rise in temperature is well known. An increase in random movements of the solute surfactant molecules also occurs on increasing the temperature because of the increase in kinetic energy. The micelles become compact with an increase in temperature owing to dehydration of the OE chains. In the presence of sugars, similar behavior has been observed with respect to temperature. However, |η| increases because of co-solubilization when the concentration of sugars is increased. Among the sugars considered, the variation is in the order of sucrose > D-glucose > D-ribose. The hydrated micellar volumes (V_h) were computed from the intrinsic viscosity by the relation $V_h = |\eta| \, M_m/2.5N_A$, where M_m (= $A_{agg}M$) is the micellar molecular weight, A_{agg} is the aggregation number obtained by SANS studies (taken from Table 6) and M is the molecular weight of $C_{12}E_{10}$. The volume of the hydrocarbon core (V_c) and the volume of the palisade layer of OE units (V_{OE}) were calculated using the following equations (10):

$$V_c = A_n V = 10^{24} A_n M_c/dN \qquad [13]$$

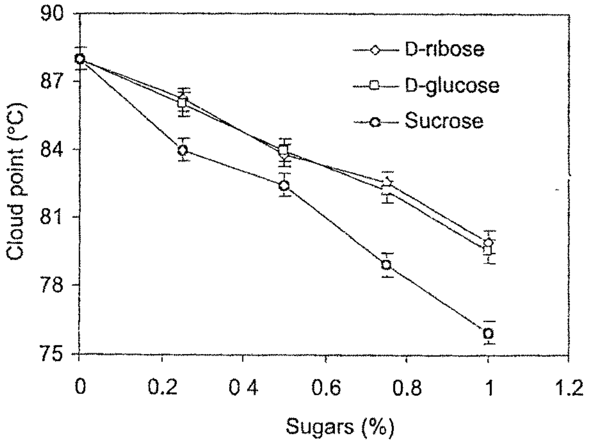

FIG. 7. Variations in the cloud point of $C_{12}E_{10}$ (1%) with weight percentage of sugars. For abbreviations see Figure 3.

and

$$V_{OE} = V_h - V_c \qquad [14]$$

where V is the volume of alkyl chain lengths in a single $C_{12}E_n$ molecule, M_c is the molecular weight (170), and d is the density of the corresponding liquid *n*-alkane at different temperatures, as already mentioned. The calculations for several systems on which SANS studies were performed are presented in Table 7. The V_h, V_c, and V_{OE} units increased as the concentration of D-glucose increased (Table 7). This may have resulted from the interaction of the OH moiety of sugars with the OE part of the nonionic surfactant at the micelle–water interface. Both V_h and V_{OE} increased as the temperature increased. This occurred because the N_{agg} of the micelle increased, which we attributed to a lateral joining of micelles. Obviously, with an increase in temperature, V_c should increase, and that was observed. The variation in the V_{OE}/V_h ratio with temperature was a function of the size and nature of the additive.

The thermodynamic activation parameters for a viscous flow were evaluated by using the Frenkel–Eyring equation (51)

$$\ln(\eta V/Nh) = \frac{\Delta H^{\circ}_{vis}}{RT} - \frac{\Delta S^{\circ}_{vis}}{R} \qquad [15]$$

where V, N, h, and R are the molar volumes, Avogadro's number, Planck's constant, and the universal gas constant, respectively. From the slope and intercept of the straight line obtained by plotting $\ln(\eta V/Nh)$ against $1/T$, the activation enthalpy ($\Delta H^{\#}_{vis}$) and activation entropy (ΔS°_{vis}) for a viscous flow were calculated.

The thermodynamic activation parameters for the system are presented in Table 8. $\Delta G^{\#}_{vis}$ was positive in all these systems, indicating a nonspontaneous flow, and it increased with an increase in the concentration of sugars in the order of: sucrose > glucose > ribose. $\Delta H^{\#}_{vis}$ values indicated that the viscous flows were endothermic. $\Delta S^{\#}_{vis}$ were positive, indicating that the micellar systems were not very well structured, either in the absence or presence of sugars.

NMR measurement. The ^1H NMR spectroscopy study of the micelle-rich solution in the presence of sugars was conducted to determine the electronic atmosphere around the protons and the additive effects on the atmosphere. Peak assignments were calculated for CH_3–$C_{\beta}H_2$–$(CH_2)_n$–$C_{\alpha}H_2$–$(OCH_2CH_2)_{10}$–OH (9,52), with the 3.69 ppm peak corresponding to the OE $(OCH_2CH_2)_m$ moiety, 3.45 for $C_{\alpha}H_2$, 1.57 for $C_{\beta}H_2$, 0.88 for CH_3, and 1.29 for the methylene protons $(CH_2)_n$. The changes in chemical shifts attributable to the addition of sugars were monitored, and the change in chemical shift of the OE units was downfield from 3.69 to 3.71 ppm. This result shows that these hydrophilic molecules were interacting with micelles through intermolecular hydrogen bonding. The

TABLE 7
Rheological Parameters of 50 mM $C_{12}E_{10}$ at Different Temperature and in the Presence of Sugars[a]

Micellar system	$\lvert\eta\rvert$ (cm^3/g)	V_h ($\times 10^4$ Å^3)	V_c ($\times 10^4$ Å^3)	V_{OE} ($\times 10^4$ Å^3)	V_{OE}/V_h
$C_{12}E_{10}$ (°C)					
30	6.60	89.7	12.5	77.2	0.94
45	6.02	137.9	21.4	116.5	0.84
60	3.99	148.5	35.4	113.1	0.76
$C_{12}E_{10}$ + 0.3 M D-glucose (°C)					
30	10.67	149.9	12.8	136.2	0.91
45	9.83	257.1	24.4	232.6	0.91
60	9.13	404.6	42.1	362.5	0.90
$C_{12}E_{10}$ + D-glucose (M) at 30°C					
0.05M	7.12	71.6	9.23	62.4	0.87
0.2M	8.63	104.1	11.1	93.0	0.89
0.3M	10.67	149.9	12.8	136.2	0.91
0.5M	14.38	203.2	13.0	190.3	0.94
$C_{12}E_{10}$ + 0.3 M sugars at 30°C					
D-Ribose	9.19	111.8	11.1	100.7	0.90
D-Glucose	10.67	149.1	12.8	136.3	0.91
Sucrose	16.60	198.1	11.0	187.1	0.94

[a]The error in the data is <5%. Abbreviations: $\lvert\eta\rvert$, intrinsic viscosity; V_h, hydrated micellar volume; V_c, volume of the hydrocarbon core; V_{OE}, volume of the palisade layer in the oxyethylene (OE) unit; for other abbreviation see Table 1.

TABLE 8

Thermodynamic Activation Parameters of the Viscous Flow of $C_{12}E_{10}$ (50 mM) in the Presence of Sugar[a]

Concentration of sugar (M)	$\Delta G^{\#}_{vis}$ (kJ mol^{-1}) at 45°C	$\Delta H^{\#}_{vis}$ (kJ mol^{-1})	$\Delta S^{\#}_{vis}$ (J mol^{-1} K^{-1})
D-Ribose			
0 0	9 15	16 9	24 3
0 1	9 23	16 1	21 5
0 3	9 37	15 5	19 3
0 5	9 46	15 5	19 1
D-Glucose			
0 1	9 26	15 8	20 6
0 3	9 45	15 8	20 0
0 5	9 67	15 8	19 3
Sucrose			
0 1	9 37	15 8	20 2
0 3	9 76	16 6	21 6
0 5	10 2	17 5	22 7

[a]The error in the data is <5% Abbreviations $\Delta G^{\#}_{vis}$, activation of micelle formation, $\Delta H^{\#}_{vis}$, activation enthalpy, $\Delta S^{\#}_{vis}$, activation entropy, for other abbreviation see Table 1

extent of intermolecular H-bonding was decreased by dilution with a nonpolar solvent and with an increase in temperature. This effect was seen in the viscosity data No change was observed in the chemical shift of the sugar proton These results show that the surfactant aggregates grew in size The main OE signals became broader and split when the sugars were added in a 1.1 ratio The NMR results suggest that the sugars were affecting the hydrophilic group, i e., OCH_2CH_2, by interacting with it, probably at the micelle–water interface, and that the electronic atmosphere of the OE group at the interface was also affected, but not strongly.

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Study of the cloud point of $C_{12}E_n$ nonionic surfactants: effect of additives

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Abstract

Nonionic surfactants are useful in the formation of emulsions. The aqueous solutions of these surfactants show complex phase behaviour including liquid–liquid phase separation at higher temperature. Addition of foreign substance to surfactant solutions does change the temperature at which the clouding phenomena occurs. In this article, we report the effect of electrolytes as well as nonelectrolytes on the cloud point (CP) of a series of nonionic surfactants of the poly(oxyethylene)ether type $C_{12}E_n$ ($n = 6, 9, 10$). It was observed that NaI and KI have different effect on the CP from that of NaCl, NaBr, KCl and KBr. Tetra butyl ammonium iodide (TBAI) acts differently on the CP from the Tetra methyl ammonium bromide (TMAB). Overall the electrolytes and nonelectrolytes have a large amount of effect on CP of nonionic surfactants, because of their effect on water structure and their hydrophilicity.

Keywords: Nonionic surfactants; Cloud Point; Electrolytes; Nonelectrolytes; Hydrophilicity

1. Introduction

Nonionic surface active agents are prepared by reacting a water insoluble material, such as an alkyl phenol with ethylene oxide to give a product which has an oil soluble group attached to a water soluble polyoxyethylene chain. The high water solubility of polyoxyethylene chain is due to hydrogen bonding between the solvent and the ether oxygen atoms in the chain. Since hydrogen bonding is temperature sensitive phenomenon, for each nonionic emulsifier molecule, there exists a temperature at which the degree of hydration of the hydrophilic portion is just insufficient to solubilize the remaining hydrocarbon portion, which is called the 'Cloud Point' [1]. At this temperature, surfactant is no longer soluble in water and solution becomes hazy or cloudy. This instant separation of nonionic surfactant upon heating into two phases, one surfactant rich and other aqueous, containing surfactant close to cmc at that temperature is the characteristic of nonionic surfactant which differentiates it from ionic surfactant. Nonionic surfactants are widely used as solubilizers, emulsifiers and detergents in many industrial processes. Therefore, the cloud point data are of considerable practical interest. For

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instance, the stability of O/W emulsions solubilized by nonionic surfactant has been related to CP [3–5]. In preparing emulsions, the CP is very important in selection of the most suitable surfactant for a given oil [3,6,7]. Moreover, pharmaceutical dosage forms consist of nonionic surfactant as stabilizer [8]. Several factors have been considered to be responsible for the CP phenomenon like structure of surfactant molecule, concentration, temperature and a third component (additive). CP is very sensitive to the presence of additives in a system, even at a very low concentration. The additives modify the surfactant–solvent interactions, change the cmc, size of micelles and phase behavior in the surfactant solutions [9]. Many efforts have been made to investigate the effect of various additives e.g. inorganic electrolytes [10,12–20], organic compounds [7,8,11,21–25], ionic surfactants [10,24–29], cationic surfactants [24,29] and zwitterionic surfactants on the cloud point of a nonionic surfactant. Some authors have also reported the CP of ionic surfactants [30–32]. This paper presents experimental results of the effect of various additives like inorganic electrolytes (NaX, KX, $Ca(NO_3)_2$ where X is halide ion) and nonelectrolytes (PEG-4000, carboxy methyl cellulose, glucose, sucrose) on the cloud points of aqueous solutions of a series of $C_{12}E_n$ ($n = 6$, 9, 10) nonionic surfactants. We have also determined the cloud point of $C_{12}E_9$ and $C_{12}E_{10}$ in presence of Triton X-100 (TX-100), which is widely used as a detergent in molecular biology [33].

2. Materials and methods

Hexa oxyethylene monododecylether, $C_{12}E_6$–$[CH_3(CH_2)_{11}(OCH_2CH_2)_6OH]$, and nona oxyethylene mono dodecylether, $C_{12}E_9$–$[CH_3CH_2)_{11}(OCH_2CH_2)_9OH]$, of Lion Corporation, Tokyo, Japan were used as received. Deca oxyethylene monododecylether, $C_{12}E_{10}$–$[CH_3(CH_2)_{11}(OCH_2CH_2)_{10}OH]$, and Triton X 100 of Sigma, USA were used without further purification. The electrolytes used in all experiments were of analytical grade. Glucose and sucrose were obtained from Qualigens, India. Carboxy methyl cellulose (M.W. ~100,000) and PEG-4000 (M.W. 4000) were obtained from Suvidinath Laboratories, Baroda, India. Doubly distilled water was used to prepare sample solutions.

Cloud points of surfactant solutions were determined visually by noting the temperature at which the turbidity was observed. The temperature at which the turbidity disappeared on cooling was also noted. Cloud points presented in this article are averages of the appearance and disappearance temperatures of the clouds. These temperatures did not differ by more than 0.4 °C.

3. Results and discussion

In Fig. 1 the variation of CP as a function of $C_{12}E_{10}$ concentration are shown. For $C_{12}E_{10}$ (1% w/v) solution the CP is 88 °C [2,34]. The cloud point increases as concentration decreases from dilute to very dilute solution (less than 1%, inset in Fig. 1). However CP decreases as the concentration becomes greater than 1% up to about 10% (w/v). Above 10% (w/v), the CP increases with increasing concentration (Fig. 1). A number of studies of CP of aqueous nonionic surfactants are reported but most of them are limited to reasonably dilute solutions [1]. The decrease in CP with increase in $C_{12}E_{10}$ concentration is due to increase in micelle concentration. The phase separation results from micelle–micelle interaction. However,

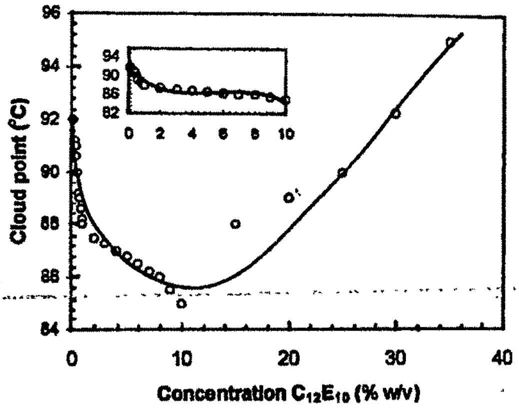

Fig. 1. Cloud point of $C_{12}E_{10}$ as a function of wt.% of $C_{12}E_{10}$ in solution.

at higher concentration (> 10%) the CP increases. This is because, at high surfactant concentration, a structured water surfactant system is present [10,35]. With increase in temperature, this structure breaks, though the molecules are not free of the surfactant effect. That is, some water molecules are not attached to a micelle in particular, but to micelle system in general, forming buffers between micelles. It has been suggested earlier that in polyglycol ether surfactant systems, the water molecules are available for total tenside molecules [36]. Thus higher temperature is required to remove these 'floating' water molecules which are barriers for micellar interaction. Thus CP is a higher temperature and at this temperature the bridge water molecules are released [10].

In Fig. 2, the effects of NaF, NaCl, NaBr and NaI on the cloud point of $C_{12}E_9$ and $C_{12}E_{10}$ (1% w/v) are reported. NaF, NaCl and NaBr decrease the cloud point of both surfactants, whereas NaI increases the cloud point. In the lyotropic series, it is expected that the effect of $F^- > Cl^- > Br^- > I^-$ on the decrease in CP, because the ionic sizes increase along the group consequently decreasing the formal charge density on anion, thus lowering the attraction on anion and thereby lowering the attraction of water. However, NaI is considered as water structure breaker, resulting in an increase in CP. Similar results for $C_{12}E_6$ were observed earlier also [37]. However, there is not much difference in the CPs of $C_{12}E_9$ and $C_{12}E_{10}$ both in the presence and absence of electrolytes. This is probably because of the polydispersity in these surfactants. The error in CPs being less than 2%.

Fig. 3 represents the change in cloud point, ΔCP (°C) of $C_{12}E_6$, and $C_{12}E_{10}$ (1% /v) in presence of KCl, KBr and KI. These electrolytes also had similar impact on the CP as did NaF, NaCl, NaBr and NaI had on $C_{12}E_6$, $C_{12}E_9$, and $C_{12}E_{10}$. NaX has more pronounced effect than KX, baring an exception of KBr, which decreased the CP to a large extent compared to NaBr.

Figs. 4 and 5 represent the effect of tetra butyl ammonium iodide (TBAI) and tetra methyl ammonium bromide (TMAB) on the cloud points of $C_{12}E_n$ ($n = 6, 9, 10$), respectively. It is clear from Fig. 4 that CP of $C_{12}E_n$ increases with increase in concentration of TBAI. The cloud point increase in this case is attributed to the mixed micelle formation of TBAI with nonionic surfactant predominating over water structure formation. Thus the mixed micelles with their cationic components have greater intermicellar repulsions and stronger interaction with water and consequently higher cloud point than the corresponding POE nonionic micelle [16]. TMAB however, decreases the CP of all three surfactants. TMAB is water structure former, thereby decreases the availability of non-

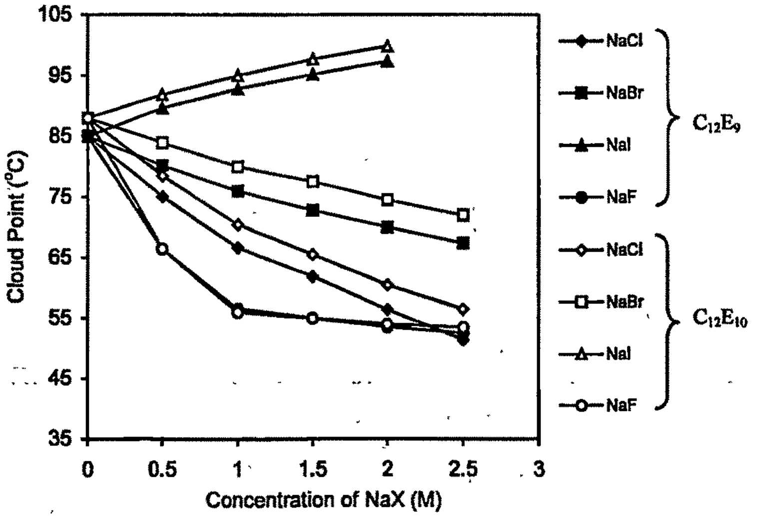

Fig. 2. Cloud point of $C_{12}E_9$ and $C_{12}E_{10}$ (1% w/v) in presence of NaX.

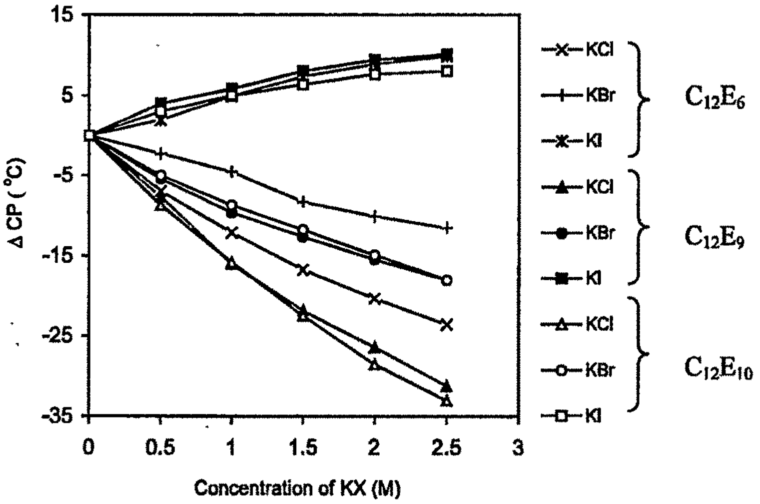

Fig. 3. Change in cloud point (ΔCP, °C) of $C_{12}E_n$ in presence of KX.

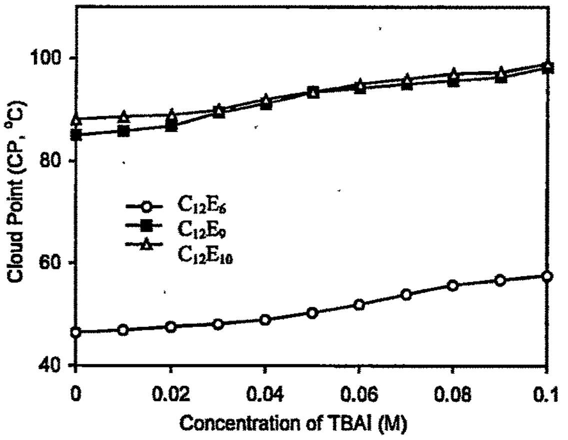

Fig. 4. Cloud point of $C_{12}E_n$ (1% w/v) in presence of tetra butyl ammonium iodide.

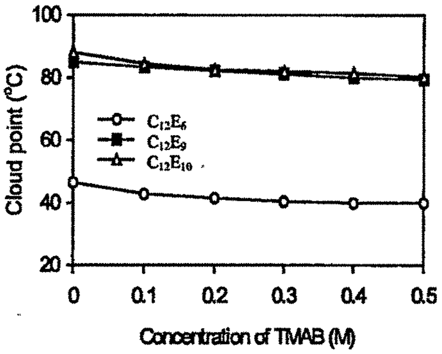

Fig. 5. Cloud point of $C_{12}E_n$ (1% w/v) in presence of tetra methyl ammonium bromide.

associated water molecules to hydrate the ether oxygens of the POE chain [2] and thus lowering the cloud point.

In Fig. 6, the cloud point of $C_{12}E_n$ (1% w/v) solution in presence of glucose, sucrose and $Ca(NO_3)_2$ is illustrated. It is clear that, glucose and sucrose both decrease the cloud point, whereas $Ca(NO_3)_2$ has negligible effect on the CP of $C_{12}E_n$. This indicates that glucose and sucrose remove nearby water molecules surrounding the micelle and helping the micelles to approach each other easily. It was suggested by Kjellander and Florin [38] that, appearance of cloud point is entropy dominated. The ethylene oxide group of POE nonionic surfactant is highly hydrated. When the additives (glucose and sucrose) are added, the water of hydration of the micelles decreases, as these additives compete for water molecules associated with the micelle. Thus with two relatively less hydrated micelles approaching each other, the hydration spheres overlap and some of the water molecules are freed to increase the entropy of the system. At the cloud point, the water molecules get totally detached from the micelles. However, some researchers [3] have suggested that the hydropho-

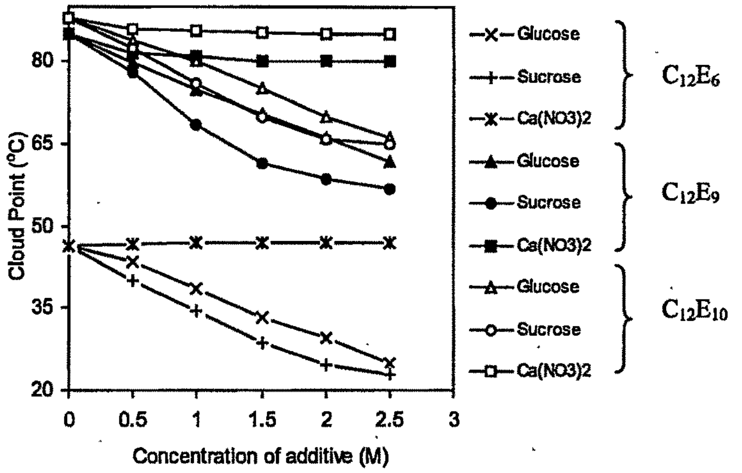

Fig. 6. Cloud point of $C_{12}E_n$ (1% w/v) in presence of different additives.

bic and hydrophilic parts of the micelle interact with water differently where temperature dependent interaction parameters come in to play. At CP the hydrophobicity has relative dominance over hydrophilicity and complete removal of water may not be necessary. With our study it is difficult to make a choice between the two ideas. In any case the overall entropy is high and hence the free energy change is relatively more negative and the appearance of cloud point is facile [39].

In Table 1, the cloud points of $C_{12}E_6$, $C_{12}E_9$ and $C_{12}E_{10}$ (1% w/v) as function of concentration of KSCN are presented. It is evident that, thiocyanate anion being a very soft lewis base and water structure breaker increases the cloud point by making more water molecules available to interact with POE chain.

Table 1
Cloud point for $C_{12}E_9$/TX-100 and $C_{12}E_{10}$/TX-100 (2% w/v) as a function of mole fraction of TX-100

$N_{TX\text{-}100}$	Cloud point (°C)	
	$C_{12}E_9$/TX-100	$C_{12}E_{10}$/TX-100
0.0	84.2	88
0.1	82.4	84
0.3	80	80.4
0.5	77.2	77
0.7	73.6	72.5
0.9	72.8	70
1.0	65.4	65.4

We have also determined the CP of $C_{12}E_9$ and $C_{12}E_{10}$ mixed with TX-100 i.e. nonionic–nonionic surfactant system. Also the CP of $C_{12}E_{10}$/TX-100 (1:1, 1% w/v) mixture in presence of NaX and KX (Fig. 7) were determined.

The cloud points of $C_{12}E_9$/TX-100 (2% w/v) as well as $C_{12}E_{10}$/TX-100 (2% w/v) mixed in various mole ratios are presented in Table 2. It is clear that, the CP of mixed surfactant system at all mole fractions in both the systems are intermediate

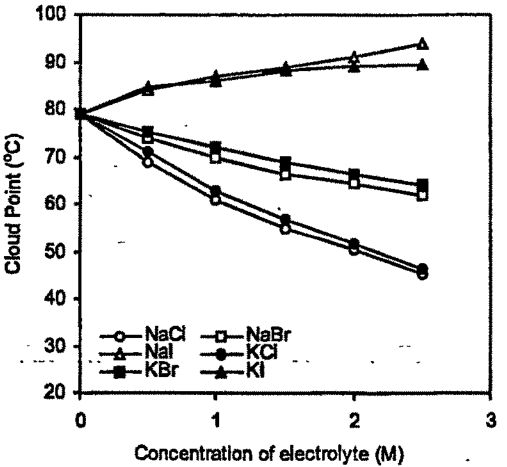

Fig. 7. Cloud point of $C_{12}E_{10}$/TX-100 (1:1, 1% w/v) in presence of electrolytes.

Table 2
Cloud point of $C_{12}E_n$ in presence of KSCN

Concentration of KSCN (M)	Cloud point (°C)		
	$C_{12}E_6$	$C_{12}E_9$	$C_{12}E_{10}$
0.0	46.5	85	88
0.1	48	87.2	89
0.2	50.6	89	91
0.3	52.8	90.2	92.5
0.4	54.2	91.6	93.3
0.5	55.4	92.8	94

between either of the pure surfactant. From Fig. 7, it is evident that the cloud point of $C_{12}E_{10}$/TX-100 mixed surfactant system in presence of NaX and KX (where $X = Cl^-$, Br^-) decreases CP whereas in presence of NaI and KI the CP increases. This is expected, because the mixed nonionic–nonionic micelle formed by adding TX-100 to $C_{12}E_{10}$ is chargeless similar to that of a pure nonionic surfactant. Thus the addition of NaX and KX will have similar effect on the CP of mixed nonionic–nonionic surfactant system, as it had on pure nonionic surfactants. Reasons for such behaviour have been described earlier in this article.

We also investigated the effect of carboxy methyl cellulose and PEG-4000 on the CP of $C_{12}E_n$ (1% w/v) solution (Table 3, Fig. 8a and b). It was suggested earlier that the solutes, which get solubilized in the POE mantle of the micelle decrease the cloud point [40]. Hence we believe that, both carboxy methyl cellulose and PEG-4000 do enter the core of the micelle, consequently decreasing the cloud point. Similar result for TX-114 on addition of PEG-200, -300 and -400 has been reported earlier [10]. However, as carboxy methyl cellulose and PEG-4000 are expected to be reasonably hydrated it is difficult to visualize these molecules in core of the micelle which is oil type but may be present at the palisade layer. Moreover, they will affect the water structure as well as the number of water molecules available for POE groups of the surfactants to be hydrated and hence the CP decreases (cf. discussion of the effect of glucose, sucrose etc., Fig. 6).

Clouding phenomenon is dependent on the structure of poly oxyethylenated nonionic surfactant. The results reported in this article also support the above-mentioned hypothesis. We have studied the effect of various foreign substances on the CP of $C_{12}E_6$, $C_{12}E_9$ and $C_{12}E_{10}$. That is, the hydrophobic group is same, only the ethylene oxide content is changing ($n = 6, 9, 10$). Higher the percentage of oxyethylene (hydrophilic) group, higher will be the cloud point, though the relation between oxyethylene percentage and cloud point is not linear. Hence the decreasing order of cloud point of CP is $C_{12}E_{10} > C_{12}E_9 > C_{12}E_6$ [2].

4. Conclusion

The effects of various electrolytes and nonelectrolytes on the cloud points of $C_{12}E_6$, $C_{12}E_9$ and $C_{12}E_{10}$ were studied. The CP of $C_{12}E_{10}$ showed a minimum in variation with concentration. Sucrose, glucose, KCl, KBr, NaCl, NaI, $(CH_3)_4NBr$ and $(C_4H_9)_4NI$ do change the cloud point to a large extent. Water structure breaking property of

Table 3
Cloud point (°C) of $C_{12}E_n$ in presence of CMC and PEG-4000

CMC (% w/v)	Cloud point (°C)			PEG-4000 (% w/v)	Cloud point (°C)		
	$C_{12}E_6$	$C_{12}E_9$	$C_{12}E_{10}$		$C_{12}E_6$	$C_{12}E_9$	$C_{12}E_{10}$
0.0	46.5	85	88	0.0	46.5	85	88
0.1	41.4	83.8	85	0.01	37.4	82.4	87
0.2	41.4	83.4	84.5	0.02	34.2	81	86.4
0.3	41.4	83	84	0.03	29.6	80.4	86
0.4	41.2	82.6	83	0.04	24	79.8	85.7
0.5	41	81.4	82.5	0.05	18.8	78.8	85.4

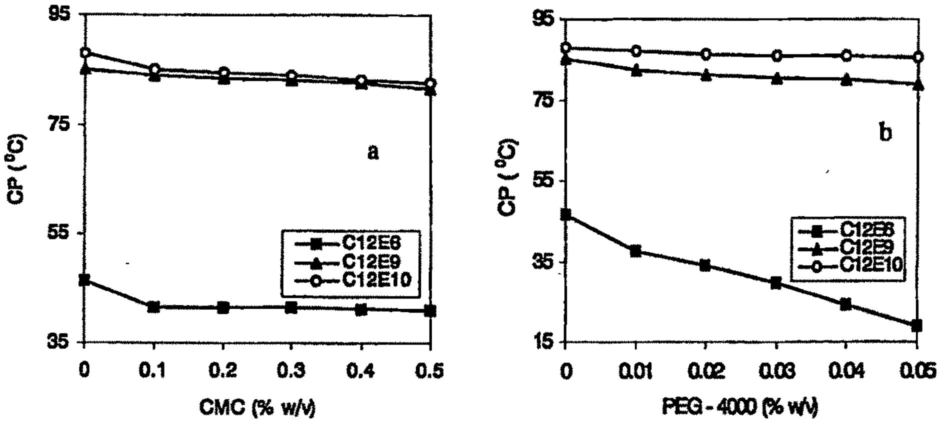

Fig. 8. (a) Cloud point of $C_{12}E_n$ in presence of CMC; (b) cloud point of $C_{12}E_n$ in presence of PEG-4000.

NaI and KI makes its effect different from that of NaCl, NaBr as well as KCl and KBr. $(C_4H_9)_4NI$ has different effect on CP than $(CH_3)_4NBr$, because of mixed micelle formation of $(C_4H_9)_4NI$ with nonionic surfactant predominating over water structure formation. Mixed nonionic–nonionic surfactant system shows clouding phenomenon at temperatures, which are intermediate to that of corresponding pure surfactants.

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Thermodynamics of micellization and interfacial adsorption of polyoxyethylene (10) lauryl ether ($C_{12}E_{10}$) in water

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The interfacial and micellization properties of nonionic surfactant, polyoxyethylene (10) lauryl ether [$C_{12}E_{10}$, $CH_3(CH_2)_{11}(OCH_2CH_2)_{10}OH$] at different *p*Hs and temperatures have been investigated from surface tension measurements. The surface excess (Γ) and the corresponding interfacial quantities have been evaluated The Gibbs free energy, enthalpy and entropy of micellization (ΔG°_{m}, ΔH°_{m}, ΔS°_{m}), and of adsorption at the air/water interface (ΔG°_{ad}, ΔH°_{ad}, ΔS°_{ad}) have also been computed Both micellization and adsorption processes have been found to be endothermic at all *p*H An enthalpy-entropy compensation effect has been observed with an isostructural temperature of 300 K for both the micellization and interfacial adsorption processes The cloud point of $C_{12}E_{10}$ is not much affected by *p*H

The interfacial and thermodynamic properties of surfactant in solution, both in presence and absence of additives, provide a wealth of information about solute-solute and solvent-solute interactions. Additives have significant effect on surfactant self-organization[1]. They can influence solvent structure and polarity and can also undergo direct interaction with the surfactants. Recently, there has been a rapid growth in commercial application of nonionic surfactants and the progress in basic research[2] Hence, in continuation of our interest in the properties of nonionic surfactants[3-5], we extended our work to study the interfacial and micellization properties of poly oxyethylene (10) lauryl ether at different *p*Hs to understand how acidity/alkalinity affect the behaviour of the surfactant in aqueous solution. The effects of change of *p*H on stability, aggregation number and titration properties of dodecyldimethylamine oxide (DDAO) surfactant has been studied extensively[6]. The effect of *p*H on other surfactants like cationic[7] hexadecyltrimethyl ammonium bromide (HTAB) and amphoteric-anionic[8] N,N-dimethyl N-lauroyl lysine (DMLL)-sodiumdodecyl sulphate (SDS) has also been studied. Herrann[9] showed that dimethyl dodecyl amine oxide (DDAO) behaves as nonionic at *p*H ≥ 7, as cationic ($DDHA^+$) at *p*H ≤ 3 and as a nonionic-cationic mixture between *p*H 3 and 7. However to our knowledge, no study dealing with the effect of *p*H on nonionic POE type surfactant has been done so far We report herein the effect of *p*H on surface excess (Γ), minimum area per molecule (A_{min}), surface pressure (π_{cmc}) and thermodynamics of micellization and adsorption of $C_{12}E_{10}$ at the air/water interface at different temperatures. The study of the effect of *p*H on micellization is important because of increasing use of nonionic surfactants in drug delivery systems and also in emulsion formulation *e.g.* shampoo.

Materials and Methods

Nonionic surfactant, polyoxyethylene (10) lauryl ether, $C_{12}E_{10}$, [$CH_3(CH_2)_{11}(OCH_2CH_2)_{10}OH$], molar mass = 626.85 (Sigma, USA) was used without any further purification. The surface tension vs concentration plot did not show any minimum. All solutions were prepared using doubly distilled water having electric conductance 2-3 μScm^{-1}. A digital *p*H meter of Weltronix CM-100 was used, following calibration using buffer solutions of *p*H 4.0, 7.0 and 9.2 obtained from Qualigens Fine Chemicals, Glaxo, India In the working solution, HCl was used to adjust the acidic *p*H, while the alkaline *p*H was adjusted by using NaOH solution. The HCl and NaOH used were of analytical grade (Suvidhinath Lab., Baroda, India).

Critical micelle concentration

The critical micelle concentration (cmc) was determined by the surface tension (γ) measurement using a du-Nouy ring tensiometer (S. C. Dey and Co Calcutta, India); measurements were taken at temperatures 308, 313, 318 and 323 K. The temperatures were maintained within ± 0.1 K by circulating thermostated water through a jacketed vessel containing the solution. Surface tension (γ) decreased with increasing surfactant concentration and reaching a plateau. The concentration of solution was varied by adding aliquots of a stock solution of known concentration with a Hamilton microsyringe to the known volume of solution taken in the jacketed vessel. 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%. The measured surface tension values were plotted as a function of the logarithm of surfactant concentration and the critical micelle concentration (cmc) was estimated from the break point in the resulting curve[10]. The reproducibility of the surface tension concentration curve was checked with duplicate runs. The reproducibility in the cmc was found to be within ±1.0%.

The required *p*H was maintained by adding aqueous HCl and NaOH for acidic and alkaline solution respectively. The *p*H of solution was determined before and after the completion of each run. It was found that there was a very small decrease in *p*H in all solutions except water (*p*H 6.8) in the presence of the surfactant. The change was of the order of 0.2 *p*H units within the experimental time span (~ 90min) and was thus neglected. However, it is not very clear why this small change in *p*H occurred.

Cloud point (CP) measurement

The cloud points of polyoxyethylene (10) lauryl ether in all *p*H were determined. The total surfactant concentration was 1% (w/v). The experimental procedure was same as reported earlier[11]. The cloud points are presented in Table 1. These are the averages of the appearance and disappearance temperatures for the clouding, the maximum difference was not greater than 0.4°C. It can be hence seen that the CP is not much affected by the change of *p*H in the acidic range. The error in CP is 0.5%.

Table 1 —Critical micelle concentration (cmc) of polyoxyethylene (10)lauryl ether ($C_{12}E_{10}$) in aqueous solution as a function of *p*H, different temperatures and its cloud point at different *p*Hs

*p*H of the solution	Critical micelle concentration (cmc)/μm at				Cloud point/°C
	308	313	318	323K	
2	6.0	5.9	5.4	4.3	86.9†
3	9.5	7.4	7.0	4.5	87.1†
4	10.0	8.1	7.9	5.0	87.3†
5	11.0	9.3	8.9	7.0	87.4†
6.8*	11.8	10.0	8.9	7.1	87.5†
9	13.1	11.2	11.0	10.9	88.4
11	14.1	13.1	11.2	11.1	89.0

* Ref 3

† These values are almost same. An average of 87.2 °C ± 0.1 can be taken as cp for these systems

Results and Discussion

Surface tension is a dependable and elegant method for the determination of cmc[12]. The cmc values of $C_{12}E_{10}$ at various *p*Hs and at different temperatures are presented in Table 1. It can be seen from the table that the critical micelle concentration values of polyoxyethylene (10) lauryl ether decrease with an increase in temperature at all *p*H, which is generally seen in case of nonionic surfactant. It is observed that at constant temperature, cmc increases with the *p*H of the solution, low *p*H favours the micellization of the surfactant.

The formation of micelle is controlled by hydrophobic interaction[13], and the London dispersion force[14]. In the case of nonionic surfactants without any additive, the cmc decreases with increasing temperature due to the dehydration of the hydrophilic moiety of the surfactant molecules and also due to breaking of water structure[15]. The ether linkages in $C_{12}E_{10}$ chain can be protonated at low *p*H, making it positively charged to behave as a pseudo ionic surfactant. At alkaline or around neutral *p*H, this surfactant is expected to remain nonionic.

From Table 1, it is seen that with decreasing [H^+], the cmc increases. Also lowering of temperature increases the cmc. Both H^+ and OH^- can form hydrogen bonds with water molecules and thereby promote water structure, which is also promoted by the hydrophobic group of the surfactant molecule. On increasing the temperature, the oxyethylene groups get dehydrated with decrease in hydrophilicity or increase in hydrophobicity causing lowering of cmc The resultant cmc is governed by the effects of various factors, synergetic and/or antagonistic.

The Gibbs free energy of micellization (ΔG°_{m}) for a nonionic surfactant is related to the cmc (expressed in mole fraction scale) by the following relation[16].

$$\Delta G^{\circ}_{m}=RT \ln \text{cmc} \qquad \ldots (1)$$

The initial standard state being the hypothetical ideal solution of unit mole fraction though behaving as if at infinite dilution and the final state being the micelle itself. In Table 2, the Gibbs free energy, enthalpy and entropy of micellization ΔG^{o}_{m}, ΔH^{o}_{m} and ΔS^{o}_{m} respectively at the standard state of unit mole fraction are reported. The free energy of micellization is relatively more negative with increasing temperature indicating relative spontaneity of the micellization process as temperature increases.

The ΔS^{o}_{m} was computed from the slope of the reasonably linear ΔG^{o}_{m} vs. T plots. The ΔH^{o}_{m} was then calculated from the equation[16],

$$\Delta H^{o}_{m} = \Delta G^{o}_{m} + T\Delta S^{o}_{m} \qquad \ldots (2)$$

The entropy of micellization (ΔS^{o}_{m}) values are all positive and large indicating that the micellization process is entropy controlled. The micellization process is endothermic in nature. High entropy changes are generally associated with a phase-change. The pseudophase micellar model is thus preferred over the mass action model. Rosen[17] has stated that the presence of hydrated oxyethylene groups of the surfactant introduces structure in the liquid phase and that the removal of the surfactant via micellization results in an increase in the overall randomness[18] and hence an increase in entropy The hydrated surfactant molecules release the water molecules during micellization on the consequence of which the entropy of the process increases

A good linear correlation between ΔH^{o}_{m} and ΔS^{o}_{m} values has been observed. On a general basis, such a compensation has been suggested by Lumry and Rajender[19]. The slope of the line i.e. the compensation temperature has been found to be 300 K, close to the expected values between 270 and 294K in aqueous medium[19]. Thus, the micellization is a function of the bulk structure of the solvent. The small variations, observed here as well as those observed earlier[20] may be due to the difference in the bulk structural property of the solution from that of water. However, deviations from Lumry *et al.* observation are well known. As mentioned by Krug *et al.*[21] error in the data may also lead to such compensation.

Table 2—Thermodynamic parameters of micellization of $C_{12}E_{10}$ at different *p*Hs and temperatures

*p*H of solution	$-\Delta G^{o}_{m}$ / kJmol^{-1} at				ΔH^{o}_{m} / kJmol^{-1}	ΔS^{o}_{m} / Jmol^{-1}K^{-1}
	308	313	318	323K		
2	41.0	41.8	42.7	44.0	20.1	198
3	39.9	41.2	42.0	43.8	37.2	250
4	39.8	41.0	41.7	43.6	34.8	242
5	39.5	40.6	41.4	42.7	24.6	208
6.8	39.3	40.4	41.4	42.6	27.8	218
9	39.0	40.1	40.8	41.5	11.4	164
11	38.9	39.7	40.7	41.4	13.5	170

The air/water interface of a surfactant solution is well populated[22] by the adsorbed amphiphile molecules. The Gibbs surface excess (Γ) for dilute solution of a nonionic surfactant is given by the adsorption equation[23]

$$\Gamma = (-1/RT)\,(d\gamma/d\ln C) \qquad \ldots (3)$$

where Γ, γ, R, T and C are the surface excess, surface tension, gas constant, absolute temperature and concentration, respectively. The slope of the tangent at the given concentration of the γ vs. log C plot has been used to calculate Γ by using curve fitting to a polynomial equation of the form, $y=ax^2+bx+c$ in microsoft excel program. The R^2 (regression coefficient) value of the fit lies between 0.9583 and 0.9957. The surface excess is an effective measure of the molecular adsorption at the air/liquid interface. The Γ values are presented in Table 3.

The surface excess increases with increase in temperature (at *p*H 6.8) due to the dehydration of the surfactant molecule. This has not been observed at lower and higher *p*H. In some cases (*p*H 2, 5 and 9) a minimum has been observed. At *p*H 4 and 11 there has been only a slight decrease with temperature. The effect of temperature on Γ at different *p*H is a complex phenomenon. This is guided by the interaction of H^+ and OH^- ions with water as well as with the surfactant. The nature of interaction is not straightforward.

Table 3— Surface excess and area per molecule of $C_{12}E_{10}$ at different *p*Hs and temperatures

*p*H of solution	$\Gamma \times 10^{10}$ / mol cm^{-2} at				$A_{min} \times 10^{2}$ / nm^{2} at			
	308	313	318	323K	308	313	318	323K
2	2.8	2.0	1.8	3.7	59.3	83.0	92.2	44.9
3	2.5	4.1	2.2	2.3	66.4	40.5	75.5	72.2
4	2.6	2.9	3.1	3.6	64.6	56.6	54.4	45.4
5	4.0	1.0	1.7	4.8	41.5	166.0	97.6	34.6
6.8	2.3	2.4	3.3	3.6	72.2	69.2	50.3	46.1
9	4.2	2.9	3.3	4.4	40.0	[illegible]7.2	50.3	37.7
11	2.8	2.8	2.3	2.8	58.3	58.9	72.2	59.3

From the surface excess quantity, it is possible to calculate the minimum area per molecule (A_{min}), by the relation,

$$A_{min}\,(\mathrm{nm}^2) = 10^{14}/N\,\Gamma_{max} \qquad \ldots (4)$$

where N is the Avogadro number. The magnitudes of A_{min} are of the order of 1.0×10^2 nm^2 or less, suggesting that the surface is a close packed one which means that the orientation of the surfactant molecules is almost perpendicular to the surface[24]. The A_{min} values of $C_{12}E_{10}$ at cmc are also presented in Table 3.The effectiveness of a surface active molecule is measured by the surface pressure (π_{cmc}). at the cmc i.e. ($\pi_{cmc} = \gamma_o - \gamma_{cmc}$ where γ_o. and γ_{cmc} are the surface tension of solvent and the surface tension of surfactant solution at cmc respectively. The value of free energy of adsorption at air/water interface (ΔG^o_{ad}) has been calculated using the relation[25].

$$\Delta G^o_{ad} = R\,T \ln \mathrm{cmc} - N\,\pi_{cmc}\,A_{min} \qquad (5)$$

The standard state for adsorbed surfactant here is a hypothetical monolayer at its minimum surface area/molecule but at zero surface pressure. As expected, the free energy of micellization, ΔG^o_m was less negative than the free energy of adsorption, ΔG^o_{ad} values at air/water interface at all temperatures, indicating that when a micelle is formed, work has to be done to transfer the surfactant molecules in the monomeric form at the surface to the micellar stage through the aqueous medium. In Table 4, the thermodynamic parameters of adsorption i.e. ΔG^o_{ad}, ΔH^o_{ad} and ΔS^o_{ad} of $C_{12}E_{10}$ at the air/solution interface at various pH are presented. The standard entropy (ΔS^o_{ad}) and enthalpy (ΔH^o_{ad}) of adsorption have been obtained from the slope of the reasonably linear ΔG^o_{ad} Vs T plot. The ΔH^o_{ad} has been obtained from the thermodynamic relation (Eq.2). It can be seen from Tables 2 and 4 that the derived enthalpy and entropy quantities have irregular relationship with pH. The error associated with these quantities is ±7%. It is difficult to say from the available data as to whether irregularity is due to this error or genuine. Hence, no reasoning is preferred. Direct measurement would give better answer. However, as mentioned in an earlier paragraph adsorption at air/water interface in these systems seems to be very much a complex phenomenon.

Table 4—Thermodynamic parameter of adsorption of polyoxyethylene (10) lauryl ether at different pHs and temperatures

pH of solution	$-\Delta G^o_{ad}$ / kJmol^{-1} at				ΔH^o_{ad}/ kJmol^{-1}	ΔS^o_{ad} / Jmol^{-1} K^{-1}
	308	313	318	323K		
2	46.2	44.5	50.4	46.6	2.1	142
3	48.1	44.6	46.7	49.5	11.2	186
4	44.5	45.2	46.9	46.9	10.3	178
5	42.3	46.9	47.1	46.0	25.7	226
6.8	42.7	43.7	43.8	44.8	-3.4	128
9	43.9	45.1	45.5	46.3	2.8	152
11	44.8	45.7	46.8	47.4	10.0	178

Like the micellization process, the adsorption at the air/water interface has been found to be also endothermic. The endothermic character of micellization and adsorption are specific to the surfactant, the additive and the temperature[4, 5, 26, 27]. The compensation temperature has been found to be 284K, somewhat different from 300K obtained for micellization phenomenon, but within the expected range for aqueous systems (270-294K) [19].

The cloud points are the manifestation of the solvation/desolvation phenomena of the nonionic surfactant in solution. The desolvation of the hydrophilic groups of the surfactant leads to phase separation i.e. clouding in the surfactant solution. It is seen that the pH has mild effect on the cloud point of $C_{12}E_{10}$, it increases only by 2°C for a change of pH from 2 to 11 (Table 1), and at the acidic region there is no effect at all.

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Small-angle neutron scattering studies of nonionic surfactant: Effect of sugars

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Abstract. Micellar solution of nonionic surfactant *n*-dodecyloligo ethyleneoxide surfactant, decaoxyethylene monododecyl ether [$CH_3(CH_2)_{11}(OCH_2CH_2)_{10}OH$], $C_{12}E_{10}$ in D_2O solution have been analysed by small-angle neutron scattering (SANS) at different temperatures (30, 45 and 60°C) both in the presence and absence of sugars. The structural parameters like micelle shape and size, aggregation number and micellar density have been determined. It is found that the micellar structure significantly depends on the temperature and concentration of sugars. The micelles are found to be prolate ellipsoids at 30°C and the axial ratio of the micelle increases with the increase in temperature. The presence of lower concentration of sugar reduces the size of micelles and it grows at higher concentration of sugar. The structure of micelles is almost independent of the different types of sugars used.

Keywords. Small-angle neutron scattering; nonionic surfactant; micellar aggregation number.

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1. Introduction

Surfactant molecules self assemble into aggregates in aqueous solution to form micelle above a concentration called critical micelle concentration (CMC) where their properties are different from those of the non-aggregated monomer molecules. The micelles are formed in various shapes such as globular, ellipsoidal, cylindrical and disc-like [1]. The structure of micelles depends on the chemical structure of surfactant molecule [2] and the solution conditions such as concentration, temperature and ionic strength. The study of these systems is a matter of common scientific and technological interest from both theoretical as well as experimental points of views.

The aggregational and surface properties of surfactant in solution are very sensitive and are influenced or controlled by solvent polarity and type, temperature, pressure, pH and presence of various additives (cosolvent) [3–7]. The nature of cosolvent decides the direction of the changes in the CMC of the surfactants. They may be distributed between aqueous and micellar phase and may accumulate both in palisade layer and inside the micelle hydrophobic core, thus favoring the stability of the system. In this paper we have undertaken small-angle neutron scattering (SANS) studies of *n*-dodecyloligo ethyleneoxide type surfactant, $C_{12}E_{10}$-aqueous-sugars ternary system, to know the interaction of nonionic additives with nonionic surfactants. It is well-known that SANS is an ideal technique to study the micellar structure of surfactants [8,9] and this has also been demonstrated for surfactant micelles in the presence of various additives [10].

2. Experimental procedures

Materials. The $C_{12}E_{10}$ was purchased from Sigma and used as supplied. D-Ribose ($C_5H_{10}O_5$), D-glucose ($C_6H_{12}O_6$) and sucrose ($C_{12}H_{22}O_{11}$) (Merck, AR) were dried in vacuum before use. Solvent D_2O (99.4 atom D %, supplied by Heavy Water Division, BARC, Mumbai) was used for SANS experiments. The use of D_2O instead of water for preparing solution provides a very good contrast between the micelles and solvent in SANS experiments.

2.1 *SANS measurement*

Small-angle neutron scattering experiments were performed on the SANS instrument at the Dhruva reactor, Mumbai [11]. The mean wavelength of the incident neutron beam is $\lambda = 5.2$ Å with a wavelength resolution of approximately 15%. The scattered neutrons are detected in an angular range of 0.5–15° using a linear position sensitive detector (PSD). The accessible wave vector transfer $Q(= (4\pi/\lambda)\sin\theta/2$, where θ is the scattering angle) range of instrument is 0.018–0.30 $Å^{-1}$. In all the measurements the concentration of $C_{12}E_{10}$ was constant (50 mM) and the concentration of sugars was varied in the range 0.05 to 0.3 M. The effect of temperature was studied in the range of 30 to 60°C. The measured data have been corrected and normalized to a cross-section unit, using standard procedure.

2.2 *SANS data analysis*

In SANS experiment one measures the coherent differential scattering cross-section per unit volume ($\mathrm{d}\Sigma/\mathrm{d}\Omega$) as a function of wave vector transfer Q. For a system of monodisperse particles, it is given by [8,11]

$$\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}(Q) = n\,(\rho_{\mathrm{p}} - \rho_{\mathrm{s}})^2\,V^2 P(Q)S(Q), \tag{1}$$

where n is the number density of the particles, ρ_{p} and ρ_{s} are, respectively, the scattering length densities of the particle and the solvent, and V is the volume of the particle. $P(Q)$ is the intraparticle structure factor and is decided by the shape and size of the particle. $S(Q)$ is the interparticle structure factor, which depends on

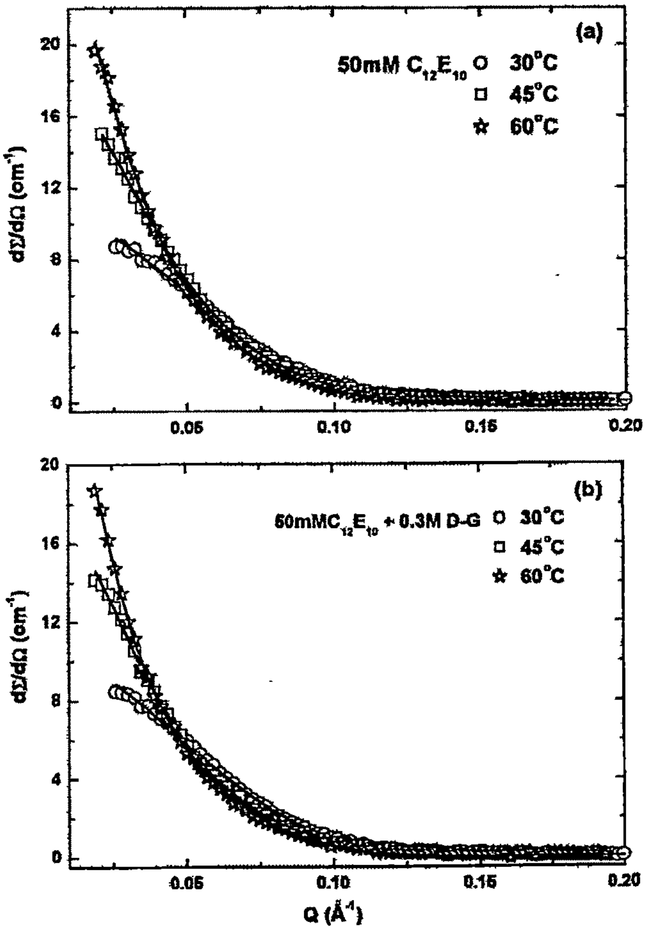

Figure 1. SANS distributions for 50 mM $C_{12}E_{10}$: (a) absence and (b) presence of 0.3 M D-glucose at different temperatures. Solid lines are theoretical fits and symbols are experimental values.

the spatial arrangement of particles and is thereby sensitive to interparticle interactions. In case of dilute solutions, interparticle interference effects are negligible, and $S(Q) \sim 1$. We have carried out the measurements at low concentration such that $S(Q) \sim 1$ and $P(Q)$ has been calculated for ellipsoidal micelles. The dimensions of the micelles, aggregation number and number density of micelles have been determined from the analysis. The semimajor axis (a) and semiminor axis ($b = c$) are the parameters in analysing the SANS data. The aggregation number is calculated by the relation $N = 4\pi ab^2/3v$, where v is the volume of the surfactant monomer. Then the number density of the micelles is determined from the surfactant concentration (C) as n_{m} (cm^{-3}) = (C-CMC)N_A10^{-3}/N.

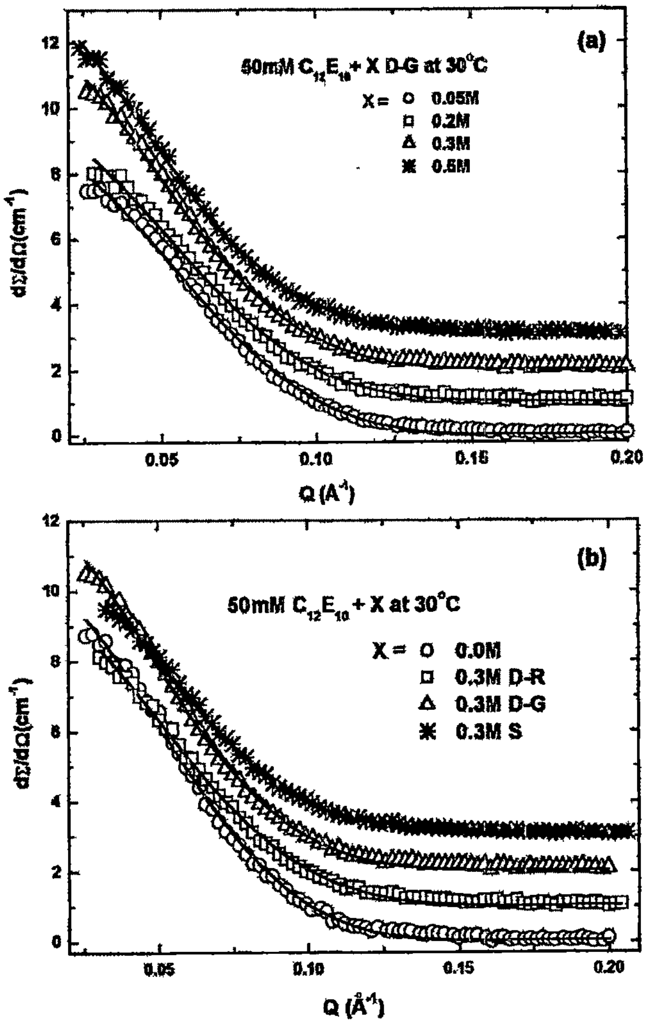

Figure 2. SANS distributions for 50 mM $C_{12}E_{10}$. (a) In the presence of D-glucose at different concentrations and (b) in the presence of D-glucose, D-ribose and sucrose at 30°C. Solid lines are theoretical fits and symbols are experiment values. For clarity, the distributions are shifted vertically by 0, 1, 2 and 3 units in the vertical direction, respectively.

3. Results and discussion

Results of SANS experiments on $C_{12}E_{10}$ are shown in figures 1 and 2. The various structural parameters of $C_{12}E_{10}$ micelles as obtained from the fit using eq. (1) to the data are given in table 1. In figure 1a, it is seen that the scattering intensity increases in the low Q region as temperature increases. The fall of the scattering curve is expected to be more for the large-sized particles. This indicates that the

Table 1. Micellar parameters of 50 mM $C_{12}E_{10}$ at different temperatures and in presence of different sugars at various temperatures.

Micellar system $C_{12}E_{10}$ (50 mM) Temp. (°C)	a (Å)	$b = c$ (Å)	N_{agg}	n_m (cm^{-3} × 10^{16})
30	41.5 ± 2.1	26.8 ± 1.3	327 ± 16	9.2 ± 0.46
45	72.2 ± 3.6	26.6 ± 1.3	551 ± 28	5.5 ± 0.28
60	101.1 ± 5.1	28.9 ± 1.4	895 ± 45	3.4 ± 0.17
+ 0.3 M D-glucose				
30	44.5 ± 2.2	26.2 ± 1.3	336 ± 17	8.9 ± 0.45
45	80.5 ± 4.0	26.9 ± 1.3	629 ± 31	4.8 ± 0.24
60	122.9 ± 6.1	28.6 ± 1.4	1066 ± 53	2.8 ± 0.14
+ D-glucose (M) at 30°C				
0.05	31.1 ± 1.6	26.6 ± 1.3	242 ± 12	12.4 ± 0.62
0.2	37.9 ± 1.9	26.4 ± 1.3	290 ± 15	10.4 ± 0.52
0.3	44.5 ± 2.2	26.2 ± 1.3	336 ± 17	8.9 ± 0.45
0.5	48.7 ± 2.4	25.2 ± 1.3	340 ± 17	8.9 ± 0.45
+ 0.3 M sugar at 30°C				
D-Ribose	41.7 ± 2.1	25.2 ± 1.3	291 ± 15	10.3 ± 0.52
D-Glucose	44.5 ± 2.2	26.2 ± 1.3	336 ± 17	8.9 ± 0.45
Sucrose	43.1 ± 2.2	24.6 ± 1.2	287 ± 14	10.5 ± 0.53

size of the micelles increases with increase in temperature. The analysis of SANS data in table 1 shows that while the semiminor axis of the micelles almost remains the same, the semimajor axis increases 2.5 times as temperature is increased from 30 to 60°C. This also suggests the increase in the aggregation number and decrease in the number density of the micelles with increase in temperature.

Figure 2a shows the effect of addition of D-glucose on the $C_{12}E_{10}$ micelles at 30°C. It is seen from table 1 that with the addition of 0.05 M D-glucose the size of the micelles decreases. For example, the aggregation number decreases from 327 to 242 with the addition of glucose. When the concentration of D-glucose is increased beyond 0.05 M, the micelle size increases with the increase in the concentration of D-glucose. However, we observe that this effect of increasing size of the micelle at higher D-glucose concentrations is much less pronounced to that of increasing the temperature. To understand the above effect of addition of D-glucose, it seems that at low concentrations molecules of D-glucose prefer to remain in the bulk water, and only start to interact with micelles at higher D-glucose concentrations.

The temperature effect on 50 mM $C_{12}E_{10}$ in the presence of 0.3 M D-glucose is shown in figure 1b. It is seen that the features of scattering data in this system are similar to that of increasing temperature in pure $C_{12}E_{10}$ micellar solution. The aggregation number and the semimajor axis of the micelles increase with the increase in temperature. A comparison of $C_{12}E_{10}$ micelles with and without D-glucose suggests that the semimajor axis or aggregation number is larger in the presence of D-glucose than without the D-glucose. It seems that the effect of the above two factors is additive.

The effect of different sugars on $C_{12}E_{10}$ micelles is shown in figure 2b. The sugars that have been used along with D-glucose are D-ribose and sucrose. The data are shown for the fixed $C_{12}E_{10}$ (50 mM) and fixed sugar concentration (0.3 M) at 30°C. The structural parameters in these systems (table 1) suggest that the micellar structure of $C_{12}E_{10}$ is almost independent of the variation in the nature of sugar.

4. Conclusions

The small-angle neutron scattering studies on micellar solution of $C_{12}E_{10}$ in aqueous solution have been performed at different temperatures both in the presence and the absence of sugars. There is a growth of the micelles and the number density of the micelle decreases with increase in temperature. In the presence of sugar, the micelle size decreases initially for the lower sugar concentration and afterwards increases at higher sugar concentrations. It seems the effect of the presence of sugar and increasing temperature is additive. The micelle structure of $C_{12}E_{10}$ is found to be independent of the variation in nature of the sugar.

Acknowledgement

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Physicochemical Studies of Nonionic Surfactants, $C_{12}E_{12}$ and $C_{12}E_{15}$: Effect of pH and NaCl

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Abstract- Aqueous micellar solutions of nonionic n-dodecyloligo ethyleneoxide surfactants, dodeca and pentadeca oxyethylene n-dodecylether, $C_{12}E_{12}$ and $C_{12}E_{15}$ [CH_3 $(CH_2)_{10}$ CH_2 $(OCH_2CH_2)_{12/15}$ OH] have been investigated at different pH (acidic to alkaline) and in the presence of NaCl at different temperatures. The interfacial and micellization properties have been studied from surface tension measurements using du Nouy tensiometer. The cmc shows maximum value at neutral pH. With increase in the concentration of NaCl and also with the increase of temperature (35–50°C), the cmc decreases. Apart from the thermodynamic quantities of micellization as well as adsorption at air/water interface, the heat capacity ($\Delta C_{p.m}$), transfer enthalpy ($\Delta H_{m.tr}$), transfer heat capacities ($\Delta C_{p\,m.tr}$), and Traube (σ) constant have been evaluated and discussed. Both micellization and adsorption processes have been found to be endothermic at all pH and in the presence of NaCl. An enthalpy-entropy compensation effect has been observed with an isostructural temperature from 299-315 K for both the micellization and interfacial adsorption processes. The CPs of $C_{12}E_{12}$ and $C_{12}E_{15}$ were significantly affected by the presence of NaCl but variation in pH does not have much effect. The micelle aggregation number (N_{agg}) has been measured by using steady state fluorescence quenching method at a total surfactant concentration ~ 10 mM at 30°C. The micropolarity and the binding constant (K_{sv}) for $C_{12}E_{12}$ and $C_{12}E_{15}$ in the presence of increasing concentration of NaCl (0.1, 0.25, 0.5, 0.75 and 1.0M) were determined from the ratio of the intensities of the first and the third vibronic peaks (I_1/I_3) of pyrene fluorescence emission spectrum. The micellar interiors were found to be reasonably polar.

Keywords : *Critical micelle concentration, nonionic surfactant, pH, aggregation number.*

INTRODUCTION

The interfacial and micellar properties of nonionic surfactants are governed by a delicate

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balance of hydrophobic and hydrophilic properties of the surfactant molecules. These properties of a surfactant are very sensitive and are influenced or controlled by the type of solvent and its polarity, temperature, pressure and also by presence of various foreign substances (cosolvent) [1-8]. They provide a wealth of information about solute-solute and solvent-solute interactions in aqueous solution, both in absence as well as in presence of additives. Additives have significant influence on surfactant self-organization [I]. They can influence solvent structure and polarity and can also undergo direct interaction with the surfactant.

Nonionic surfactant of the alkyl polyoxyethylene (POE) type are widely used in detergency, cosmetics, fabric softening, emulsion formulations like shampoo, paints, etc. as well as in pharmaceutical dosages and in drug delivery systems, which are pH sensitive phenomena. So we were interested to study the interfacial and micellization properties of POE surfactants at various pH to understand how acidity/alkalinity affect the behaviour of these surfactants in aqueous solution. The hydration of POE chains of these surfactants leads to the aqueous solubility of the molecules; their temperature induced dehydration is chiefly responsible for the inverse relationship between aqueous solubility and temperature, observed in these amphiphilic compounds. Maeda [9] emphasized the formation of hydrogen bonds between the cationic-nonionic and cationic-cationic species, where they studied the effect of change of pH on stability, aggregation number and titration properties of dodecyldimethylamine oxide (DDAO) surfactant. Herrmann [10] showed that DDAO behaved as a nonionic surfactant at pH ≥ 7, a cationic ($DDHA^+$) at pH ≤ 3 and a nonionic -cationic mixture between pH 3 and 7. The deinking of printed film by surfactant also depends on the pH [11]. Nonionic surfactant is effective above the cmc at very basic (~ pH 12) condition [11]. The effect of salinity on the phase behaviour in microemulsion can be counter balanced by adjustment of pH [12,13]. The effect of pH on solutions of other surfactants like cationic cetyltrimethylammonium bromide (CTAB) [14], amphoteric-anionic N,N-dimethyl N-lauryl lysine (DMLL), anionic sodium dodecyl sulphate (SDS) [15] and fatty acid soap [16] were also studied. However to our knowledge, no study dealing with the effect of pH on nonionic POE type surfactant has been done so far. We report herein the effect of pH and salt on cmc, minimum area per molecule (A_{min}) and thermodynamics of micellization and adsorption at the air/water interface, of n-dodecyloligoethylene oxides $C_{12}E_{12}$ and $C_{12}E_{15}$ at different temperatures. We also determine the aggregation number of both the nonionic surfactants in the absence and in the presence of NaCl of different concentrations.

EXPERIMENTAL

Materials : $C_{12}E_{12}$ and $C_{12}E_{15}$, $[CH_3(CH_2)_{11}(OCH_2CH_2)_{12/15}OH]$, MW 714 and 846 respectively were obtained from Lion Corp. Tokyo, Japan and used without any further purification. The surface tension vs concentration plot did not show any minimum. All solutions were prepared by using doubly distilled water having specific conductance 2-3 µS cm^{-1}. HCl, NaOH and NaCl used for experiments were of analytical grade (Qualigens, India). Cetyl pyridinium chloride (Loba Chemie, Baroda, India) was recrystallized twice from benzene. Pyrene (Fluka, Germany) was recrystallized from cyclohexane.

Methods : The critical micelle concentration (cmc) was determined by the surface tension (γ) measurement using a du-Noüy ring tensiometer (S. C. Dey and Co. Kolkata, India) at different temperatures, viz., 35, 40, 45 and 50°C. The temperature was maintained within ± 0.1°C by circulating thermostated water through a jacketed vessel containing the solution. Other conditions were the same as reported in our recent papers. [5,17-19]. Representative plots of surface tension (γ) against Log_{10} C (C in molarity) are shown in Fig. 1 and 2. The reproducibility in the cmc was found to be within ± 1.0%.

A digital pH meter of Weltronix CM-100, India was used, which was calibrated

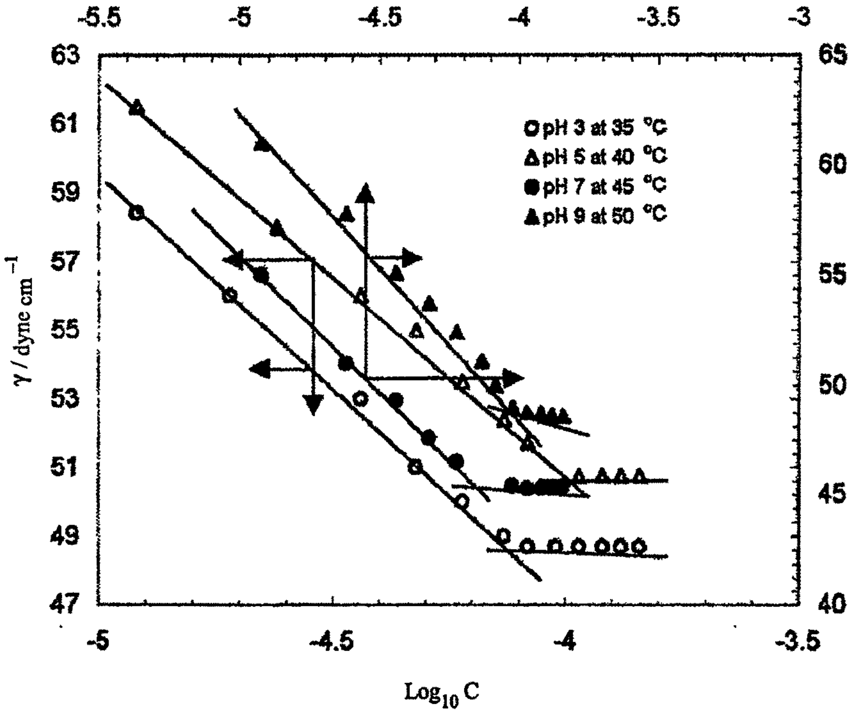

Fig. 1. Representative plots of Surface tension (γ) vs. logarithm of molar concentration (C) of $C_{12}E_{12}$ at different pHs.

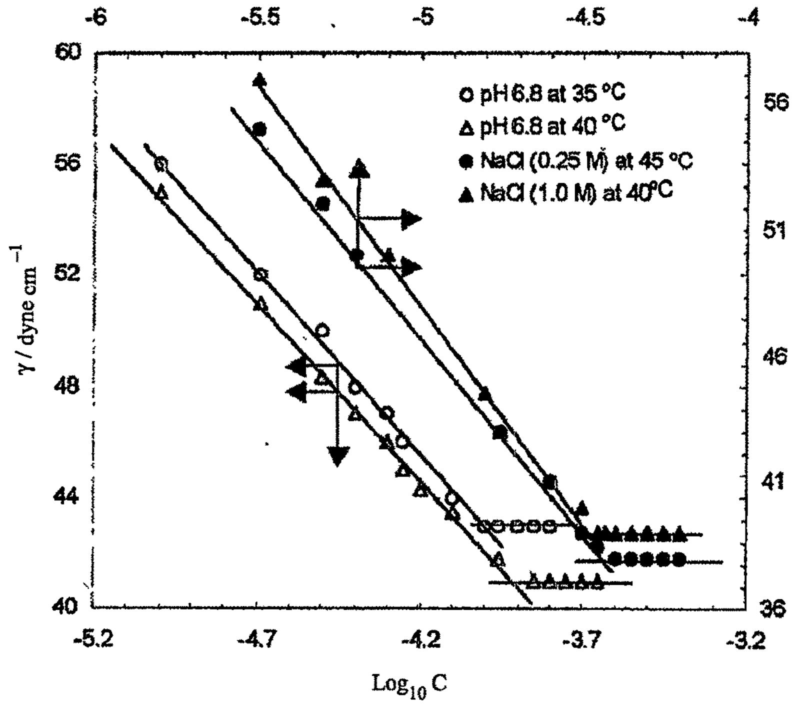

Fig. 2. Representative plots of Surface tension (γ) vs. logarithm of molar concentration (C) of $C_{12}E_{15}$ at different pHs and in the presence of NaCl

by using buffer solutions of pH 4.0, 7.0 and 9.2 obtained from Qualigens Fine Chemicals, India prior to pH measurements [20]. In the working solution, HCl was used to adjust the acidic pH while the alkaline pH was adjusted by using NaOH solution. The pH of solution was noted before and after the completion of each run, a negligible change in pH was observed at the end of each experiment which lasted for more than an hour.

The micellar aggregation number (N_{agg}) of surfactant solutions was determined by steady state fluorescence quenching measurements. Pyrene was used as the probe and cetyl pyridinium chloride as the quencher. The fluorescence emission spectra of pyrene monomers in the surfactant solutions were determined with a Shimadzu RF-5301 PC spectrofluorimeter at the excitation and emission wavelengths, 335 and 385 nm respectively. Excitation and emission band pass were 3 and 1.5 nm respectively. Each spectrum had five vibronic peaks from shorter to longer wavelengths (Fig. 3). All fluorescence measurements were carried out at room temperature, (~ 30 °C).

An aliquot of the stock solution of pyrene in ethanol was transferred into a flask

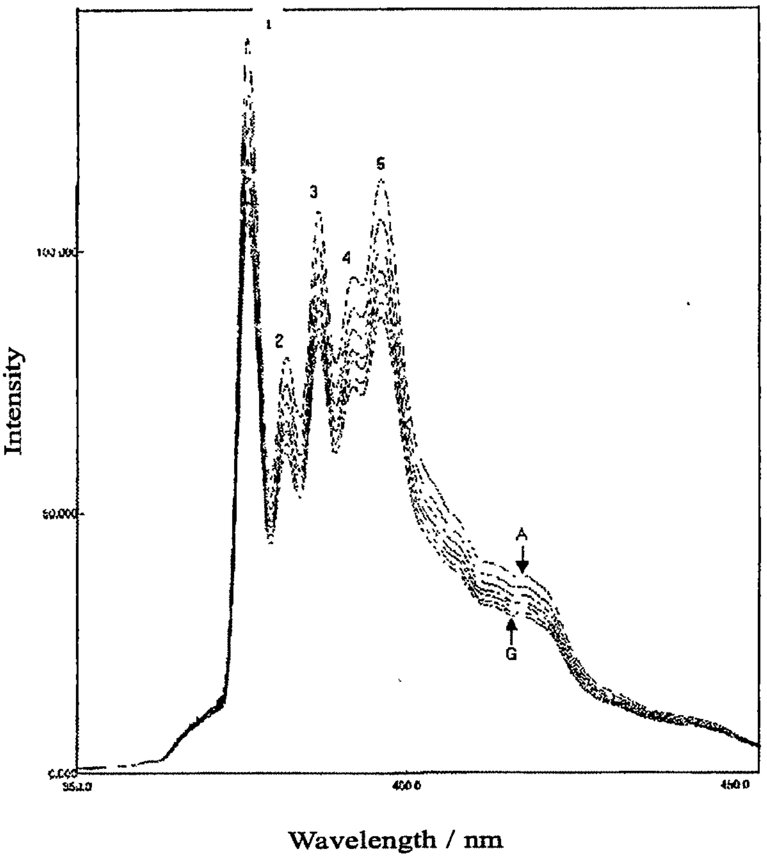

Fig. 3. Representative fluorescence (emission) spectra of 10^{-5} M pyrene in aqueous micellar solution of $C_{12}E_{12}$ in presence 0.25 M NaCl at various quencher concentrations. From top to bottom A (zero), B (1.8×10^{-5} M), C (3.3×10^{-5} M), D (4.6×10^{-5} M), E (5.7×10^{-5} M), F (6.6×10^{-5} M) and G (7.5×10^{-5} M) respectively.

and the solvent was evaporated with nitrogen. The surfactant solution (10 mM) was added and pyrene concentration was kept constant at 10^{-6} M. The quencher concentration was varied from 0 to 8×10^{-5}M.

The micellar aggregation number ($N_{agg.}$) was deduced from the equation [21,22],

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

where [Q] and [S] are the concentrations of the quencher and the total surfactant respectively. The ratio of the intensities of the first (I_1, 375 nm) and the third (I_3, 395 nm) vibronic peaks, i.e.,I_1/I_3 of the monomeric pyrene fluorescence emission spectrum in presence of surfactants is considered to be the index of micropolarity of the system, i.e., it gives an idea of the microenvironment in the micelle. A low value of this ratio ($I_1/I_3 < 1$) is generally taken as the pyrene having nonpolar surroundings whereas higher value ($I_1/I_3 > 1$) suggests that pyrene has polar surroundings [23].

The CP of surfactant concentration (1% w/v) in presence of NaCl (0.5-4.0 M) and at all pH were determined. The experimental procedure was the same as reported earlier [8]. The CP presented here are the averages of the appearance and the disappearance temperatures of the cloud. The experiments were repeated twice and the error was about 0.5%.

RESULTS AND DISCUSSION

Critical micelle concentrations

Effect of pH : Surface tension is a dependable and an elegant method for the determination of cmc [24]. The cmc values of $C_{12}E_{12}$ and $C_{12}E_{15}$ at various pH and in presence of NaCl of different concentrations at different temperatures are presented in Table 1. It is evident from the Table 1 that, the cmc values of these POE surfactants decrease with an increase in temperature at all pH, which is expected for nonionic surfactants of POE class. This is due to the dehydration of the hydrophilic moiety of the surfactant molecules and also due to the breaking of water structure [5]. As the dielectric constant of water decreases with temperature, hydration of POE chains diminishes when the solution is heated. It is observed that at a given temperature, the pH vs. cmc plot shows a maximum at pH ~ 7. As the hydrophilicity of POE nonionic surfactant (number of POE units) increases, the cmc increases, thus $C_{12}E_{15}$has higher value of cmc than $C_{12}E_{12}$ at neutral pH. The formation of micelle is controlled by hydrophobic interaction and the London dispersion forces [25]. The ether linkages in $C_{12}E_{12}$ and $C_{12}E_{15}$ chain can be protonated at low pH, and thus the surfactants acquire a weak cationic character and behave as a pseudo ionic surfactant. At alkaline or around neutral pH these surfactants are expected to remain nonionic.

It is seen that in the acidic region with decreasing [H^+], the cmc increases. With increase in alkalinity the cmc decreases. Also lowering of temperature increases the cmc. Both H^+ and OH^- can form hydrogen bonds with water molecules and thereby promote water structure, which is also promoted by the hydrophobic group of the surfactant molecule. On increasing the temperature, the oxyethylene groups get dehydrated, i.e., there is a decrease in hydrophilicity or an increase in hydrophobicity causing the lowering of cmc. The resultant cmc is governed by the effects of various factors, synergistic and/or antagonistic. It is however obvious that the presence of excess H^+ or OH^- induces early

TABLE 1

Critical micelle concentrations of $C_{12}E_{12}$ and $C_{12}E_{15}$ in aqueous solution as a function of pH and different concentrations of NaCl at various temperatures.

	Critical micelle concentration × 10^5 M							
	$C_{12}E_{12}$				$C_{12}E_{15}$			
pH	35	40	45	50°C	35	40	45	50°C
1.0	8.3	7.9	70.0	6.6	5.4	4.4	4.1	5.2
3.0	8.3	8.1	7.9	7.6	9.1	8.70	8.1	7.2
5.0	9.9	9.3	8.6	8.2	9.8	7.41	6.0	6.66
6.8	10.2	9.8	9.1	8.5	12.8	10.2	9.5	8.5
9.0	8.3	7.6	6.9	6.3	7.4	4.7	5.4	4.9
11.0	7.4	5.9	6.3	5.8	6.5	5.7	5.4	5.2
NaCl / M	$C_{12}E_{12}$				$C_{12}E_{15}$			
0.10	7.9	7.0	6.0	5.8	6.5	5.2	4.9	4.5
0.25	7.0	6.0	6.0	5.2	4.9	4.4	4.0	3.7
0.50	5.8	5.5	4.8	3.8	4.5	3.8	4.1	2.8
1.00	4.8	4.0	4.6	3.3	4.1	3.3	2.9	2.7

micellization probably because of more structured solvent.

Effect of Salt : The effect of salt on the cmc's of the POE nonionic surfactants are expected to be less complicated, due to the absence of charge-charge interactions. However, such studies have been less systematic and the nature of the effect has been attributed to various phenomena. The cmc's of $C_{12}E_{12}$ and $C_{12}E_{15}$ also decreased by the added NaCl. Various interpretations have been proposed for the observed effects. According to Shinoda et.al [26], the change in cmc is due to the decreased hydration of the surfactant resulting in an increase in their effective concentration. This is due to the amount of added salt, and their hydration. Hsiao et. al [27] attributed the lowering in cmc to the decrease in hydration of the EO chain, caused by added electrolytes, and probably due to the breaking of hydrogen bonds. Becher [28] first interpreted the lowering of the cmc due to decrease in the water activity, but later discounted this possibility. Schick [29] attributed the effect to the salting out of the EO chains. However, Mukerjee [30] concluded that the salting out of the hydrocarbon moiety of the surfactant is responsible for the lowering of cmc and not of the hydrophilic head group as proposed by Schick [29]. However we feel that probably both Schick's and Mukerjee's suggestions hold good. This is because NaCl is certainly going to affect the amount of water available for the surfactants. The hydrophilic group will therefore have less amount of water though the iceberg structure around the hydrophobic groups will be completely devoid of water, both resulting in an early micelle formation.

Thermodynamics of micellization and adsorption

The Gibbs free energy of micellization (ΔG^0_m) for a nonionic surfactant is related to the cmc (expressed in mole fraction scale) by the following relation [31],

$$\Delta G^0_m = RT \ln \text{cmc} \qquad (2)$$

the standard state being the hypothetical ideal solution of surfactant at unit mole fraction. Standard free energy of micellization, ΔG^0_m, thus evaluated from eqn. 2 are presented in Table 2. It is evident from Table 2 that the free energy of micellization is relatively more

TABLE 2

The free energy (ΔG^0_m), enthalpy (ΔH^0_m) and entropy (ΔS^0_m) of micellization of $C_{12}E_{12}$ and $C_{12}E_{15}$ at different pHs and different concentrations of NaCl.

	$C_{12}E_{12}$						$C_{12}E_{15}$					
	$-\Delta G^0_m$ kJmol^{-1}				ΔH^0_m kJmol^{-1}	ΔS^0_m Jmol^{-1}K^{-1}	$-\Delta G^0_m$ kJmol^{-1}				ΔH^0_m kJmol^{-1}	ΔS^0_m Jmol^{-1}K^{-1}
pH	35	40	45	50°C			35	40	45	50°C		
1.0	34.4	35.1	35.9	36.6	12.9	153	35.4	36.6	37.3	37.3	3.73	128
3.0	34.3	34.9	35.5	36.3	4.3	125	34.1	34.8	35.5	36.4	12.8	152
5.0	34.0	34.6	35.4	36.1	9.4	141	33.9	35.2	36.3	36.6	22.6	184
6.8	33.8	34.5	35.2	36.0	11.2	146	33.2	34.4	35.1	35.9	20.9	176
9.0	34.3	35.1	35.9	36.8	15.4	161	34.6	36.4	36.6	37.4	18.0	172
11.0	34.6	35.8	36.2	37.0	22.9	186	34.9	35.9	36.6	37.3	13.7	158
NaCl (M)												
0.1	34.4	35.3	36.3	37.0	18.2	171	34.9	36.1	36.8	37.7	21.1	182
0.25	34.8	35.7	36.3	37.3	15.3	163	35.7	36.6	37.4	38.2	15.4	166
0.5	35.3	36.0	36.9	38.1	18.6	174	35.9	36.9	37.3	38.9	19.4	180
1.0	35.8	36.8	37.0	38.5	21.7	186	36.1	37.3	38.2	39.0	25.6	200

negative with increasing temperature, indicating relative spontaneity of the micellization process as the temperature increases. The free energy of micellization, ΔG^0_m values are more negative in presence of NaCl of different concentrations as compared to that in pure water, suggesting that the micellization of both the surfactants is more favoured in presence of NaCl.

The standard entropy of micellization (ΔS^0_m) and enthalpy of micellization (ΔH^0_m) were computed from the slope and the intercept respectively of linear ΔG^0_m vs. T plots. The entropy of micellization values are all positive and large indicating that the micellization process is entropy controlled. Overall micellization process for both the surfactants at different pH and in presence of NaCl is endothermic in nature. High entropy changes are generally associated with a phase-change; the pseudophase micellar model is thus preferred over the mass action model and has been used by us. Rosen [4] has stated that the presence of hydrated oxyethylene groups of the surfactant introduces structure in the liquid phase and that the removal of the surfactant molecules via micellization wherein the hydrated surfactant molecules release the water molecules resulting in an increase in overall entropy of the system.

Linear correlation between enthalpy and entropy, i.e., enthalpy-entropy compensation phenomenon for micellization process is observed for both the surfactants (Fig. 4). Such a compensation was suggested by Lumry and Rajender [32] and the slope of the line, i.e., the compensation temperature was found to be 300 K for micellization, which is close to the expected values between 270 and 294K in aqueous medium [32]. The observed value is a little higher than the suggested value and this may be due to the effect of additives. Moreover, the small variations, we observe here as well as those observed earlier [7] may be due to the differences in the bulk structural property of the solution from that of water.

The heat capacities for the micelle formation ($\Delta C_{p.m.}$) were also evaluated from the plot of ΔH_mvs T, the slope being $\Delta C_{p.m.}$ (Table 3). The variation of heat capacities with both pH and concentration of NaCl did not show any regularity; this was observed earlier in calorimetric studies [33]. The transfer enthalpies ($\Delta H_{m.tr}$) and transfer heat capacities ($\Delta C_{p.m.tr.}$) of micelle from water to aqueous solution were obtained using the relations [34],

$$\Delta H_{m.tr.} = \Delta H_m \text{ (aq.additive)} - \Delta H_m \text{ (aq.)} \tag{3}$$

$$\Delta C_{p.m.tr.} = \Delta C_{p.m} \text{ (aq.additive)} - \Delta C_{p.m.} \text{ (aq.)} \tag{4}$$

The transfer enthalpies of micelle were found to be negative (Table 3) but few are positive also. Such transfer enthalpies were also reported for the transfer of NaCl and amino acids from water to aqueous urea solution by Ahluwalia et. al [33b]. It shows that transfer of hydrophilic (OE) groups from water (pH 6.8) to acidic or basic solution is exothermic, whereas that of hydrophobic group is endothermic. The transfer heat capaci-

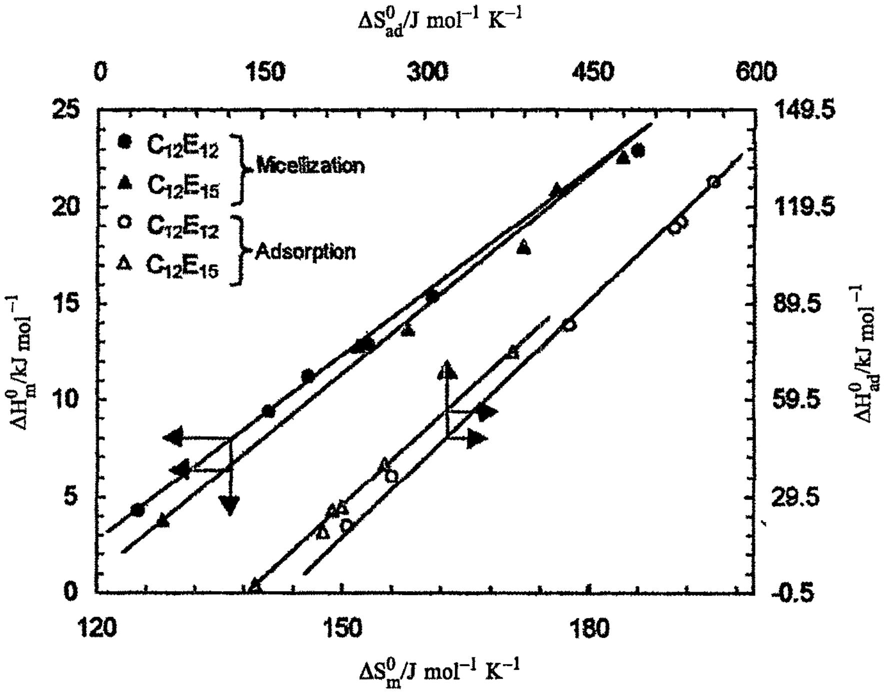

Fig. 4. Enthalpy-entropy compensation plot for micellization and adsorption taking all systems together.

ties of micellization $\Delta C_{p.m.tr.}$ for the transfer of micelle from water (pH 6.8) to acidic or basic solution are negative indicating increased hydration of micelles due to greater extent of hydrogen bonding between OE and additives present in the solution. The $\Delta C_{p.m.tr.}$ values remain more or less constant throughout for all the systems indicating no obvious structural transition.

The air/water interface of a surfactant solution is well populated [33] by the adsorbed amphiphile molecules. The surface excess concentration, Γ_{max}, of the surfactant molecules in the surface layer compared to the bulk and the area per molecule, A_{min} in the surface monolayer were calculated by the standard procedure [4,34]. The slope of the tangent, at a given concentration of the γ vs. $\text{Log}_{10}C$ plot has been used to calculate Γ_{max}, by fitting a curve to a polynomial equation of the form, $y = ax^2 + bx + c$ in Microsoft excel. The regression coefficient (R^2) value of the fit, lies between 0.9645 and 0.9968. The effect of temperature on Γ_{max} at different pH did not show any regular variation (data not given), thus the interaction seems not to be straightforward. This may be guided by

TABLE 3

The heat capacities ($\Delta C_{p.m.}$) and the transfer enthalpies ($\Delta H_{m.tr.}$) and heat capacities ($\Delta C_{p.m.tr.}$) of Micellization of $C_{12}E_{12}$ and $C_{12}E_{15}$ in Aqueous Solutions of various pH and NaCl concentrations at 45°C.

pH	$C_{12}E_{15}$			$C_{12}E_{15}$		
	$\Delta C_{p.m}$ ($Jmol^{-1}K^{-1}$)	$\Delta H_{m.tr}$ ($kJmol^{-1}$)	$\Delta C_{p.m.tr}$ ($Jmol^{-1}K^{-1}$)	$\Delta C_{p.m}$ ($Jmol^{-1}K^{-1}$)	$\Delta H_{m.tr}$ ($kJmol^{-1}$)	$\Delta C_{p.m.tr}$ ($Jmol^{-1}K^{-1}$)
1.0	0.005	1.52	–0.001	–0.062	–17.47	–0.048
3.0	–0.007	–6.98	–0.013	0.012	–8.03	0.026
5.0	–0.001	–1.79	–0.007	–0.056	1.33	–0.042
6.8	0.006	0.0	0.0	–0.014	0.0	0.0
9.0	–0.005	4.07	–0.011	0.028	–2.78	0.042
11.0	0.034	11.72	0.28	–0.024	–7.43	–0.01
NaCl (%)						
0.10	0.001	6.85	–0.005	–0.008	0.29	0.006
0.25	0.001	4.3	–0.005	–0.004	–5.48	0.01
0.50	–0.012	7.2	–0.018	–0.008	–0.93	0.006
1.00	0.02	10.92	–0.014	–0.01	4.53	0.004

(The error in the data is <2%)

the interaction of H^+ and OH^- ions with water as well as the surfactant. The increase in the temperature (in presence of H^+ or OH^-) hinders the adsorption of surfactants at air/water interface. This is because of (i) the changed nature of water due to presence of H^+ and OH^- ions and (ii) the possibility of interaction between the surfactant and the H^+ ions, due to the presence of unpaired electrons on the oxygen of oxyethylene groups.

The A_{min}. values of $C_{12}E_{12}$ and $C_{12}E_{15}$ at cmc are presented in Table 4. The magnitudes are of the order of ~1.0 nm^2 or less, suggesting that the surface is a close packed one which means that the orientation of the surfactant molecules is almost perpendicular to the surface [35]. The effectiveness of a surface active molecule is measured by the surface pressure (π_{cmc}) at the cmc, i.e., $\pi_{cmc} = \gamma_o - \gamma_{cmc}$ where γ_o and γ_{cmc} are the surface tension of pure solvent and the surface tension of the surfactant solution at cmc respectively.

The value of free energy of adsorption of the surfactant at the air/water interface

TABLE 4.

Minimum area per molecule A_{min} of $C_{12}E_{12}$ and $C_{12}E_{15}$ at different pHs and different concentrations of NaCl.

	A_{min} (nm^2)							
System	$C_{12}E_{12}$				$C_{12}E_{15}$			
pH	35	40	45	50°C	35	40	45	50°C
1.0	0.58	0.90	0.83	0.99	0.62	0.74	0.53	0.84
3.0	0.75	0.79	0.85	0.84	0.73	0.69	0.84	0.92
5.0	0.60	0.66	0.83	0.76	0.70	0.80	0.76	0.51
6.8	0.82	0.89	0.98	0.83	0.71	0.72	0.80	0.89
9.0	0.71	0.98	0.73	0.70	0.85	0.52	0.69	0.63
11.0	0.86	0.89	1.03	1.03	0.73	0.58	0.68	0.66
NaCl / M								
0.10	1.03	1.11	1.11	1.20	0.77	0.84	0.83	0.78
0.25	1.03	0.90	0.92	1.08	0.83	0.84	0.83	0.76
0.50	1.40	1.09	0.70	0.80	0.90	0.85	0.77	0.80
1.00	1.14	0.87	1.14	1.03	0.81	1.10	1.10	1.00

(ΔG^0_{ad}) was calculated using the relation [36],

$$\Delta G^0_{ad} = RT \ln \text{cmc} - N\pi_{cmc}A_{min} \qquad (5)$$

The standard state for the adsorbed surfactant here is a hypothetical monolayer at its minimum surface area/molecule but at zero surface pressure.

As expected, the free energy of micellization, (ΔG^0_m) was less negative than the free energy of adsorption, ΔG^0_{ad} values at air/water interface at all temperatures, suggesting that when a micelle is formed, work has to be done to transfer the surfactant molecules in the monomeric form at the surface to the micellar stage through the aqueous medium. In Table 5, the thermodynamic parameters of adsorption, i.e., ΔG^0_{ad}, ΔH^0_{ad} and ΔS^0_{ad} of $C_{12}E_{12}$ and $C_{12}E_{15}$ at the air/solution interface, at various pHs and in NaCl solutions of different concentrations are presented.

The standard entropy (ΔS^0_{ad}) and enthalpy (ΔH^0_{ad}) of adsorption were obtained from the slope and intercept respectively of the reasonably linear ΔG^0_{ad} vs T plot. The ΔS^0_{ad} values are all positive and greater than those of ΔS^0_m values, reflecting greater freedom

TABLE 5

The free energy (ΔG^0_{ad}), enthalpy (ΔH^0_{ad}) and entropy (ΔS^0_{ad}) of adsorption and Traube's constant ($\times 10^{-7}$) $C_{12}E_{12}$ and $C_{12}E_{15}$ at different pHs and different concentrations of NaCl.

	$C_{12}E_{12}$						$C_{12}E_{12}$					
pH	$-\Delta G^0_{ad}$ kJmol^{-1}				ΔH^0_{ad}	ΔS^0_{ad}	$-\Delta G^0_{ad}$ kJmol^{-1}				ΔG^0_{ad}	ΔG^0_{ad}
	35	40	45	50°C	kJmol^{-1}	Jmol^{-1} K^{-1}	35	40	45	50°C	kJmol^{-1}	Jmol^{-1} K^{-1}
1.0	48.3	53.4	53.7	57.1	114.8	532.2	42.8	44.6	43.8	49.4	74.7	380
	(15.5)	(81.6)	(66.2)	(172)			(1.81)	(2.78)	(1.6)	(9.8)		
3.0	51.1	51.9	54.8	53.9	20.1	231.4	41.1	43.1	43.4	44.6	25.1	216
	(46.4)	(45.9)	(100)	(52.1)			(0.93)	(1.6)	(1.4)	(1.6)		
5.0	45.8	47.0	53.9	52.9	127.3	561.6	42.3	45.7	45.9	46.0	26.3	226
	(5.87)	(6.98)	(71.4)	(35.9)			(1.49)	(4.2)	(3.5)	(2.8)		
6.8	47.3	53.5	58.0	53.0	83.3	431.2	41.9	43.1	44.9	45.7	39.4	264
	(10.5)	(84.8)	(337)	(37.3)			(1.28)	(1.6)	(2.4)	(2.5)		
9.0	47.6	54.7	52.0	51.3	35.6	271.3	46.5	44.9	47.8	49.0	18.6	208
	(11.8)	(135)	(34.8)	(19.8)			(7.7)	(3.1)	(7.1)	(8.4)		
11.0	48.0	52.1	56.1	55.5	113.3	526.8	44.0	42.1	44.9	45.5	1.9	146
	(13.8)	(49.5)	(164)	(94.5)			(2.9)	(1.1)	(2.4)	(2.3)		
NaCl (M)												
0.10	42.2	54.8	60.0	62.6	173.5	717.4	45.5	49.0	50.0	50.9		
	(1.44)	(140)	(718)	(1330)			(5.2)	(15.1)	(16.3)	(17.0)	59.7	344
0.25	57.5	54.1	55.5	59.2	125.0	570.0	46.4	46.7	47.4	50.2	28.7	242
	(565)	(107)	(131)	(375)			(7.4)	(6.2)	(6.1)	(13.1)		
0.50	47.7	565	52.8	53.1	61.8	355.4	49.5	47.3	50.5	47.7	62.6	44
	(12.3)	(269)	(47.1)	(38.7)			(24.8)	(7.8)	(19.7)	(5.18		
1.00	59.4	60.1	62.2	58.4	26.5	279.0	50.5	53.5	58.0	54.2		
	(1190)	(1070)	(1650)	(278)		36.7	84.8	337	58.3	44.4	312	

*The values in the parentheses are Traube's constant

of motion of the hydrocarbon chain at the planar air/water interface compared to that in the cramped interior beneath the convex surface of micelle [36]. It is evident from Tables 2 and 5 that the derived enthalpy and entropy quantities have irregular variation with pH. However, in the presence of NaCl, the enthalpy and entropy of micellization increase while for adsorption of surfactant at air/water interface, the corresponding values decrease on increasing the concentration of NaCl. The error associated with the values of these quantities is ±5%.

Like micellization process, the adsorption of surfactant at air/water interface has also been found to be endothermic in nature. The endothermic character of micellization and adsorption are specific to the surfactant, the additive and the temperature of micellization [37-41]. The ΔH^0_{ad} vs ΔS^0_{ad} compensation plot of the adsorption phenomenon is observed for both the surfactants and is illustrated in Fig. 4. The compensation temperature is observed to be 305 and 315K for $C_{12}E_{12}$ and $C_{12}E_{15}$ respectively, slightly different from 300K obtained for the micellization phenomenon, but around the expected region for aqueous systems (270-294K) [32].

It has been suggested by Weiner and Zografi [41] that,

$$\Delta G^0_{ad} = -RT \ln \sigma \tag{6}$$

where 'σ' 'is known as Traube's constant and is defined by the relation

$$\sigma = (\partial\pi/\partial C)_{c\to 0} = -(\partial\gamma/\partial C)_{c\to 0} \tag{8}$$

This means σ is the rate of change of surface pressure per unit concentration change at infinite dilution. The σ values are given in Table 5. It can be noted that the σ of the pure $C_{12}E_{12/15}$ is similar to the data given in Table 4 of Meguro et.al [42] thereby suggesting that our adsorption data are reasonable. We computed the effect of different pH and NaCl concentration on σ where unfortunately, no regularity was observed.

Micellar aggregation number (N_{agg})

The micellar aggregation numbers of $C_{12}E_{12}$ and $C_{12}E_{15}$ evaluated using steady state fluorescence quenching measurements with varying NaCl concentration are tabulated in Table 6. It is evident that, the $N_{agg.}$ of $C_{12}E_{12}$ is higher than that of $C_{12}E_{15}$. However, in presence of NaCl, though the $N_{agg.}$ changes, there is no regular change with increasing NaCl concentration. A minimum is observed for both the surfactants, though at different NaCl concentrations. However, at higher concentration of NaCl, the $N_{agg.}$ increases due to the decrease in the steric hindrance between ethylene oxide moieties of the polyoxyethylene chain due to the presence of NaCl. Table 6 also illustrates the intensity ratio of the first and the third vibronic peaks (I_1/I_3) in the monomeric pyrene fluorescence emission spectrum, which is sensitive to the local polarity around the probe (pyrene). It is evident that, all the values of I_1/I_3 are > 1 suggesting polar environment around pyrene. However I_1/I_3 values are almost constant ($I_1/I_3 \sim 1.30$) for both the surfactants irrespective of NaCl concentration in the present study. This indicates that by the presence of NaCl there is no significant change in polarity around pyrene.

TABLE 6

Aggregation number (N_{agg}) and micropolarity (I_1/I_3) of $C_{12}E_{12}$ and $C_{12}E_{15}$ in the presence of NaCl at 30°C.

Concentration of NaCl / M	Aggregation number (N_{agg})	
	$C_{12}E_{15}$	$C_{12}E_{15}$
0.00	74 ± 4 (1.30)	51 ± 3 (1.30)
0.10	51 ± 3 (1.30)	46 ± 2 (1.31)
0.25	33 ± 2 (1.31)	57 ± 3 (1.30)
0.50	46 ± 2 (1.31)	56 ± 3 (1.31)
1.00	53 ± 3 (1.30)	58 ± 3 (1.31)

Micropolarity values are given in in parentheses

Cloud points

Cloud points are the manifestation of the solvation/desolvation phenomena in nonionic surfactant solution. The desolvation of the hydrophilic groups of the surfactant

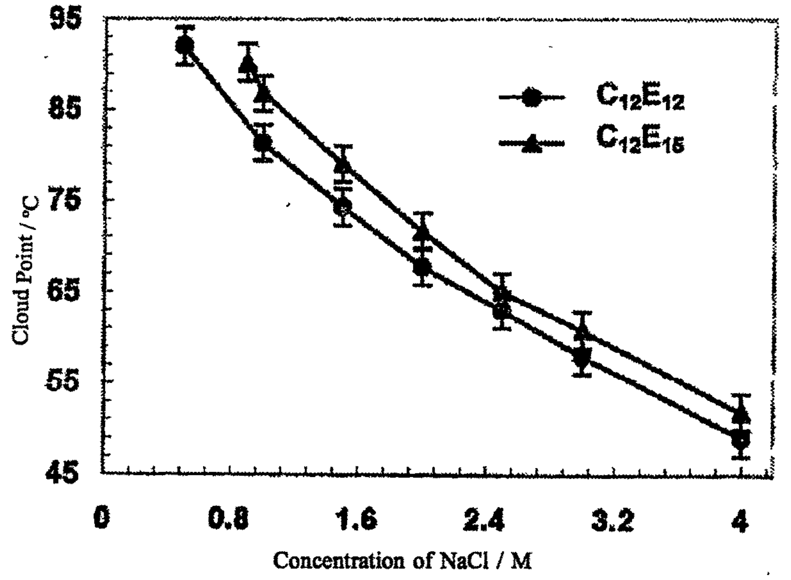

Fig. 5. Cloud point vs NaCl concentration plot for $C_{12}E_{12}$ and $C_{12}E_{15}$ surfactants.

leads to the formation of cloud in the surfactant solution. It is seen that pH does not have any effect on the cloud points of $C_{12}E_{12}$ and $C_{12}E_{15}$ but NaCl being a water structure maker, lowers the CP of POE surfactants by decreasing the availability of water molecule to hydrate the ether oxygen of the POE chain (Fig 5). Similar results were also observed with other $C_{12}E_n$ (n=9,10) surfactants [43]. However, it has been stated that when temperature dependent interaction parameters exist, the hydrophilic and hydrophobic parts of micelles interact with water in different ways [44]. Clouding of surfactant is thus dependent on balance of hydrophobicity and hydrophilicity. Hence at CP, hydrophobicity is more dominating than hydrophilicity and the complete removal of water from the molecule is not essential. Therefore we can say that the H^+ and Cl^- ions affect the hydrophobicity or hydrophilicity to the same extent but in opposite direction which is also true for Na^+ and OH^- ions. Hence the CP does not change on changing the pH. However the effect of Na^+ and Cl^- are not of same magnitude and hence there is a change in CP.

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