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CMC Determination of an Odd Carbon Chain Surfactant ($C_{13}E_{20}$) Mixed with Other Surfactants Using a Spectrophotometric Technique

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Micellization of seven binary surfactant mixtures (containing an odd carbon chain nonionic surfactant, tridecanol ethoxylates (20 mol of ethylene oxide/mol of tridecanol), represented as $C_{13}E_{20}$, and a nonionic or cationic surfactant) was studied by dye absorption method. Critical micelle concentrations (CMCs) of these mixed surfactant systems in water were obtained spectrophotometrically using Eosin Y dye. A pseudo-phase separation model was employed for mixed micellization analysis. The Margules equation with one constant was employed to describe nonideal mixing behavior in micelles of surfactant mixtures. The nature of nonideality is accounted for by intermolecular interactions and micellar composition. The composition of mixed micelle x_1 and x_2 and the interaction parameter β were determined from the CMCs of different binary systems, employing the Margules equation. Mixtures of nonionic surfactants show antigistic interactions while cationic−nonionic surfactant mixtures show strong synergistic interactions.

Introduction

Surfactants employed industrially almost always consist of a mixture of surfactants. Even if surfactant mixtures are not intentionally made, they result from the natural polydispersity in the carbon chain derived from fatty acids and the nature of ethylene oxide reaction with fatty alcohol and other species.[1,2] Chemically pure species are very rarely used individually as surfactants as it is not economical to synthesize them. A mixed surfactant system is also often superior in performance to individual components. There is a substantial difference in the micellization tendency of mixtures of two or more surfactants as compared to a single pure species. This results in a dramatic change in properties and behavior of mixed surfactants as compared to any single surfactant. It is therefore important to investigate the nature of interactions (synergistic or antigistic) and the factors (counterion valence, addition of electrolyte, pH, temperature variation, etc.) affecting them. A lower of mixture CMC than of individual surfactants is often synergy, and synergistic effects seem to be negligible for mixtures of nonionic surfactants.[3−5] There is appreciable synergism in ionic−nonionic mixtures,[6,7] while cationic−anionic surfactant mixtures show the strongest synergistic effects.[8] The interaction is often analyzed by finding the interaction parameter.[9] The interaction parameter is a measure of the extent of interaction between the surfactants resulting in a deviation of the CMC from the ideal behavior. Negative values of the interaction parameter indicate synergism, and positive values indicate antagonism.

In the present work, we report spectrophotometric studies of interaction of an odd carbon chain nonionic surfactant, tridecanol ethoxylates (20 mol of ethylene oxide/mol of tridecanol), represented as $C_{13}E_{20}$, with seven other surfactants using Eosin Y dye. The binary mixtures of an odd carbon chain nonionic surfactant like $C_{13}E_{20}$ with other surfactants are rarely studied and reported in the literature. Hence, we have studied the interactions of $C_{13}E_{20}$ with other nonionic and cationic surfactants by measuring the CMCs and evaluated the interaction parameter β. The interaction of a cationic surfactant stertile (cocoamidopropyl dimethyl hydroxyethyl ammonium chloride), with $C_{13}E_{20}$ is also studied for the first time. Most often, fatty acids/triglycerides containing an even carbon chain are used as a raw material for the synthesis of surfactants. The manufacturing of such even carbon chain surfactants is comparatively more economical than that of odd carbon chain surfactants. Some properties of odd carbon chain surfactants are different from those of even carbon chain surfactants. The structure of a hydrophobic group in a surfactant molecule has pronounced effect on the physicochemical properties like solubility, adsorption, surface/interfacial tension, melting point, etc.

Experimental Procedures

Modeling of Mixed Micellization. Models for mixed micellization are based on an equilibrium thermodynamic approach.[10] The pseudo-phase separation model assumes that the mixed micelle (surfactant aggregate) can be treated as a separate phase. Although micelles do not constitute a true thermodynamic phase, they do show phase-like behavior. There is a dynamic equilibrium between surfactant monomers and micelles in the solution. The pseudo-phase separation approach is a very useful tool for the description of micelle formation.[11] In comparison to single surfactant systems, relatively few experimental measurements of monomer concentrations and micelle compositions are available in the literature.[9,12−14]

The CMC of the ideal mixture of two surfactants is given by eq 1, proposed by Clint:[15]

$$\frac{1}{C_{\text{mix}}} = \frac{x_1'}{C_1} + \frac{(1 - x_1')}{C_2} \tag{1}$$

where x_1' is the bulk solution mole fraction of surfactant 1 in the mixture; C_1, C_2, and C_{mix} are the CMCs of surfactants 1, 2, and the mixed system, respectively. The ideal solution theory has been successful in explaining the properties of mixtures composed of surfactants with similar chemical structures;[16] however, deviations occur for mixtures containing chemically

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dissimilar surfactants.[17−21] Rubingh[16] proposed a model incorporating activity coefficient of surfactants 1 and 2 to account for the nonideal behavior of mixed surfactant systems employing the Regular Solution Theory. Thus, the nonideal form of eq 1 will be given by eqs 2 to 4:

$$\frac{1}{C_{\mathrm{mix}}} = \frac{x_1'}{C_1 f_1} + \frac{(1 - x_1')}{C_2 f_2} \tag{2}$$

$$\ln(f_1) = \beta(1 - x_1)^2 \tag{3}$$

$$\ln(f_2) = \beta(x_1)^2 \tag{4}$$

where x_1 and x_2 are the mole fractions of surfactant 1 and surfactant 2, respectively, in the mixed micelle. β is the interaction parameter that is usually obtained by fitting the experimental data of mixture CMCs as a function of bulk mole fraction x_1' of surfactant. Assuming a constant value of interaction parameter β, across the whole range of mole fractions, it is possible to solve for x_1 and hence to predict the mixed CMCs. The interaction parameter β is a measure of the extent of net (pairwise) interaction between the surfactants within the micelles resulting in their deviation from the ideal behavior. In order to obtain valid interaction parameter β values that do not change significantly with change in the ratio of surfactant in the mixture, the following conditions must be met:[2]

(1) The two surfactants must be molecularly homogeneous and free from surface-active impurities.

(2) Since the derivation of eqs 2 to 4 are based upon the assumption that the mixed micelle or monolayer can be considered to contain only surfactants, these structures are considered to contain no free water, and all the present water can be considered to be bound to the hydrophilic head groups.

(3) Since eqs 2 to 4 neglect counterion effects, all solutions containing ionic surfactants should have the same total ionic strength, with a swamping excess of any counterion.

Treatment of Binary Surfactant Mixtures. The surfactant is present in the form of either monomer or as aggregates in a solution. When the total surfactant concentration is just incrementally larger than C_{mix}, then the momomer composition coincides with the overall surfactant composition. It indicates that a greater number of surfactant monomers are present in a solution as compared to micelles. The number of micelles will be increased with an increase in total surfactant concentration. The mixture CMC, C_{mix}, is fitted with eq 2, which is also known as a Margules one-constant equation. Such a treatment gives a constant value of interaction parameter β at all bulk solution mole fractions x_1'. The value of interaction parameter β is then substituted in eq 2 to compute the values of micellar mole fraction x_1 at each bulk solution mole fraction x_1'. The plots of C_{mix} against $C_{13}E_{20}$ bulk solution mole fraction x_1' are shown in Figures 3 and 4 where β from eqs 3 and 4 is the parameter describing nonideality. The values of interaction parameter obtained in these cases are positive. The deviations from ideal behavior could be attributed to repulsive interactions (negative synergism/antagonism) between surfactants in mixed micellar systems as has been reported in the literature.[6−8]

The conditions for synergism or negative synergism in a mixture containing two surfactants (in the absence of second liquid phase) have been shown mathematically[25] to be the following:

(1) For synergism, the interaction parameter β must be negative and $|\beta| > |\ln(C_1/C_2)|$.

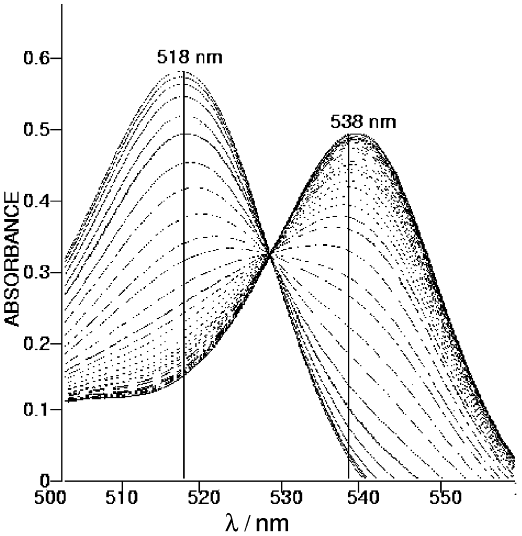

Figure 1. Plot of dye absorbance against wavelength λ for a mixture of nonionic surfactants $C_{13}E_{20}$ and Brij 35 at a fixed mole fraction of 0.8 and a concentration range of (0 to 0.35) mol·m^{-3} to determine the wavelength maximum. Eosin Y concentration: 0.009 mol·m^{-3}.

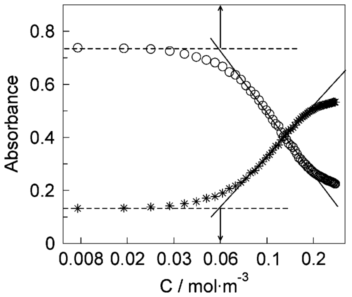

Figure 2. Plot of dye absorbance against concentration C of a mixture of nonionic surfactants $C_{13}E_{20}$ and Brij 35 at a fixed mole fraction of 0.8 for the CMC determination. Eosin Y concentration: 0.009 mol·m^{-3}. Horizontal dashed lines (− −) represent dye absorbance in water in the absence of surfactant; ○, 518 nm; ★, 538 nm.

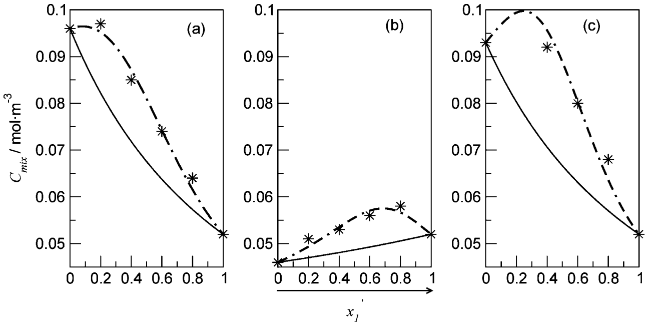

Figure 3. Plots of C_{mix} against $C_{13}E_{20}$ bulk solution mole fraction x_1' for the three nonionic mixed surfactant systems: (a) Tween 20, (b) Tween 40, and (c) Tween 80. The solid lines in the figures correspond to the ideal C_{mix} values, and the stars represent measured C_{mix} values that are fitted with the one-constant Margules equation, shown by dashed lines, to determine the best fit interaction parameter β.

(2) For negative synergism or antagonism, the interaction parameter β must be positive and $|\beta| > |\ln(C_1/C_2)|$ where C_1 and C_2 are the CMCs of individual surfactants.

Materials. Polyoxyethylene(20) sorbitan monolaurate (Tween 20), polyoxyethylene(20) sorbitan monopalmitate (Tween 40), polyoxyethylene(20) sorbitan monoleate (Tween 80), polyoxyethylene(23) lauryl alcohol ether (Brij 35), polyoxyethylene(20) cetyl alcohol ether (Brij 58), and DTAB were procured from Aldrich Chemical Co. with 98 % to 99 % purity.

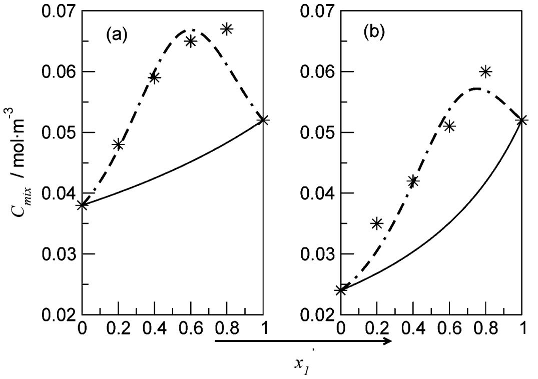

Figure 4. Plots of C_{mix} against $C_{13}E_{20}$ bulk solution mole fraction x_1' for the two nonionic mixed surfactant systems: (a) Brij 35 and (b) Brij 58. The solid lines in the figures correspond to the ideal C_{mix} values, and the stars represent measured C_{mix} values that are fitted with the one-constant Margules equation, shown by dashed lines, to determine the best fit interaction parameter β.

Tridecanol ethoxylates (20 mol of ethylene oxide/mol of tridecanol with 98 % purity), represented as $C_{13}E_{20}$, were gifts from ICI-Uniqema Ltd (Thane, India). Cocoamidopropyl dimethyl hydroxyethyl ammonium chloride (stertile) was a gift from Galaxy Surfactants Ltd (Navi Mumbai, India). Eosin Y with 99 % purity was obtained from Acros Organics. All the surfactants were used without further purification. Distilled water was used in all the experiments for the preparation of solutions (specific conductivity of 1 μS·cm^{-1} and surface tension of 72.2 mN·m^{-1} at 298 K.

Methods. The absorbance spectra of 0.009 mol·m^{-3} Eosin Y dye in pure as well as mixed surfactant solutions were recorded on an Agilent 8453 UV−vis Spectroscopy System at 298 K. Eosin Y shows an absorbance maximum at 518 nm in water. In the presence of nonionic surfactant micelles, the absorbance maximum at 518 nm shifts to 538 nm (see Figure 1), while in the case of cationic surfactants, the absorbance maximum shifts to 528 nm. The decrease in absorbance at 518 nm at a fixed concentration of Eosin Y dye was followed as a function of surfactant concentration. The sudden deflection in absorbance was taken to be the surfactant CMC (see Figure 2). The surface tension of pure components at the liquid−vapor interface was measured at 298 K by the Wilhelmy plate method using a Kruss tensiometer (model K11). The CMC was also determined from a plot of surface tension against surfactant concentration. The uncertainties in the measurements of surface tension, temperature, concentration, and absorbance of surfactants are 0.10 %, 0.10 %, 0.001 %, and 0.0001 %, respectively.

Results and Discussion

Ionic surfactants usually possess higher CMCs than nonionic surfactants.[3,13,22,23] This is attributed to the electrostatic repulsions among head groups of ionic surfactants. The hydrophobic groups of a nonionic surfactant are easily separated from the aqueous medium, whereas for ionic surfactants, high concentrations are necessary to overcome the electrostatic repulsion between ionic head groups during aggregation. Table 1 shows the CMC values measured by the surface tension and dye absorption methods. The CMC values measured by dye absorption method are higher than those measured by surface tension method. The dye method is a micelle-based phenomenon and detects the presence of micelles in the solution where as the surface tension method depends on the surface concentration of all surface-active species. Properties of commercial grade surfactants that contain a small amount of some other surface-active compound, like long chain alcohols, were studied with a view to generate data that may be useful for practitioners. The surface tension method is a surface phenomenon and is highly sensitive to surface-active impurities in the surfactant solution that often significantly reduce the CMC of surfactant. Nonionic surfactant properties are a strong function of the ethylene oxide (EO) distribution; hence, differences between the literature values of CMC and our observed values shown here are expected. The dye method can overcome the problems caused by a small amount of surface-active impurities and can be a suitable method for CMC determination of surfactants.[14,24]

Table 1. Critical Micelle Concentration (CMC) Values of Surfactants at 298 K

	CMC/(mol·m^{-3})		
	measured		literature[14]
surfactant	dye absorption method	surface tension method	surface tension method
$C_{13}E_{20}$	0.052	0.024	
Tween 20	0.096	0.029	0.012
Tween 40	0.046	0.012	0.007
Tween 80	0.093	0.021	0.018
Brij 35	0.038	0.053	0.068
Brij 58	0.024	0.009	0.010
DTAB	14	14	16
stertile	0.026	0.021	

Nonionic−Nonionic Mixed Systems. Mixed surfactant systems of $C_{13}E_{20}$ with five nonionic surfactants (Tween 20, Tween 40, Tween 80, Brij 35, and Brij 58) were investigated. Mixed CMC values obtained experimentally are higher than those obtained by assuming ideal behavior.

$C_{13}E_{20}$/Tweens Mixed System. Figure 3 shows plots of C_{mix} against $C_{13}E_{20}$ solution mole fraction x_1' for three nonionic Tweens mixed surfactant systems. The measured C_{mix} values are fitted with the one-constant Margules equation (eq 2) to determine the best fit interaction parameter β. The interaction parameter β values for each system are listed in Tables 2 and 3. The average number of hydrophilic polyoxyethylene group in each case is 20. Since the hydrophilic groups interacting with each other are similar, the hydrophilic−hydrophilic interactions between nonionic−nonionic mixed surfactant systems are not significant. However, there is an increase in the number of carbon atoms in the hydrophobic chain from Tween 20 (dodecyl hydrophobe) to Tween 80 (octadecyl hydrophobe). Tween 80 contains an octadecyl hydrocarbon chain with one carbon−carbon double bond that plays an important role in hydrophobic interactions with $C_{13}E_{20}$. Hence the interaction parameter β for Tween 80 is more positive than for other nonionics of Tween type. The sorbitan group in each Tween with six carbon atoms in a closed chain may also take part in hydrophobic interactions with $C_{13}E_{20}$. Thus, the hydrophobic−hydrophobic interactions are more pronounced resulting in a positive deviation from ideality due to steric hindrance of different chain lengths.[26] The micellar mole fractions x_1 of $C_{13}E_{20}$ in the mixed micelle at different solution mole fractions are computed using eq 2, considering the best fit interaction parameter β. Figure 6 shows plots for the computed micellar mole fraction x_1 of $C_{13}E_{20}$ as a function of its solution mole fraction x_1' in its mixtures with Tween type surfactants. In the case of Tween 20 and Tween 80, positive deviations are observed from ideality up to a $C_{13}E_{20}$ solution mole fraction of 0.6 followed by negative deviation at higher mole fractions. This indicates that there is a major contribution of $C_{13}E_{20}$ molecules in the mixed micelle up to a bulk solution mole fraction of 0.6 beyond which the Tweens contribute more. In the case of $C_{13}E_{20}$/Tween 40 mixed system, positive deviations are observed from ideality up to the $C_{13}E_{20}$

Table 2. $C_{13}E_{20}$ Bulk Solution Mole Fraction x_1', Mixture CMC C_{mix}, Micellar mole Fraction x_1, and Interaction Parameter β for Nonionic−Nonionic Systems at 298 K

surfactant	x_1'	C_{mix} measured mol·m^{-3}	C_{mix} ideal mol·m^{-3}	x_1	β
Tween 20	0.0	0.096	0.042	0.0	
	0.2	0.097	0.082	0.44	0.72
	0.4	0.085	0.072	0.58	
	0.6	0.074	0.064	0.61	
	0.8	0.064	0.057	0.65	
	1.0	0.052	0.052	1.0	
Tween 40	0.0	0.046	0.046	0.0	0.54
	0.2	0.051	0.047	0.27	
	0.4	0.053	0.048	0.33	
	0.6	0.056	0.049	0.43	
	0.8	0.058	0.051	0.50	
	1.0	0.052	0.052	1.0	
Tween 80	0.0	0.093	0.028	0.0	
	0.2	0.10	0.080	0.43	1.1
	0.4	0.092	0.071	0.60	
	0.6	0.080	0.063	0.61	
	0.8	0.068	0.057	0.65	
	1.0	0.052	0.052	1.0	
Brij 35	0.0	0.038	0.068	0.0	
	0.2	0.048	0.040	0.23	1.6
	0.4	0.059	0.043	0.34	
	0.6	0.064	0.045	0.57	
	0.8	0.067	0.048	0.61	
	1.0	0.052	0.052	1.0	
Brij 58	0.0	0.024	0.010	0.0	
	0.2	0.035	0.027	0.39	1.5
	0.4	0.042	0.030	0.41	
	0.6	0.051	0.035	0.41	
	100	0.060	0.042	0.57	
	1.0	0.052	0.052	1.0	

Table 3. $C_{13}E_{20}$ Bulk Solution Mole Fraction x_1', Mixture CMC C_{mix}, Micellar Mole Fraction x_1, and Interaction Parameter β for Nonionic−Cationic Systems at 298 K

surfactant	x_1'	C_{mix} measured mol·m^{-3}	C_{mix} ideal mol·m^{-3}	x_1	β
DTAB	0.0	14	16	0.0	
	0.2	0.11	0.25	0.20	−1.3
	0.4	0.079	0.13	0.37	
	0.6	0.077	0.087	0.70	
	0.8	0.063	0.065	0.85	
	1.0	0.052	0.052	1.0	
stertile	0.0	0.026	0.026	0.0	
	0.2	0.023	0.029	0.44	−1.1
	0.4	0.025	0.033	0.47	
	0.6	0.028	0.037	0.53	
	0.8	0.031	0.043	0.82	
	1.0	0.052	0.052	1.0	

solution mole fraction of 0.3 beyond which negative deviations are observed. It shows that there is considerable micellar contribution of Tween 40 beyond a solution mole fraction of 0.3.

$C_{13}E_{20}$/Brij Mixed System. Figure 4 shows a plot of C_{mix} against the solution mole fraction x_1' of $C_{13}E_{20}$ in mixture with Brij series of surfactants. The measured C_{mix} values were fitted with the one-constant Margules equation (eq 2) to determine the best fit interaction parameter β. Brij 35 shows a comparatively higher value of β than Brij 58. Brij 35 contains 23 mol of hydrophilic ethylene oxide (EO) groups per mol of dodecanol. As $C_{13}E_{20}$ contains 20 mol of hydrophilic ethylene oxide groups per mol of tridecanol, hydrophilic−hydrophilic interactions are observed between $C_{13}E_{20}$ and Brij 35. Scamehorn[1] reported that oxonium ions are formed in the hydrophilic portion of nonionic surfactants consisting of ethylene oxide groups. The oxonium ion formation brings considerable intramicellar head group repulsions resulting in antagonism. This suggests that, in the mixed system of $C_{13}E_{20}$/Brij 35, hydrophilic−hydrophilic interactions between ethylene oxide groups are more dominant than hydrophobic−hydrophobic interactions between hydrophobic chains. On the contrary, in the mixed system of $C_{13}E_{20}$/Brij 58, the hydrophilic ethylene oxide groups are same (20 mol) but the hydrophobic groups are different, as Brij 58 contains 16 carbon atoms in its hydrophobic tail. The hydrophobic−hydrophobic interactions in this case are more pronounced with comparatively lower value of interaction parameter β than the mixed system of $C_{13}E_{20}$/Brij 35. The plots of micellar mole fraction x_1 against $C_{13}E_{20}$ bulk solution mole fraction x_1' in $C_{13}E_{20}$/Brij mixed surfactant systems are shown in Figure 7. In the mixed systems of $C_{13}E_{20}$/Brij 35, positive deviations are observed from ideality up to $C_{13}E_{20}$ bulk solution mole fraction of 0.2, beyond which negative deviations are observed. It shows that there is major micellar contribution of Brij 35 beyond 0.2. In the $C_{13}E_{20}$/Brij 58 mixed system, the micellar contribution of Brij 58 is more beyond a $C_{13}E_{20}$ bulk solution solution mole fraction of 0.4.

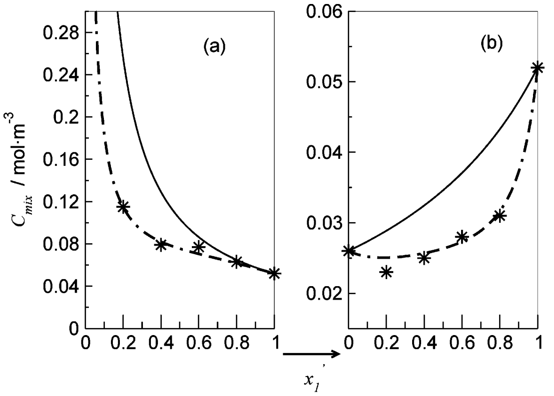

Figure 5. Plots of C_{mix} against $C_{13}E_{20}$ bulk solution mole fraction x_1' for the two nonionic/cationic mixed surfactant systems: (a) DTAB and (b) stertile. The solid lines in the figures correspond to the ideal C_{mix} values, and the stars represent measured C_{mix} values that are fitted with the one-constant Margules equation shown by dashed lines to determine the best fit interaction parameter β.

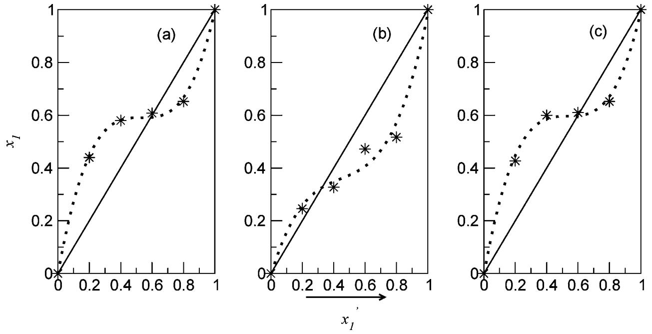

Figure 6. Plots of $C_{13}E_{20}$ micellar mole fraction x_1 against solution mole fraction x_1' for the nonionic mixed surfactant systems: (a) Tween 20, (b) Tween 40, and (c) Tween 80. The solid lines in the figures correspond to the ideal behavior, and the stars represent calculated values of x_1 computed from the one-constant Margules equation considering the best fit interaction parameter β.

Nonionic−Cationic Mixed System. Mixed surfactant systems of $C_{13}E_{20}$ with two cationic surfactants DTAB and stertile were studied. The measured CMCs are found to be lower than those obtained by assuming ideal behavior. The plots of C_{mix} against $C_{13}E_{20}$ bulk solution mole fraction x_1' are shown in Figure 5. The interaction parameter β is obtained as a best fit. The negative deviations could be attributed to strong attractive interactions (positive synergism) between nonionic−cationic

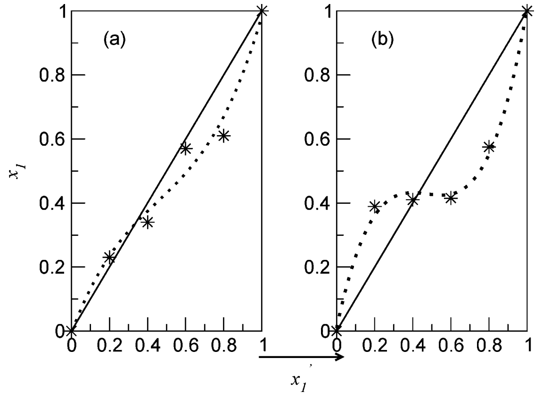

Figure 7. Plots of $C_{13}E_{20}$ micellar mole fraction x_1 against solution mole fraction x_1' for the nonionic mixed surfactant systems: (a) Brij 35 and (b) Brij 58. The solid lines in the figures correspond to the ideal behavior, and the stars represent calculated values of x_1 computed from the one-constant Margules equation considering the best fit interaction parameter β.

surfactants in mixed micellar systems. The hydrophilic−hydrophilic interactions are more pronounced as compared to hydrophobic−hydrophobic interactions as the surfactant molecules possess a similar number of carbon atoms in the hydrophobic tails. This synergistic behavior can be explained assuming that ethoxylated chains of the nonionic surfactant molecules in the mixed micelle coil around charged head groups (quaternary ammonium ion) of the cationic surfactant molecules thereby minimizing electrostatic repulsions between the positively charged surfactant head groups, favoring micelle formation.[27] During micellization, nonionic surfactant molecules orient themselves between cationic surfactant molecules minimizing the head group repulsion. This also reduces steric interactions in-between surfactant tails and results in lowering of CMC value as compared to individual surfactants. The $C_{13}E_{20}$/DTAB mixed system shows stronger synergistic interactions with higher negative value of interaction parameter β as compared to $C_{13}E_{20}$/stertile system. In both mixed surfactant systems, the head groups of the cationic surfactants are similar but the hydrophobic chains are different. stertile, with more hydrophobic substituents along with the dodecyl group, shows hydrophobic−hydrophobic interactions with tridecyl hydrophobes of $C_{13}E_{20}$. The $C_{13}E_{20}$/stertile system, therefore, shows comparatively weaker synergistic interactions than the $C_{13}E_{20}$/DTAB system, as shown by a lower interaction parameter β. The plots for the calculated micellar mole fraction x_1 of $C_{13}E_{20}$ against its bulk solution mole fraction x_1' for $C_{13}E_{20}$/DTAB and $C_{13}E_{20}$/stertile mixed systems are shown in Figure 8. In the mixed system of $C_{13}E_{20}$/DTAB, positive deviations are observed from ideality beyond $C_{13}E_{20}$ solution mole fraction of 0.4, indicating major micellar contribution of $C_{13}E_{20}$. In the mixed system of $C_{13}E_{20}$/stertile, positive deviations from ideality are observed up to 0.5 bulk solution mole fraction, indicating major micellar contribution of $C_{13}E_{20}$, beyond which stertile molecules have a higher contribution to the micelle.

Conclusions

Spectrophotometric study of micellization of an odd carbon chain nonionic surfactant $C_{13}E_{20}$ with seven other surfactants—five nonionics and two cationics—was carried out by dye absorption method. The CMCs of these mixed surfactant systems in water at different mole fractions were obtained at 298 K. Positive deviations from ideality in the mixed CMCs of five nonionic−nonionic mixtures were observed, which are due to stronger antigistic interactions showing negative synergism. This is attributed to the difference in the structure and size of surfactant molecules, steric interactions of hydrophobic tails of nonionic surfactants, and formation of oxonium ions in the hydrophilic portion of surfactants. On the contrary, mixed CMCs of two nonionic−cationic mixtures deviate negatively from ideality. This is due to incorporation of $C_{13}E_{20}$ monomers in-between cationic surfactant monomers in a mixed micelle, decreasing electrostatic repulsions between positively charged head groups of cationic surfactants. This also results in decrease in steric interactions of hydrophobic tails of nonionic surfactants. resulting in stronger positive synergism.

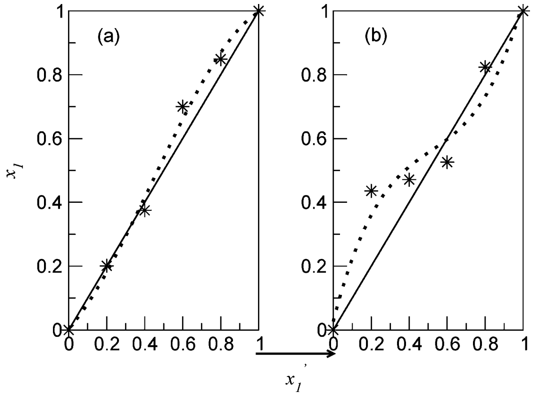

Figure 8. Plots of $C_{13}E_{20}$ micellar mole fraction x_1 against solution mole fraction x_1' for the nonionic/cationic mixed surfactant systems: (a) DTAB and (b) stertile. The solid lines in the figures correspond to the ideal behavior, and the stars represent calculated values of x_1 computed from the one-constant Margules equation considering the best fit interaction parameter β.

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