Chapter II A

Studies of Mixed Surfactant Solutions of Cationic Dimeric (gemini) Surfactant with Nonionic Surfactant $C_{12}E_6$ in Aqueous Medium

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 (τ_{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/$C_{12}E_6$ systems 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 these systems.

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 Krafft 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 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-bishexadecyldimethyl ammoniumbromide [$(C_{16}H_{33}N^+(CH_3)_2(CH_2)_4N^+(CH_3)_2C_{16}H_{33})2Br^-$], referred to as 16–4–16, and the conventional ethoxylated nonionic surfactant $C_{12}E_6$, hexaoxyethylene *n*-dodecyl ether, [$CH_3\ (CH_2)_{10}CH_2\ (OCH_2CH_2)_6OH$]. 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 (τ_{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.

EXPERIMENTAL

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-bishexadecyl dimethylammonium bromide [$(C_{16}H_{33}N^+(CH_3)_2\ (CH_2)_4N^+(CH_3)_2\ C_{16}H_{33}\ )2Br^-$], referred as16–4–16, 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 μScm^{-1}, *p*H 6.8 at 303 K was used throughout as the solvent for all measurements.

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 logarithmof 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.

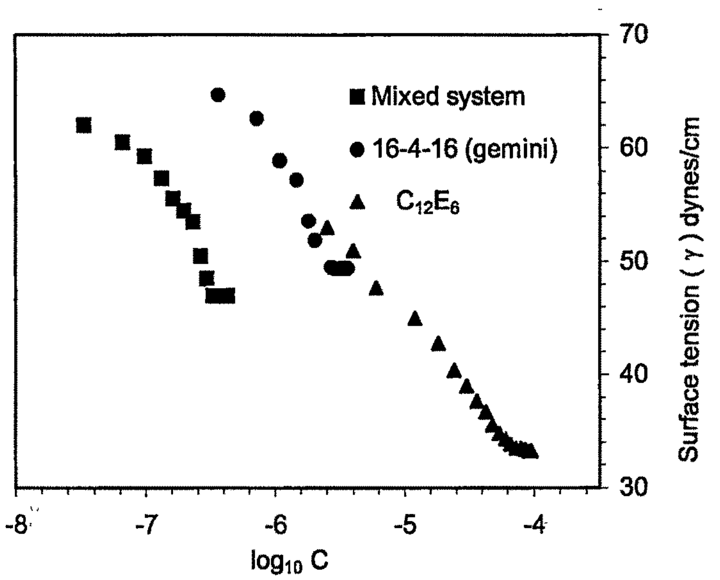

Fig.1 Representative plots of surface tension vs. $\log_{10}$ C for (■) Mixed 16-4-16: $C_{12}E_6$ (5:5), (•)Pure 16-4-16, (▲) Pure $C_{12}E_6$ at 30°C.

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 °C ±0.1 °C).

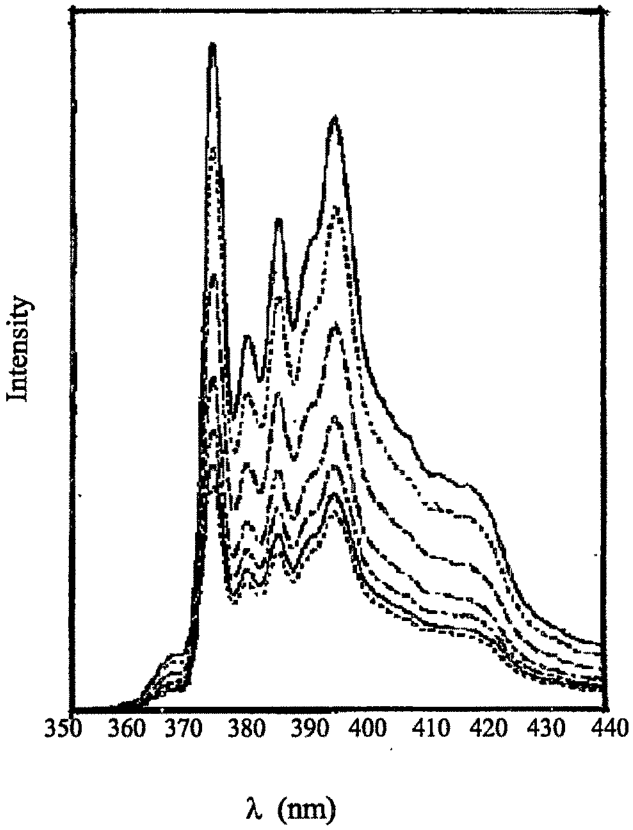

Fig.2 Representative fluorescence (emission) spectra of 10^{-5} M pyrene in aqueous micellar solution of 16-4-16: $C_{12}E_6$ (5:5) at different quencher concentrations (maximum Intensity indicates no quencher and minimum intensity indicates maximum amount of quencher).

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 x 10^{-5}M. The micellar aggregation number (N_{agg}) was deduced from the equation [28,29]

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

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

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

$$I_0/I = 1 + K_{SV}[Q] \tag{2}$$

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].

RESULTS AND DISCUSSION

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

Table 1. Critical Micelle Concentration Values for 16-4-16:$C_{12}E_6$ Mixed Surfactant Systems in Aqueous Medium at Different Temperatures.

	Critical micelle concentration (μ M)		
$N_{16\text{-}4\text{-}16}$	303	308	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] Ref 34-36

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.

The surface excess (τ_{max}/ molcm^{-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 (τ_{max}) and minimum area per molecule (A_{min}) values were calculated by the Gibbs adsorption equation [40],

$$\tau_{max}\left(molcm^{-2}\right)=\left(\frac{-1}{nRT}\right)\left(\frac{d\gamma}{d\ln C}\right) \tag{3}$$

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

where dγ/dlnC is the maximum slope in each case and R, T, C, and N are the gas constant, absolute temperature, concentration, and Avogadro number, respectively.

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.

	$\Gamma \times 10^{10}$ (molcm^{-2})			A_{min} (nm^2)		
$N_{16\text{-}4\text{-}16}$	303	308	313 K	303	308	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

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.

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]

$$\frac{X_1^{\,2}\ln\left(\alpha_1 C_{12}/X_1 C_1\right)}{(1-X_1)^2\ln\left[(1-\alpha_2)C_{12}/(1-X_1)C_2\right]}=1 \tag{5}$$

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

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 systems are listed in Table 3.

Table 3 Interaction Parameter Values for 16-4-16:$C_{12}E_6$ Mixed Surfactant Systems in Aqueous Medium at Surface Tension 55 dynes/cm (β^{σ}) and at cmc (β^{m}).

$N_{16\text{-}4\text{-}16}$	β^{σ}			β^{m}		
	303	308	313	303	308	313
0.1	-18.1(0.46)*	-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)

*In the parenthesis the value of X (ionic) is given.

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 dynes 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

$$\Delta G_m = RT(B_0 + B_1X_2 + B_2X_2^2) \tag{9}$$

$$\textit{where } B_o = \ln C_1 \quad (C_1 \text{ is the cmc of the nonionic surfactant}) \tag{10}$$

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

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

Table 4: B_0, B_1 and B_2 Values for 16-4-16:$C_{12}E_6$ Mixed Surfactant Systems.

		$C_{12}E_6$	
$N_{16\text{-}4\text{-}16}$	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(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.

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 differentmole 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 behavior was expected. However, by SANS studies [20], it was not possible to obtain the aggregation number of 16–4–16 gemini surfactant.

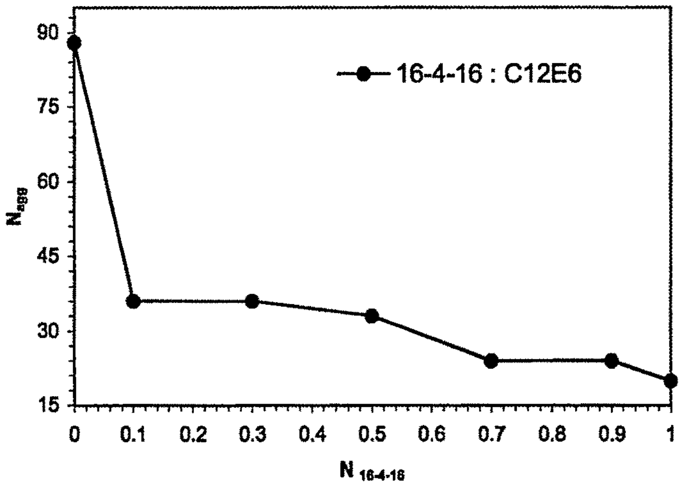

Fig.3 Variation of the aggregation Number (N_{agg}) for 16-4-16:$C_{12}E_6$ with the mole fraction of ionic surfactant in mixed surfactant systems. The solid lines are guide to the eyes.

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

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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.

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

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

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} (x10^5)	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).

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.

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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Chapter II B

Self Aggregation of Binary Surfactant Mixture of Cationic Dimeric (gemini) Surfactant with Nonionic Surfactants in Aqueous Medium II

ABSTRACT

Solubility, tensiometric, fluorometric and dynamic light scattering (DLS) measurements have been used to elucidate the self aggregation of a mixture of alkanediyl-α,ω type cationic gemini surfactant, $[(C_{16}H_{33}N^+(CH_3)_2(CH_2)_{10}N^+(CH_3)_2C_{16}H_{33})2Br^-]$,16-10-16, $2Br^-$ with POE nonionic surfactants, $[CH_3(CH_2)_{10}CH_2\text{-}(OCH_2CH_2)_6OH]$, $C_{12}E_6$ and $[(CH_3)_3CCH_2C(CH_3)_2C_6H_4\text{-}(OCH_2CH_2)_{9.5}OH]$ Triton X-100. The critical micelle concentrations (cmc) of the binary mixtures have been investigated at well above their Krafft temperatures in aqueous medium by tensiometric (at different temperatures at 5°C interval) measurements. Surprisingly it was observed that the Krafft temperatures of binary mixtures were higher than the pure gemini surfactant. Application of the regular solution model to the experimental data yield the interaction parameter at mixed micelles (β^m), and at the air – water interfaces (β^σ), which indicate an attractive interaction and reflect the synergistic behavior in both 16-10-16,$2Br^-$ /$C_{12}E_6$ and 16-10-16,$2Br^-$ /TX 100 systems. The micelle aggregation numbers (N_{agg}) of the binary combinations fall between those of constituent surfactants. The micropolarity values of various combinations and the binding constants (K_{sv}) were determined from the ratio of intensity of peaks (I_1/I_3) of pyrene fluorescence emission spectrum. The micellar interiors were found to be reasonably polar. By using Maeda's concept, it was observed that the chain-chain interactions were very important for stability of mixed micelle in these systems. The hydrodynamic radius (R_h) of TX 100 was higher than that of 16-10-16, $2Br^-$ while the mixed aggregates have intermediate values of R_h.

INTRODUCTION

Dimeric or Gemini surfactants, made up of two amphiphilic moieties connected at the level of hydrophilic groups or very close to these groups by spacer groups which can be either hydrophobic or hydrophilic, rigid or flexible, straight or branched are attracting considerable interest in both academic and industrial research [1-10]. The micellization behaviour of bis (quaternary ammonium) dimeric surfactant in which two cationic surfactant moieties (for instance, alkyl dimethyl ammonium bromide) are connected by a polymethylene chain (i.e. spacer), is the most investigated gemini surfactant [10-14]. Besides their unusual physicochemical properties [2-7], these surfactants show a very potent bactericidal activity [15,16], much larger than the conventional monoquaternary ammonium bromide, and are also useful as phase transfer catalysts [17] and in synthesizing ordered silicate mesoporous structure that are the analogs of lyotropic liquid crystals formed by the surfactants: hexagonal, cubic or lamellar [18]. These surfactants are currently extensively investigated for their possible use in various formulations by mixing with conventional ionic [19], nonionic [19-21], zwitterionic [21] and/or sugar based surfactants [22]. Mixtures of surfactant solutions form mixed micellar aggregates that exhibit characteristic properties, which are superior to those of the individual components and synergism can often be observed. An important mixed system is cationic gemini surfactant with a nonionic surfactant. In an earlier paper [23], we reported the self aggregation of binary surfactant mixtures of cationic gemini surfactant, butanediyl - α,ω–bisalkyldimethylammoniumbromide, 16-4-16,$2Br^-$ with $C_{12}E_6$ (hexaoxyethylene monododecyl ether). This paper aims to further extend the investigation of molecular interaction in mixed micellization of 1,10-decanediyl α–ω bishexadecyldimethylammoniumbromide[$(C_{16}H_{33}N^+(CH_3)_2(CH_2)_{10}N^+(CH_3)_2C_{16}H_{33})2Br^-$], 16-10-16,$2Br^-$ and the conventional ethoxylated nonionic surfactant having similar hydrophilic group (POE) but different hydrophobic tail part, $C_{12}E_6$ and Triton X-100 (TX 100). Both $C_{12}E_6$ and TX 100 having POE hydrophilic moieties are the most widely used nonionic surfactants. The hydration of these POE chains leads to the aqueous solubility of the molecules, and their temperature induced dehydration is chiefly responsible for the inverse relationship between aqueous solubility and temperature observed among these amphiphilic compounds. We studied the mixed surfactant properties well above the Krafft temperature (T_k) of gemini surfactant, as Fung et.al [24] mentioned that below T_k, the surfactant concentration is not high enough to form micelles. So it was essential to perform the experiments above the T_k [24]. Unfortunately, the cmc reported for several m-s-m dimeric surfactants were determined at 25°C, without considering their T_k [25]. On the one hand Rosen [1] stated that ionic gemini surfactants have much lower Krafft points and higher solubility in water than conventional surfactant, while on the other hand Zana [26] recently reported the Krafft temperature of series of 12-s-12, 16-s-16 and other cationic gemini surfactants and showed that the Krafft temperature may even be >45°C. Therefore, knowledge of the Krafft temperature of the surfactant is important which give information about the conditions in which a surfactant acts. This is useful to select an appropriate surfactant for a special application. In this article the mixed micelle of 16-10-16, $2Br^-$ with $C_{12}E_6$ and TX 100 are characterized by their solubility, tensiometric, fluorometric and light scattering techniques. The nature and strength of the interaction between the surfactant mixtures in monolayer at air/water interface and in micelle were obtained by calculating the values of their β parameters. We also obtained the micropolarity and binding constant for 16-10-16,$2Br^-$ / $C_{12}E_6$ mixed systems.

EXPERIMENTAL SECTION

Materials

$C_{12}E_6$,[MW=450.68, Lion corporation, Tokyo, Japan], and TX 100 [MW=625, Fluka, Germany] were used without further purification. Cationic dimeric (gemini) surfactant 16-10-16, $2Br^-$ was a gift sample from Prof. S. Bhattacharya, IISc, Banaglore, India and used as obtained. The synthesis and purification of this surfactant have been described earlier by Bhattacharya et. al. [13,14]. The surface tension vs concentration plot of these samples did not show any minimum. Cetyl pyridinium chloride (Loba Chemie, Baroda, India) was recrystallized twice from benzene. Pyrene (Fluka, Germany) was recrystallized from cyclohexane.. For Krafft temperature and CMC determination, triple distilled water was used as solvent and for fluorescence and DLS experiments the milli Q water was used.

Krafft temperature (T_k) measurements

The Krafft temperatures of 16-10-16, $2Br^-$ pure and mixed systems have been determined by electrical conductivity method [24,26,27]. The aqueous solution of surfactant (3 mM, i.e. well above the cmc) were prepared by warming it to ~ 40°C and placed in a refrigerator at ~5°C for at least 24 h where in the precipitation of the surfactant hydrated crystal occurred. Then temperature of the precipitated system was raised gradually under constant stirring and the conductance (κ) was measured using Welltronix digital conductivity meter CM 100 having cell constant 1.00 cm^{-1}. The Krafft temperature was taken as the temperature where the conductance vs temperature plots showed an abrupt change in slope. This temperature was the same as that required to completely dissolve the hydrated solid surfactant and it can also be judged visually to be the point of complete clarification of the surfactant system. The reproducibility of T_k measurements was ± 0.1°C.

Surface tension measurements

The surface tension (γ) of the aqueous surfactant solutions was measured by duNoüy tensiometer at 30, 35 and 40°C. The experimental method was same as reported elsewhere [23,27,28]. 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.

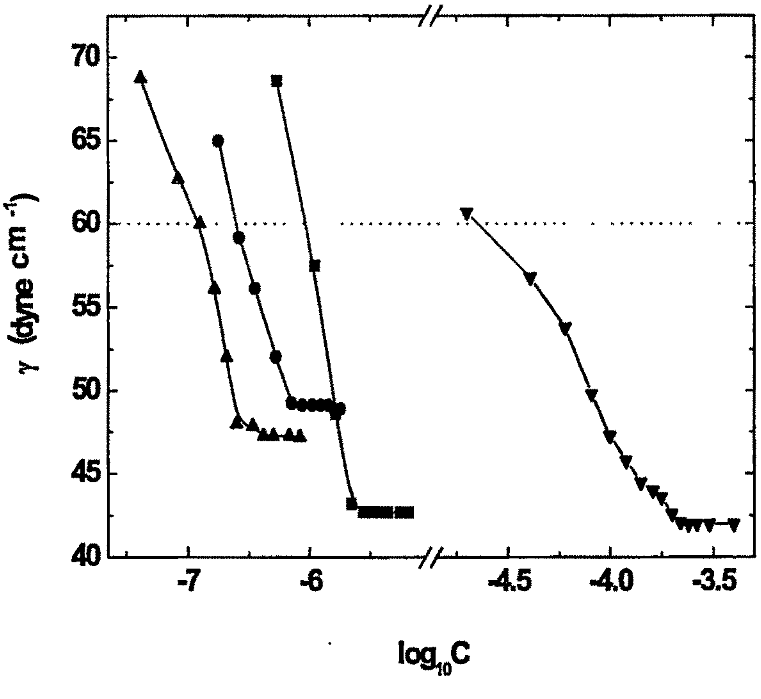

Fig. 1 Representative plots of surface tension vs. $\log_{10}$ C for (■) pure 16-10-16,2Br$^-$, (●)16-10-16,2Br$^-$:TX 100 (3:7), (▲)16-10-16,2Br$^-$:TX 100 (7:3), (▼) TX 100 at 35°C. The $\log_{10}$C values at 60 dyne cm^{-1} were used to calculate the β^{σ}s.

Fluorescence Measurements

The micellar aggregation number (N_{agg}) of single and mixed surfactant solutions were determined by steady state fluorescence quenching measurements[23] at 25±0.1 °C. 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 x 10^{-5}M. The N_{agg}, binding constant and micropolarity were determined by using various required equations as present in the literature [23,29-31].

Dynamic Light Scattering (DLS).

Multiangle DLS measurements were carried out for 16-10-16, $2Br^-$:TX 100 surfactant system (total concentration 5 mM) at five different scattering angles (50, 70, 90, 110 and 130°) using a Malvern 4800 photon correlation spectrometer[27]. 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 intensity correlation function was measured 5 times for each sample at each angle. The surfactant solutions were filtered through 0.2 μm millipore nylon filter directly in to the sample cell, and the cells were sealed until use. The average decay rate was obtained from the measured autocorrelation function using the method of cumulants employing a quadratic fit [32] and the error in these repeated measurements was approximately 5%.

RESULTS AND DISCUSSION

Krafft temperature (T_k) of pure dimeric and mixed surfactant solutions

The Krafft temperature can be defined as the melting point of hydrated surfactant [33 a]. It is observed that at low temperature, conductance of pure as well as mixed hydrated surfactant mixtures increase slowly because the solubility of the ionic surfactants are quite limited. During the temperature transition stage, conductance increases sharply with increasing temperature, due to larger dissolution of the surfactant until the T_k. Then after T_k, the conductance increases slowly due to the increase in ionic mobility with increasing temperature [24]. The T_k of pure 16-10-16, $2Br^-$ was found to be 12.5°C , which is nearer to 16-12-16,$2Br^-$ (13.5 °C) [26] than for 16-4-16,$2Br^-$ which was 34.5°C (determined by us), which are in good agreement with reported values 33.6 [24], and 35.0 [26]. Fung et.al [24] observed that T_k does not change regularly with the change of spacer, and concluded that enlargement of the spacer not only increases the hydrophobicity of the surfactant but also decrease the columbic interaction between the positive charges in the head group as well as their interaction with the bromide ions, and the two effects counteract each other to a large extent. The Krafft temperatures of $C_{12}E_6$ and TX 100 were found to be <1°C as it was observed visually that the pure aqueous surfactant solutions of these surfactants did not show any turbidity even at 1°C. The T_k of dimeric surfactant increases with the increasing ratio of nonionic monomeric surfactant (Table 1) as nonionic surfactant makes gemini surfactant less soluble. However addition of nonionic surfactant increases this value, which is a bit surprising.

Table 1 Krafft temperature values for 16-10-16,2Br$^-$:$C_{12}E_6$ and 16-10-16,2Br$^-$:Triton X-100 (TX 100) mixed surfactant systems in aqueous medium at different mole fractions of gemini surfactant.

$\alpha_{16\text{-}10\text{-}16,2Br^-}$	$C_{12}E_6$	TX 100
	Temperature °C	
1.0	12.5	12.5
0.9	13.0	24.0
0.7	15.6	23.2
0.5	15.8	21.2
0.3	16.0	17.0
0.1	<0	<0
0.0	<0	<0

Hence we believe that gemini surfactant is probably interacting strongly with nonionic surfactant and behaves as one single species possibly because of favourable packing conditions. As nonionics did not show any T_k even at 1°C, we believe the T_ks that we obtained were those of the mixtures. It was not that of pure gemini. However it has been noted that the variation in T_k is not always regular and sometimes quite dramatic changes are observed [33 b]. Mixture of 16-10-16, 2Br$^-$ and TX 100 has less solubility in water than the mixture of 16-10-16, 2Br$^-$ and $C_{12}E_6$. This may be due to demicellization of cationic gemini surfactant by TX 100 surfactant. However for 16-10-16, 2Br$^-$ / TX 100 mixed system the T_k first increase, then decrease progressively on addition of TX-100. However mixed systems show higher Krafft temperature than pure gemini, 16-10-16,2Br$^-$. For 1:9 (Gemini: Nonionic surfactant) ratio of mixed system as well as for pure nonionic we could not obtain any T_k value.

Surface properties of surfactant mixtures

The cmc values of single as well as binary surfactant mixtures are presented in Table 2. The cmc values of pure $C_{12}E_6$ and TX 100 at a given temperature are in good agreement with reported values in literature [34,35]. However, the cmc values for 16-10-16, 2Br$^-$ as well as 16-4-16,2Br$^-$ [23] that we determined are ~10 times lower than the literature value determined by fluorescence technique [13].

Table 2. Critical micelle concentration values for 16-10-16, 2Br$^-$:$C_{12}E_6$ and 16-10-16, 2Br$^-$: TritonX-100 (TX 100) mixed surfactant systems in aqueous medium at different temperatures. (α=mole fraction)

	Critical micelle concentration (10^{-6} M)					
$\alpha_{16\text{-}10\text{-}16}$	$C_{12}E_6$			TX 100		
	303	308	313	303	308	313 K
0.0	71.0 (71.0^a)	62.0	51	250	220	200
0.1	1.0	0.85	0.74	2.75	2.57	2.34
0.3	0.67	0.60	0.55	1.05	0.79	0.71
0.5	0.50	0.45	0.39	0.79	0.56	0.50
0.7	0.40	0.35	0.31	0.50	0.42	0.34
0.9	0.33	0.26	0.23	0.37	0.33	0.22
1.0	3.2	2.5	2.2	3.2	2.5	2.2

^{a} Ref. 34

Zana et. al [36] mentioned that the fluorescence technique is not a good method for determining cmc for gemini surfactant, and suggested that surface tension is a more suitable method for cmc determination. Also conductometric method is not very suitable when dealing with mixed systems of nonionic (with very low cmc) with ionic [27]. The cmc values of conventional nonionic $C_{12}E_6$ and TX 100 as well as dimeric 16-10-16, 2Br$^-$ were found to decrease with the increase in temperature (Table 2). This phenomenon is generally seen for nonionic surfactant [37]. With an increase in the temperature, the dehydration of hydrophilic groups of $C_{12}E_6$ and TX–100 take place, which results in an increase in hydrophobic interaction and consequently the cmcs decrease. Surfactants with long POE chains have the greatest solubility in water because of extensive hydrogen bonding with the solvent. As the dielectric constant of water decreases with temperature, hydration of the POE chains diminishes when the solution is heated. In TX 100, the phenyl group of the hydrophobic tail is equivalent to three and one half methylene group [37]. As $C_{12}E_6$ has higher number of C-atom in their hydrophobic moiety than TX 100 and as TX 100 has more number of OE units than $C_{12}E_6$, the cmc of TX 100 is higher than that of $C_{12}E_6$. The decrease in the cmc for 16-10-16, $2Br^-$ with increasing temperature may be due to enhancement of hydrophobicity of the surfactant molecules with increase in temperature due to dehydration. However if we had measured cmc at still higher temperature we might have seen a minimum due to breaking of ice berg structure which does not favour micellization i.e. we should have gotten higher cmc as is generally the case for an ionic surfactant. The cmc values of 16-10-16,$2Br^-$/ $C_{12}E_6$ and 16-10-16,$2Br^-$/TX 100 mixed systems, as well as those of the pure surfactants were evaluated by surface tension (γ) measurement only. From Table 2, it can be seen that in the mixed surfactant systems at any mole ratio, the cmc value is lower than either pure 16-10-16, $2Br^-$ or $C_{12}E_6$ / TX 100 surfactant, indicating a synergistic behavior (Figure 1). The cmc values of mixed systems were also found to decrease with increasing temperature. The decrease in cmc values indicate that the surfactant molecules in mixed systems 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.

Surfactant-surfactant Interaction

The cmc values for the mixed surfactant system (c_{12}) can be calculated theoretically using the Clint's equation [38]

$$\frac{1}{c_{12}} = \frac{\alpha_1}{c_1} + \frac{1-\alpha_1}{c_2} \qquad (1)$$

where 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-α_1) is the mole fraction of surfactant 2 in solution respectively. The cmc values thus obtained from equation 1 and experimentally (cmc_{exp}) are plotted as a function of mole fraction of 16-10-16, 2Br⁻ in Figure 2, that cmc_{exp} values are lower than c_{12} values which indicate that there are interactions between the constituent surfactants in the mixed micelle resulting in nonideal behavior.

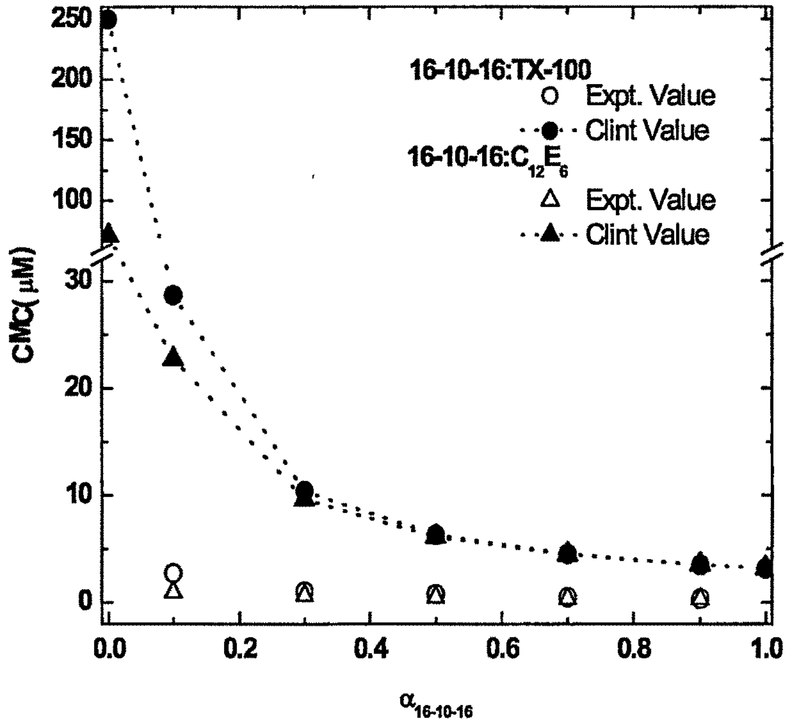

Fig. 2 Plot of mole fraction of 16-10-16 ($\alpha_{16\text{-}10\text{-}16}$) vs CMC for 16-10-16,2Br⁻:TX 100 and 16-10-16, 2Br⁻: $C_{12}E_6$ mixtures at 30°C.

Hence in order to investigate the nature of interaction between the surfactants in the mixed micelle, we calculated the interaction parameter using Rubingh as well as Maeda's theory [39,40] respectively.

Interaction parameter (β^{σ}) for mixed monolayer at the air/water interface as well as in the mixed micelle (β^{m}) were calculated by the usual equations that exist in literature [23,37]. The β^{σ} values change with overall surface tension and hence they were computed at a fixed γ values of the solution, 60 dynes cm^{-1} (see Fig 1). The β^{σ} or β^{m} values for these mixed systems are listed in Tables 3 and 4.

Table 3 Interaction parameter (β^{σ}) values for 16-10-16, 2Br$^-$:$C_{12}E_6$ and 16-10-16, 2Br$^-$:Triton X-100 (TX 100) mixed surfactant systems in aqueous medium at different temperatures at surface tension 60 dynes/cm. (α=mole fraction)

α 16-10-16	β^{σ} at air/water interface					
	$C_{12}E_6$			TX 100		
	303	308	313	303	308	313 K
0.1	-5.6 (0.34) *	-8.6 (0.42)	-6.9 (0.40)	-12.1 (0.51)	-11.9 (0.54)	-17.8 (0.59)
0.3	-7.0 (0.44)	-8.9 (0.48)	-7.0 (0.48)	-10.0 (0.57)	-9.0 (0.61)	-16.6 (0.63)
0.5	-9.4 (0.49)	-8.8 (0.52)	-8.9 (0.52)	-9.5 (0.61)	-11.7 (0.62)	-15.1 (0.69)
0.7	-8.9 (0.53)	-8.7 (0.56)	-7.1 (0.57)	-15.7 (0.60)	-13.2 (0.63)	-17.2 (0.67)
0.9	-10.9 (0.58)	-8.7 (0.62)	-8.3 (0.63)	-17.4 (0.62)	-15.6 (0.65)	-16.8 (0.71)

*In the parenthesis the value of $X_{16\text{-}10\text{-}16}$ at interface is given.

Table 4 Interaction parameter (β^{m}) values for 16-10-16, 2Br$^-$:$C_{12}E_6$ and 16-10-16, 2Br$^-$: Triton X-100 (TX 100) mixed surfactant systems in aqueous medium at different temperatures. (α=mole fraction)

α 16-10-16	β^{m} for mixed micelle formation					
	$C_{12}E_6$			TX 100		
	303	308	313	303	308	313 K
8	-12.8 (0.53)	-12.7 (0.53)	-12.6 (0.53)	-11.0 (0.58)	-10.5 (0.52)	-10.4 (0.60)
0.3	-12.5 (0.58)	-12.1 (0.58)	-11.8 (0.58)	-12.7 (0.62)	-13.0 (0.62)	-13.0 (0.62)
0.5	-12.9 (0.60)	-12.6 (0.61)	-12.5 (0.61)	-13.1 (0.64)	-13.7 (0.64)	-13.6 (0.64)
0.7	-13.9 (0.62)	-13.6 (0.63)	-13.4 (0.63)	-14.9 (0.65)	-14.8 (0.66)	-15.2 (0.66)
0.9	-15.7 (0.65)	-15.9 (0.65)	-15.7 (0.65)	-17.2 (0.67)	-16.7 (0.68)	-18.0 (0.67)

*In the parenthesis the value of $X_{16\text{-}10\text{-}16}$ in micelle is given.

The tables indicate that the composition of mixed micelles and mixed monolayers are independent of the composition of surfactant solution as well as temperature. That is the mixed systems are very stable. As seen from the tabulated data both β^{σ} or β^{m} values are negative throughout, showing attractive interaction (synergism) between the constituent surfactant molecules. 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 component of the mixtures [41]. The nonionic surfactants of POE class have a large number of oxygen with unpaired electrons. These will have a tendency to react coulombically with the cationic gemini surfactant. The β^{σ} values for 16-10-16, 2Br$^-$ /$C_{12}E_6$ system are less negative than the β^{m} in all cases, which may be due to the difficulty of incorporating tightly packed chains into a monolayer than a micelle. However in the case of 16-10-16, 2Br$^-$ / TX 100 both β^{σ} and β^{m} are more or less same. The β^{m} values for a system where the chains are not tightly packed are generally similar to the β^{σ} [37]. The activity coefficients were calculated using the relation [37]

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

$$\ln(f_2) = \beta^{m}(X_1)^2 \quad (3)$$

where X_1 is the mole fraction of surfactant 1 in the micelle and f_1 & f_2 are the activity coefficients of surfactants 1 & 2 respectively, in the mixed micelle. The activity coefficient values (f_1 and f_2) of 16-10-16, 2Br$^-$/$C_{12}E_6$ and 16-10-16, 2Br$^-$/ TX 100 mixed surfactant systems in aqueous medium at different temperatures were computed. Activity coefficient 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 non ideal behaviour and attractive interaction between the surfactants in the micelle (data are not given). The activity coefficient values of 16-10-16, 2Br$^-$ are high in both the mixed systems and f_2 values of $C_{12}E_6$ and TX 100 are low, indicating negative deviation from ideality and an attractive interaction. It is also interesting to note that the X values, both in the mixed micelles and in mixed monolayers, are almost (though not exactly) the same, with a little higher value in micellar state. The temperature does not seem to have any effect on the composition of either micelle or surfactants at 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 [40] as well as Ruiz et al. [41] have stated that both chain - chain and head group – head group interactions are present in a mixed system. According to Maeda, β^m values obtained by the use of regular solution theory encompass the head group – head group interactions but not the hydrocarbon chain – chain interactions, particularly when the chains are of dissimilar length. Maeda [40] 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 molecule between the head groups. He suggested that besides the regular solution interaction parameter, there could be another parameter (B_1) which 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

$$\Delta G_m = RT(B_0 + B_1X_2 + B_2X_2^2) \tag{4}$$

where $B_o = \ln C_1$ (C_1 is the cmc of the nonionic surfactant) (5)

$B_1 + B_2 = \ln\left(\frac{C_2}{C_1}\right)$ (C_2 is the cmc of the ionic surfactant) (6)

$$B_2 = -\beta^m \tag{7}$$

where B_1 is associated with standard free energy change when an ionic surfactant replaces a nonionic surfactant (cmc of which is related with B_o). B_2 is the regular solution theory interaction parameter but with opposite sign. 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 5. Hence ΔG_m can be calculated.

Table 5: B_0, B_1 and B_2 values for 16-10-16, $2Br^-$:$C_{12}E_6$ and 16-10-16, $2Br^-$: Triton X-100 (TX 100) mixed surfactant systems. (α=mole fraction)

$\alpha_{16\text{-}10\text{-}16}$	$C_{12}E_6$			TX 100		
	B_0 (avg)	B_1	B_2	B_0 (avg)	B_1	B_2
0.9	-13.7	-20.4	17.34	-12.3	-23.6	19.2
0.7		-17.7	14.6		-20.2	15.8
0.5		-16.0	12.9		-17.4	13.1
0.3		-14.8	11.7		-15.9	11.5
0.1		-13.8	10.7		-15.4	11.0

We expect the chain-chain interaction to be independent of head group-head group interaction in the above calculations. However as the β^m values increase with the increase in gemini surfactant concentration it is suggested that some nonelectrostatic interaction may also be present. Hence we believe that chain-chain and head group- head group interactions are not totally independent of each other. Also the standard free energy of micellization of nonionic surfactant is given by the relation [37]

$$\Delta G_m^o = RT \ln X_{cmc} \qquad (8)$$

where X_{cmc} is the cmc in mole fraction scale, whereas for an ionic as well as mixed surfactant system,

$$\Delta G_m^o = (2-a) RT \ln X_{cmc} \qquad (9)$$

where a is the degree of ionization of micelle which is computed from the ratio between slopes of the post micellar and premicellar regions of the conductance – concentration profile of ionic as well as ionic/nonionic binary surfactant mixture. However, we did not observe break point in the conductance – concentration profile for both 16-10-16,$2Br^-$/$C_{12}E_6$ and 16-10-16, $2Br^-$/TX 100 mixed surfactant system and hence treated the mixed systems as nonionic one and evaluated ΔG_m^o using equation 8. It is interesting to note that the ΔG_m^o values calculated by using

Eq. 8 and by Maeda's method (equ. 4) agree reasonably well (within ±3%). This indicates that the degree of counter ion binding of the mixed micelles is probably negligible. The B_1 values are highly negative, 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 nonionic surfactant $C_{12}E_6$ and TX 100 have 12 and 7.5 carbons respectively. Hence according to Maeda, as the chain lengths are very different; there should be strong chain – chain interaction helping in the stability of the micelle. However the B_1 values seem to be a function of composition of a system as well as the head groups.

Micellar Aggregation numbers (N_{agg}) in Cationic Gemini/Nonionic surfactant mixtures

Fluorescence method is a convenient method to determine the micelle aggregation numbers (N_{agg}) [41]. We determined N_{agg} by steady state fluorescence quenching method at different mole ratios of the binary 16-10-16, $2Br^-$ / $C_{12}E_6$ mixtures. The values N_{agg} of pure and mixed surfactants are given in Table 6.

Table 6: Aggregation number (N_{agg}), Micropolarity (I_1/I_3) Binding constant (K_{sv}) and apparent dielectric constant (ε) for 16-10-16, $2Br^-$:$C_{12}E_6$ mixed surfactant systems. (α=mole fraction)

$\alpha_{16\text{-}10\text{-}16}$	N_{agg}	$X_{16\text{-}10\text{-}16}$ at micelle	I_1/I_3	K_{sv} (10^5)	Expt ε^a	Calc ε^b
1.0	12	-	1.38	0.85	30.0	30.0
0.9	13	0.65	1.36	0.88	28.4	21.3
0.7	18	0.62	1.35	1.46	27.6	20.4
0.5	23	0.60	1.35	1.85	27.6	19.9
0.3	25	0.58	1.32	2.09	25.2	19.3
0.1	35	0.53	1.25	3.98	19.6	18.1
0.0	88	-	1.17	9.69	13.2	13.2

ε^a calculated from eqn 14, *ε^b calculated from eqn 15*

It is evident that the $N_{agg.}$ values of the mixed surfactant system are larger than 16-10-16, 2Br$^-$ but lower than $C_{12}E_6$ single surfactant at all mole ratios. Such behavior was expected. However by small angle neutron scattering studies it was found that N_{agg} of 25, 50, 75 and 100mM of 16-10-16, 2Br$^-$ are 47, 50, 80 and 87 respectively [13]. These results indicate the increase in number density of 16-10-16, 2Br$^-$ micelle from sphere to ellipsoid or oblate ellipsoid [13]. However these concentrations were very high. We decreased the surfactant concentration to 2mM and by fluorescence study the N_{agg} was found to be 12 and at the same concentration N_{agg} for 16-4-16,2Br$^-$ was 20 [23]. The decrease *of* N_{agg} in the mixed 16-10-16, 2Br$^-$ /$C_{12}E_6$ system, is obviously associated with the increased average repulsive interaction between head groups with increasing 16-10-16, 2Br$^-$, as nonionic surfactant molecules are progressively replaced by cationic dimeric surfactants as well as a more difficult geometry of association of the system. 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 16-10-16, 2Br$^-$ 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.

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]. The I_1/I_3 values (>1) suggest a polar environment around pyrene. I_1/I_3 and K_{sv} are presented in Table 6. Representative plot of In I_0/I vs concentration of quencher [Q] for different mixed systemsare presented in figure 3. K_{sv} is the ratio of bimolecular quenching constant to unimolecular decay constant. Also K_{sv} is the product of k_q, the rate constant of quenching process and τ, the actual life time of probe in absence of bimolecular quenching [30]. Thus from the values of K_{sv}, we can assume that quenching is efficient; also the life time 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.

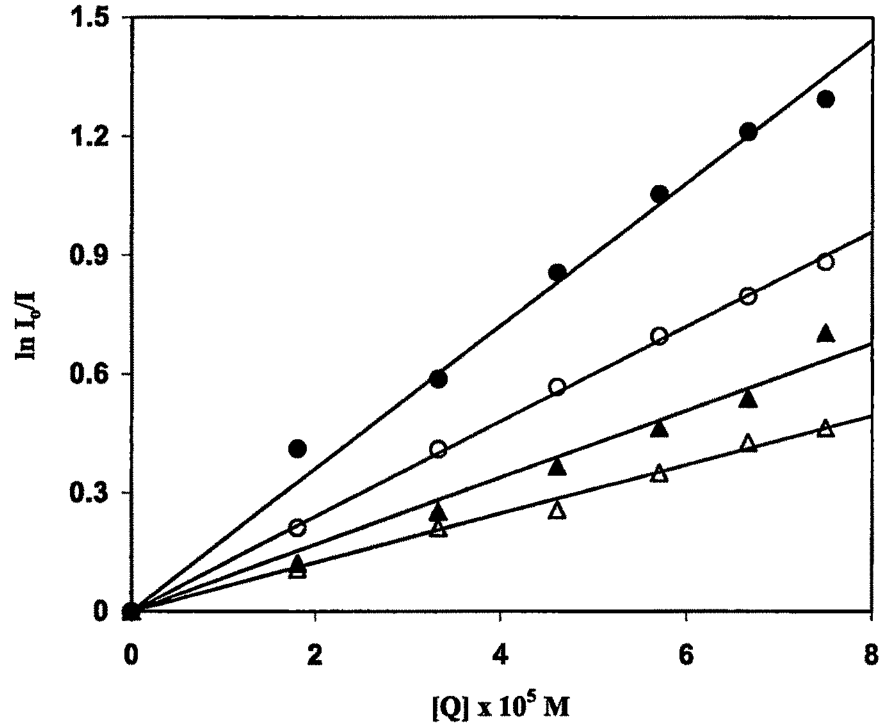

Fig. 3 Representative plot of ln I_o/I vs concentration of quencher [Q] for different mixed systems 16-10-16,2Br⁻:$C_{12}E_6$ ● 1:9, o 3:7, ▲ 7:3, Δ pure 16-10-16,2Br⁻ at 25°C.

The apparent dielectric constant (ε) of the medium (in this case the pyrene environment inside the micelle) can be estimated [42] by employing the following relation

$$I_1/I_3 = 1.000461 + 0.01253\varepsilon \qquad (10)$$

In our present study we have computed the apparent dielectric constant of the interior of pure micelles as well as of 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 [38]. The observed results are reasonable where we compare two nonionic surfactants $C_{12}E_6$ and $C_{12}E_8$ as the more the oxyethylene group in the system, the higher the dielectric constant should be. According to Turro [42], the dielectric constant inside the mixed micelle can be computed from the following relation

$$\varepsilon_{12} = \Sigma X_i \, \varepsilon_i \tag{11}$$

In Table 6 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 interaction inside the micelle.

Dynamic Light Scattering (DLS)

Figure 4 represents the average decay rates of electric field correlation functions (Γ) as a function of q^2 for 5mM 16-10-16/Triton X-100 mixed surfactant system. The magnitude of the scattering vector (q) is given by [43]

$$q = \frac{4\pi n \sin(\theta/2)}{\lambda} \tag{12}$$

where n, θ and λ are refractive index of solvent, scattering angle (50 – 130°) and wave length of laser in vacuum respectively. The diffusion coefficient (D_0) values were obtained from the slope of Γ vs q^2 plot. The corresponding equation being $\Gamma = D_o q^2$.

For small, dilute, noninteracting spheres the hydrodynamic radius, (R_h) can be obtained from translational diffusion coefficient values by applying the well known Stokes-Einstein equation

$$R_h = \frac{k_B T}{6\pi \eta_o D_0} \tag{13}$$

where k_B is the Boltzmann constant, T and η_0 are the absolute temperature and solvent viscosity respectively. The diffusion coefficient (D_o) and hydrodynamic radius of micelle *(R_h)* values are plotted as a function of mole fraction of 16-10-16 in Figure 5.

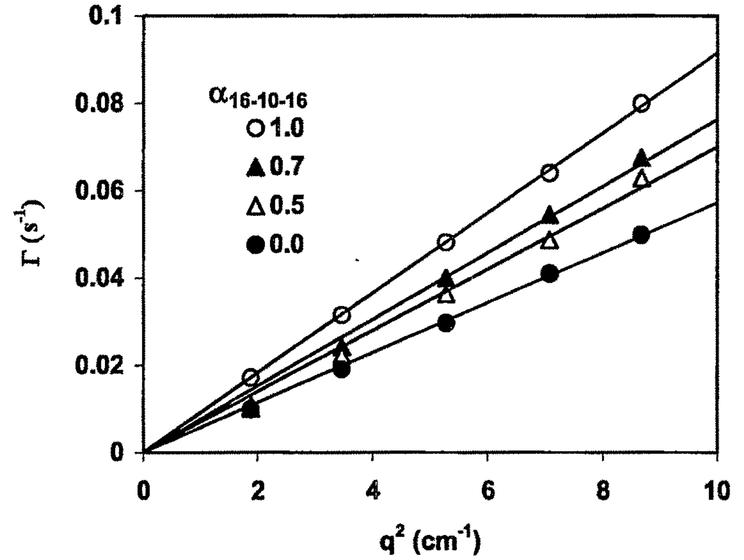

Fig. 4 Average decay rate of the electric field correlation function (Γ) as a function of q^2 for 5mM Triton X 100 at varying mole fraction of 16-10-16 ($\alpha_{16\text{-}10\text{-}16}$) at 25°C.

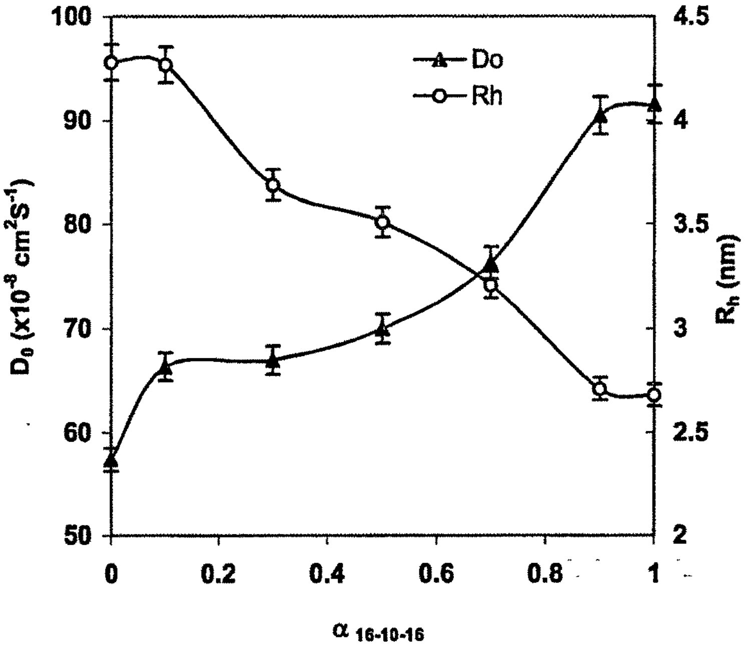

Fig 5 Apparent diffusion coefficients (D_o) and hydrodynamic radius (R_h) as a function of the mole fraction of 16-10-16, $X_{16\text{-}10\text{-}16}$ in 16-10-16/TX 100 mixture at 25°C.

It is evident from Figure 5 that the R_h values for mixed system are higher than that of 16-10-16 but lower then TX-100. This is because the head group-head group repulsions between the gemini molecules are reduced due to the presence of TX 100 in the mixed molecule.

CONCLUSIONS

The interfacial and micellar behavior in a mixture of cationic dimeric surfactant, 16-10-16, 2Br$^-$ with the POE nonionic surfactants $C_{12}E_6$ and TX 100, systems were studied well above the Krafft temperature. The Krafft temperature of dimeric surfactant increases with the increasing ratio of nonionic monomeric surfactant, as nonionic surfactant make 16-10-16, 2Br$^-$ less soluble. Mixture of 16-10-16, 2Br$^-$ and TX 100 has less solubility in water than 16-10-16, 2Br$^-$ and $C_{12}E_6$. The cmc value in mixed surfactant systems at any mole ratio is less than either of pure 16-10-16, 2Br$^-$ or $C_{12}E_6$/TX 100, by which we observed, the attractive interaction in the mixed micelle both at the monolayer at the air/water interface as well as in micelle. The interaction parameter in micelle (β^m), and at the monolayer air – water interface (β^σ), indicate an attractive interaction and reflect the synergistic behavior in both the systems. Aggregation number values of the mixed surfactant systems lie between the pure constituent surfactants at all mole ratios. The micropolarity values of mixed systems are almost same but binding constant values decrease on increasing the mole fraction of 16-10-16,2Br$^-$. The hydrodynamic radius of mixed micelle are higher than that of 16-10-16, 2Br$^-$ but lower than TX 100. The chain – chain interactions seem to be very important for the stability of mixed micelles.

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