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Properties of Mixed Aqueous Micellar Solutions Formed by Cationic Alkanediyl-α,ω-bis(tetradecyldimethylammonium bromide) and Alkyltrimethylammonium Bromides: Fluorescence and Conductivity Studies[†]

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Mixed micellization behavior of three dimeric cationic surfactants alkanediyl-α,ω-bis(tetradecyldimethylammonium bromide) (referred to as 14−*s*−14, where *s* = 4, 5, 6) with two cationic conventional surfactants (hexadecyltrimethylammonium bromide and tetradecyltrimethylammonium bromide) have been studied using conductance and fluorescence techniques. Critical micelle concentration for different mixing mole fractions, their ideal values, interaction parameters, micellar mole fractions, and activity coefficients have been evaluated using Rubingh's theory. Motomura's theory is also used to calculate the micellar mole fractions. All these parameters indicate nonideal but synergistic behavior. Aggregation numbers from fluorescence quenching suggest that contribution of the conventional surfactants is always greater than that in the ideal state.

Introduction

Surfactants are found throughout a wide spectrum of biological systems and medical applications, soil remediation techniques, and other environmental, health, and safety applications. They may also be applied to advantage in the production and processing of food, pharmaceuticals, laundry products, and petroleum.

Most of the practical surfactant applications rely on mixtures of surfactant/surfactant[1,2] or surfactant/polymer,[3] either because commercial surfactants are always mixtures due to raw materials used and method of manufacture or because of their improved action over single pure surfactants.[1,4] For example, liquid detergents usually contain synthetic anionic surfactants, nonionic surfactants, and natural soaps.[5]

From a purely fundamental point of view, the study of surfactant mixtures contributes to the understanding of the process of micellization.[6] Practically, this understanding is of utmost importance in view of appropriate industrial applications of these systems which pave the way to locate the most suitable mixture with desired surface activity from application as well as economics points of view.[7]

Mixtures of surfactants often exhibit nonideal behavior which can also be influenced by a difference in surfactant structures such as sizes of surfactant heads or tails. The interactions which lead to nonideality in solutions may be either favorable or unfavorable. Favorable interactions (or synergistic interactions) have been shown by ionic/nonionic, ionic/zwitterionic, and cationic/anionic surfactant mixtures.[8−10] These interactions result in critical micelle concentration (cmc) and interfacial tensions that are quite different than would be expected on the basis of the properties of pure surfactants.

Several theories have been developed by different investigators for predicting the interactions in binary surfactant systems. The first model given by Lange[11] and used by Clint[12] focused on ideal mixing. Rubingh,[13] Rosen,[14] and others[15−17] considered mixed micellization as a nonideal process. They treated binary mixtures using the pseudophase separation model. In this treatment, nonideality is included in the form of activity coefficients of each component in the bulk phase. More recently, Rodenas[18] used a simple theoretical treatment, based on Lange's model that utilizes the Gibbs−Duhem equation, to relate the activity coefficients of the surfactants in the mixed micelles. Although these models give satisfactory results, they are sometimes criticized on thermodynamic grounds.[19,20] Motomura,[21,22] Georgiev,[23] Maeda,[24] and Blankschtein[17,25−29] have thermodynamically formulated their models for mixed systems. In this respect, the contribution by Blankschtein's[17,25−29] group needs special mention whose molecular-thermodynamic approach has been successful for predicting solution properties of mixed surfactant systems.

Nowadays, a new class of surfactants known as gemini are attracting considerable interest in both academic and industrial research laboratories. These surfactants are amphiphilic molecules consisting of two hydrophobic tails and two hydrophilic head groups covalently attached to a spacer. The spacer group can be hydrophilic or hydrophobic, short or long, and rigid or flexible.[30−33] Hence, the spacer represents a new structural parameter to tune the behavior and properties of the amphiphile, in addition to the classical variation of the nature of the hydrophilic headgroup and the hydrophobic tail. The presence of the spacer group connecting the amphiphilic moieties permits the synthesis of dimeric surfactants with an enormous variety of structures and thus possibly opens the door to properties that cannot be achieved with pure conventional surfactants.

All the gemini surfactants show two important features, viz., much lower cmc values and high efficiency to reduce the surface tension of water.[34] Due to their high cost of preparation, they are likely to be used in combination with conventional surfactants. In such mixtures, favorable or synergistic interactions may be found, which make these systems even more attractive and useful.[35,36]

Keeping this in mind, we have selected some combinations of three cationic gemini surfactants, alkanediyl-α,ω-bis(tetradecyldimethylammonium bromide) (referred to as 14−*s*−14, where *s* = 4, 5, 6) with two conventional cationic surfactants, hexadecyltrimethylammonium bromide (CTAB), and tetrade-

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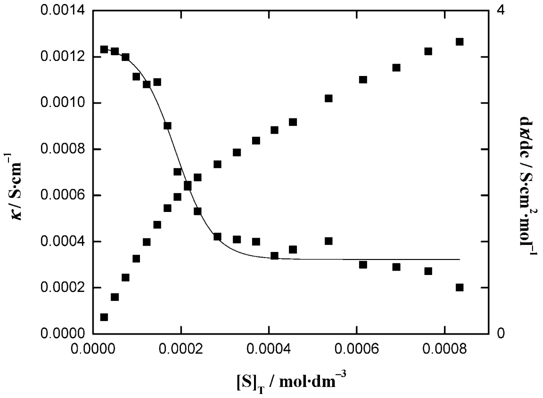

Figure 1. Plots of conductivity (κ) and first derivative of conductivity (dκ/dc) of 14−4−14 + CTAB versus total surfactant concentration $[S]_T$ at α_{CTAB} = 0.2.

cyltrimethylammonium bromide (TTAB), to study their mixed micellar properties with the help of conductivity and fluorescence measurements. The aim of selecting these surfactants is to have insight on various factors which may affect the behavior of mixed micelles, e.g., headgroup variation, chain length variation, and effect of incompatible/compatible chain lengths.

Materials and Methods

CTAB (98 %, Merck, Germany) and TTAB (99 %, Sigma, Germany), due to their high purities, were used as received. Pyrene (98 %, Acros Organics) was purified by recrystallizing several times from hexane. The gemini surfactants (symbolized as 14−4−14, 14−5−14, and 14−6−14) were synthesized according to the literature method.[37] The purity of the materials was checked by ^{1}H NMR spectroscopy.

(a) Determination of cmc and Degree of Counterion Binding (χ). A series of mixed surfactant systems of different mole fractions were prepared from equimolar stock solutions of conventional and gemini surfactants (for gemini + CTAB or TTAB the concentrations were $5 \cdot 10^{-3}$ mol·dm^{-3}). Stock solutions of surfactants were prepared by dissolving the calculated amount of surfactant in double distilled water of specific conductivity: (10 to 50) μS·cm^{-1}. An ELICO conductivity bridge, model CM82T, and dip cell (cell constant: 1.02 cm^{-1}) were employed to perform the conductivity measurements at 303 K. The conductivity at each mole fraction was measured by successive addition of concentrated solution of surfactant mixture in pure water. Differential conductivity (dκ/dc) plots in all cases were used to determine the cmc; they are considered to give more accurate cmc values than the values evaluated only from κ plots. A representative example of dκ/dc is given in Figure 1. The degree of counterion binding (χ) was determined from the ratio of the slopes of the conductivity versus surfactant concentration plots above and below the cmc.

(b) Determination of Micelle Aggregation and Stern−Volmer Constant (K_{sv}). A $3 \cdot 10^{-3}$ mol·dm^{-3} pyrene solution was prepared in ethanol. An aliquot of this solution was transferred into a standard volumetric flask, and the solvent was evaporated. The surfactant solution was added so that the pyrene concentration became $2 \cdot 10^{-6}$ mol·dm^{-3}, which was kept constant in all experiments. The total surfactant concentration for CTAB + gemini was $2 \cdot 10^{-3}$ mol·dm^{-3}, while for TTAB + gemini it was $5 \cdot 10^{-3}$ mol·dm^{-3}. Cetylpyridinium chloride (CPC) was used as a quencher, and its concentration was varied from (0 to $6 \cdot 10^{-5}$) mol·dm^{-3}, confirming full solubilization of probe in the micelles and the Poisson distribution for quencher. It was ensured that the fluorescence lifetime of pyrene was longer than the residence time of the quencher in the micelle. Fluorescence measurements were taken in a Hitachi F-2500 Fluorescence spectrometer at an excitation wavelength of 337 nm. Excitation and emission slit widths were fixed at 2.5 nm, and emission spectra were recorded in the range (350 to 450) nm. All spectra had one to five vibronic peaks. The fluorescence intensities of the peaks decreased with an increase in the quencher concentration without the appearance of any new peak.

If a micellar solution contains an unknown micelle concentration [M] and a quencher of concentration [Q], adding a luminescent probe, pyrene, to the micellar system will enable it to partition both among micelles with quencher and with empty micelles. If the probe molecule is luminescent only when it occupies an empty micelle, then the measured ratio of intensities in the presence (I) and absence (I_o) of quencher is related as[38]

$$\ln\left(\frac{I}{I_o}\right) = -\frac{[Q]}{[M]} \tag{1}$$

[M] can be written as

$$[M] = \frac{[S]_T - C}{N_{agg}} \tag{2}$$

where $[S]_T$ is the total concentration of surfactant mixture; C is the critical micelle concentration of the mixture; and N_{agg} is the micellar aggregation number.

Combining eqs 1 and 2 leads to

$$\ln\left(\frac{I_o}{I}\right) = \frac{N_{agg} \cdot [Q]}{[S]_T - C} \tag{3}$$

Equation 3 predicts a linear plot between $\ln(I_o/I)$ and [Q] with a slope equal to $N_{agg}/([S]_T - C)$, which gives the values of N_{agg}. The aggregation number of gemini component (N_{gem}) was calculated using eq 4

$$N_{gem} = \{[\text{gemini}] - \alpha_2 \cdot C\} \cdot \frac{N_{agg}}{[S]_T - C} \tag{4}$$

where α_2 is the mole fraction of gemini surfactant. The ratio of I_o and I was used to calculate the Stern−Volmer binding constant, K_{sv} (or first-order quenching rate constant)

$$\frac{I_o}{I} = 1 + K_{sv} \cdot [Q] \tag{5}$$

In eq 4, the composition of mixed micelles is taken equal to the overall solvent-free composition of the surfactant mixture in the solution.

Results and Discussion

(a) Critical Micelle Concentration (C). The experimental cmc along with ideal values (C^*) and degree of counterion binding (χ) for the mixed gemini-conventional systems are given in Tables 1 to 3. The cmc values for the pure components are compared with the values available in the literature and are

Table 1. Various Physicochemical Parameters for 14−4−14 + CTAB/TTAB Mixed Systems at $T = 303$ K Evaluated on the Basis of Conductivity Measurements[a]

								average values			
α_1	$C\cdot10^3$ / $\text{mol}\cdot\text{dm}^{-3}$	$C^*\cdot10^3$ / $\text{mol}\cdot\text{dm}^{-3}$	χ	X_1	$\bar{X}_1^{\text{mic}}$	X_1^{ideal}	β	β	f_1	f_2	ΔG_{ex} / $\text{J}\cdot\text{mol}^{-1}$
					CTAB						
0	0.150		0.68					−0.815	0.597	0.966	−335
0.2	0.170	0.180	0.74	0.086	0.081	0.037	−1.093				
0.4	0.224	0.227	0.71	0.103	0.113	0.092	−0.149				
0.6	0.290	0.305	0.62	0.216	0.323	0.186	−0.325				
0.8	0.381	0.466	0.51	0.415	0.621	0.379	−0.855				
1	0.984 (0.823)[39]		0.70								
					TTAB						
0	0.150		0.68					−1.575	0.305	0.973	−455
0.2	0.180	0.186	0.70	0.038	0.097	0.009	−1.564				
0.4	0.240	0.244	0.65	0.039	0.142	0.024	−0.545				
0.6	0.294	0.355	0.51	0.171	0.428	0.053	−1.986				
0.8	0.454	0.653	0.37	0.281	0.676	0.129	−2.204				
1	4.040 (3.510)[39]		0.73								

[a] Uncertainties on C are estimated to be less than or equal to $\pm\,(0.5\cdot10^{-5})\ \text{mol}\cdot\text{dm}^{-3}$.

Table 2. Various Physicochemical Parameters for 14−5−14 + CTAB/TTAB Mixed Systems at $T = 303$ K Evaluated on the Basis of Conductivity Measurements[a]

								average values			
α_1	$C\cdot10^3$ / $\text{mol}\cdot\text{dm}^{-3}$	$C^*\cdot10^3$ / $\text{mol}\cdot\text{dm}^{-3}$	χ	X_1	$\bar{X}_1^{\text{mic}}$	X_1^{ideal}	β	β	f_1	f_2	ΔG_{ex} / $\text{J}\cdot\text{mol}^{-1}$
					CTAB						
0	0.164		0.68					−1.417	0.466	0.905	−697
0.2	0.174	0.197	0.67	0.128	0.108	0.040	−1.692				
0.4	0.206	0.246	0.67	0.204	0.226	0.100	−1.405				
0.6	0.263	0.328	0.59	0.292	0.391	0.200	−1.196				
0.8	0.353	0.492	0.55	0.441	0.644	0.400	−1.375				
1	0.984 (0.823)[39]		0.70								
					TTAB						
0	0.164		0.68					−2.278	0.210	0.935	−817
0.2	0.190	0.203	0.63	0.065	0.109	0.010	−2.211				
0.4	0.219	0.266	0.61	0.150	0.253	0.026	−2.677				
0.6	0.311	0.386	0.64	0.186	0.417	0.057	−2.102				
0.8	0.493	0.705	0.52	0.287	0.665	0.139	−2.121				
1	4.040 (3.510)[39]		0.73								

[a] Uncertainties on C are estimated to be less than or equal to $\pm\,(0.5\cdot10^{-5})\ \text{mol}\cdot\text{dm}^{-3}$.

Table 3. Various Physicochemical Parameters for 14−6−14 + CTAB/TTAB Mixed Systems at $T = 303$ K Evaluated on the Basis of Conductivity Measurements[a]

								average values			
α_1	$C\cdot10^3$ / $\text{mol}\cdot\text{dm}^{-3}$	$C^*\cdot10^3$ / $\text{mol}\cdot\text{dm}^{-3}$	X	X_1	$\bar{X}_1^{\text{mic}}$	X_1^{ideal}	β	β	f_1	f_2	ΔG_{ex} / $\text{J}\cdot\text{mol}^{-1}$
					CTAB						
0	0.170		0.63					−1.481	0.456	0.896	−739
0.2	0.185	0.204	0.68	0.114	0.112	0.041	−1.413				
0.4	0.207	0.254	0.55	0.216	0.246	0.103	−1.534				
0.6	0.257	0.338	0.59	0.310	0.418	0.206	−1.433				
0.8	0.347	0.503	0.57	0.450	0.662	0.409	−1.543				
1	0.984 (0.823)[39]		0.70								
					TTAB						
0	0.170		0.63					−3.089	0.143	0.877	−1273
0.2	0.201	0.210	0.68	0.050	0.134	0.010	−1.789				
0.4	0.221	0.276	0.57	0.161	0.298	0.027	−2.835				
0.6	0.259	0.400	0.54	0.251	0.488	0.059	−3.343				
0.8	0.306	0.728	0.34	0.362	0.717	0.144	−4.391				
1	4.040 (3.510)[39]		0.73								

[a] Uncertainties on C are estimated to be less than or equal to $\pm\,(0.5\cdot10^{-5})\ \text{mol}\cdot\text{dm}^{-3}$.

found to be in good agreement with each other[39] (literature values are provided in Tables 1 to 3).

The mixing behavior of present cationic surfactants is expected to be different from that of mixtures of surfactants of homologous series, e.g., CTAB + TTAB or CTAB + DTAB, due to various structural dissimilarities. Clint's[12] equation can be used to find the ideality/nonideality in mixed micelle formation. For ideal mixing, the ideal cmc (C^*) of mixtures is related to the cmc's of pure components as

$$\frac{1}{C^*} = \frac{\alpha_1}{C_1} + \frac{\alpha_2}{C_2} \tag{6}$$

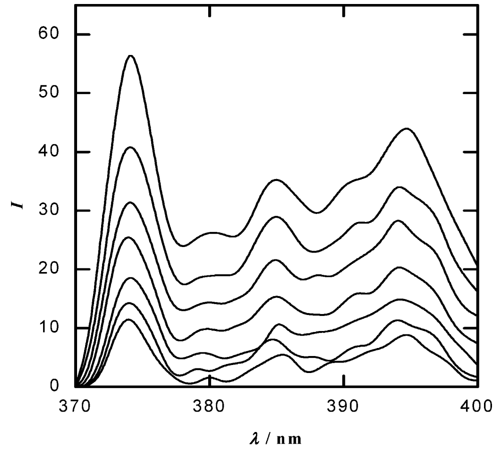

Figure 2. Representative fluorescence (emission) spectra of $2 \cdot 10^{-6}$ $\text{mol} \cdot \text{dm}^{-3}$ pyrene in aqueous micellar solution of 14−4−14:CTAB (0.8: 0.2) at different quencher concentrations. The maximum intensity is for no quencher, and the successive curves are for [Q] = (1.0, 1.99, 2.97, 3.95, 4.92, and 5.82)$\cdot 10^{-5}$ $\text{mol} \cdot \text{dm}^{-3}$.

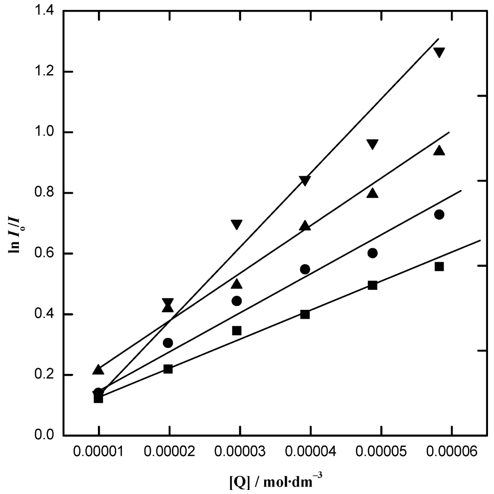

Figure 3. Plots (according to eq 3) for determination of aggregation number of the 14−6−14/TTAB system as a function of TTAB mole fraction: ■, 0.2; ●, 0.4; ▲, 0.6; ▼, 0.8.

where α_1 and C_1 are the mole fraction and cmc of pure conventional surfactant and C_2 is the cmc of pure gemini and C^* is ideal value. The difference in C and C^* indicates nonideality. This theory neglects the interaction among different surfactants in the aggregated state and, thus, can be applied only on dilute systems. One can see from the data (Tables 1 to 3) that the C values are always smaller than the C^* values, and the difference between the two increases with the increase in mole fraction of the conventional surfactant. A lower C value than the corresponding C^* value indicates that mixed micellization is due to some sort of attractive interactions operating between the two components of the mixtures (synergism). The intercalation of two hydrophobic tails of gemini into the TTAB/CTAB micelles improves the hydrophobic environment in the mixed state in comparison to that in the pure state. As a result, C values are lower than C^* values. The C values increase slowly with the increase in mole fraction of CTAB/TTAB in a nonlinear manner. These results indicate that 14−*s*−14 partitions in CTAB/TTAB micelles but the conventional surfactants do not partition easily into the 14−*s*−14 micelles. As the mole fraction of conventional surfactant increases in the mixture, the deviation from ideal behavior increases in the system.

(b) Molecular Interactions. To investigate the nature of interactions among the components, we calculated various other parameters (presented in Tables 1 to 3), using Rubingh's model.[13]

The model is based on regular solution theory for nonideal mixed systems. This model is an iterative algorithm. The micellar mole fraction (X_1) of a surfactant in the mixed micelle and the micellar molecular interaction parameter (β) are the optimization parameters which can be calculated using the model in the form

$$\frac{[X_1^2 \cdot \ln(C \cdot \alpha_1 / C_1 \cdot X_1)]}{(1 - X_1)^2 \cdot \ln[C \cdot (1 - \alpha_1) / C_2 \cdot (1 - X_1)]} = 1 \qquad (7)$$

$$\beta = [\ln(C \cdot \alpha_1 / C_1 \cdot X_1)] / (1 - X_1)^2 \qquad (8)$$

Equation 7 was solved iteratively to obtain the value of X_1. The interaction parameter β is related to activity coefficients (f_1 and f_2) of the surfactants within the micelles by

$$f_1 = \exp[\beta \cdot (1 - X_1)^2] \qquad (9)$$

and

$$f_2 = \exp(\beta \cdot X_1^2) \qquad (10)$$

Thermodynamically, Motomura[21,22] considered mixed micelles as a macroscopic bulk phase and proposed that the related parameters can be calculated from the excess thermodynamic quantities. This theory takes the dissociation of ionic surfactants also in consideration. For a mixed system constituted by two ionic surfactants, which dissociate into $\nu_1 (= \nu_{1a} + \nu_{1c})$ and $\nu_2 (= \nu_{2b} + \nu_{2d})$ ions (a and c and b and d are the respective ions given by the two ionic surfactants 1 and 2), the micellar composition can be calculated by the following equations

(i) when both surfactants have common counterions, i.e., c = d

$$\bar{X}_2^{\text{mic}} = \bar{\alpha}_2 - \left(\frac{\bar{\alpha}_1 \cdot \bar{\alpha}_2}{\bar{C}}\right) \cdot \left(\frac{\partial \bar{C}}{\partial \bar{\alpha}_2}\right)_{T,P} \cdot \left[1 - \frac{\delta_d^c \cdot \nu_{1,c} \cdot \nu_{2,d}}{\nu_{1,c} \cdot \nu_2 \cdot \bar{\alpha}_1 + \nu_{2,d} \cdot \nu_1 \cdot \bar{\alpha}_2}\right] \qquad (11)$$

where

$$\bar{\alpha}_i = \frac{\nu_i \cdot \alpha_i}{\sum \nu_i \cdot \alpha_i}$$

and

$$\bar{C} = C \cdot \sum \nu_i \cdot \alpha_i$$

Kronecker delta δ, is 1 for c = d and 0 for c ≠ d.

(ii) when both surfactants have different counterions, i.e., c ≠ d

$$\bar{X}_1^{\text{mic}} = \bar{\alpha}_1 \cdot \bar{C} / \bar{C}_1 \qquad (12)$$

Table 4. Average Aggregation Numbers (N_{agg}), Aggregation Numbers of Gemini (N_{gem}), Aggregation Numbers of Conventional Surfactants (N_{conv}), and Stern−Volmer Constants (K_{sv}) for the 14−*s*−14 + CTAB/TTAB Mixed Systems Evaluated on the Basis of the Steady State Fluorescence Quenching Technique (Equations 3 and 5)

	$s = 4$				$s = 5$				$s = 6$			
α_1	N_{agg}	N_{gem}	N_{conv}	$K_{sv}\cdot 10^{-4}$/mol$^{-1}\cdot$dm^3	N_{agg}	N_{gem}	N_{conv}	$K_{sv}\cdot 10^{-4}$/mol$^{-1}\cdot$dm^3	N_{agg}	N_{gem}	N_{conv}	$K_{sv}\cdot 10^{-4}$/mol$^{-1}\cdot$dm^3
							CTAB					
0	42	42	0	4.1	29	29	0	2.3	31	31	0	2.6
0.2	50	40	10	5.7	43	34	09	3.9	30	23	07	2.4
0.4	56	33	23	8.0	52	31	21	5.5	34	20	14	3.1
0.6	59	24	35	9.5	59	23	36	6.5	37	15	22	3.4
0.8	85	17	68	15.2	85	17	68	14.8	49	10	39	5.7
1	86	0	86	57.9	84	0	86	57.9	84	0	86	57.9
							TTAB					
0	86	86	0	2.8	58	58	0	1.6	45	45	0	1.2
0.2	73	59	14	2.3	62	49	13	1.8	49	39	10	1.3
0.4	85	51	34	2.7	75	45	30	2.4	63	38	25	1.8
0.6	88	35	53	4.5	84	33	51	3.6	79	32	47	2.5
0.8	91	18	73	13.8	96	19	77	5.9	99	20	79	3.7
1	89	0	89	20.5	89	0	89	20.5	89	0	89	20.5

Also, the micelle mole fraction in the ideal state (X_1^{ideal}) has been computed using the equation

$$X_1^{ideal} = [(\alpha_1 \cdot C_2)/(\alpha_1 \cdot C_2 + (1 - \alpha_1) \cdot C_1)] \qquad (13)$$

It is clear from the data that X_1 values (either X_1 or $\bar{X}_1^{mic}$) are always more than X_1^{ideal}, which means that, even in a low conventional surfactant region (i.e., with low α_1 values), the mixed micelles are rich in conventional surfactants in comparison to that in the ideal mixing state (i.e., X_1^{ideal}). It is also clear from Tables 1 to 3 data that, as the content of conventional surfactant in the mixture increases, the deviation in X_1 values from X_1^{ideal} increases. Further, as the length of the spacer increases from 4 to 6, the value of X_1 becomes larger, and the difference between X_1 and X_1^{ideal} values increases. This means that at the same mixture composition, as the spacer chain length changes from 4 to 6, the contribution of the gemini surfactant decreases and the gemini molecules contribute less as compared to their ideal state. Zana et al.[30] observed that the cmc values show a peaked behavior with the spacer length having a maximum at $s = 5$ or 6. This is the equilibrium distance between the two head groups. Surfactants with a spacer length of less than 5 or 6 micellize easily, while a spacer of 5 or 6 carbon atoms prefers to lie in stretched rather than in the curved form. Therefore, the contribution of 14−5−14 and 14−6−14 gemini molecules is less in mixed micelles as compared to 14−4−14. The χ values decrease with the increase in TTAB/CTAB content in the system, suggesting loose micellar aggregates.

The β values demonstrate the extent of interaction between the two surfactants which leads to the deviation from ideality. Negative β values mean attractive interactions between the two components in a mixed micelle more than the self-attraction of the two surfactants before mixing. A zero value indicates ideal mixing, while positive values show less attraction after mixing than before mixing (antagonism).

In our case, as is clear from Tables 1 to 3, the average values of β come out to be:

(i) −0.815, −1.417, and −1.481 for 14−4−14, 14−5−14, 14−6−14, and CTAB systems, respectively.

(ii) −1.575, −2.278, and −3.089 for 14−4−14, 14−5−14, 14−6−14, and TTAB systems.

Thus, the β values are all negative, and the magnitude is greater with TTAB for all the geminis.

The values of activity coefficients, f_1 and f_2, calculated from eqs 9 and 10, are found to be less than unity showing nonideal behavior of the mixed systems.

The activity coefficients can also be used to calculate excess free energy of mixing by the relation

$$\Delta G_{ex} = RT[X_1 \cdot \ln f_1 + (1 - X_1) \cdot \ln f_2] \qquad (14)$$

where R and T have their usual meanings. The negative ΔG_{ex} values thus obtained suggest (Tables 1 to 3) that the mixed micelles are more stable than the micelles of individual components.

(c) Micelle Aggregation and Micropolarity. Figure 2 depicts the fluorescence spectra of $2 \cdot 10^{-6}$ mol·dm^{-3} pyrene in an aqueous micellar solution of 14−4−14:CTAB (0.8:0.2) at different quencher concentrations. From the data of such spectra, plots were drawn between $\ln(I_o/I)$ and [Q] (shown in Figure 3). The values of N_{agg} obtained for different systems are provided in Table 4. In general, N_{agg} values fall in between the values for pure gemini and pure conventional surfactants. For all three geminis, as the mole fraction of conventional surfactant increases, N_{gem} decreases, whereas with the spacer chain length increase, the value of N_{agg} decreases for both CTAB and TTAB, which is in conformity with the χ variation.

Conclusions

Mixed micellization of dimeric cationic surfactants with monomeric cationic surfactants is investigated, and the results of the study allow us to conclude that:

1. Gemini/conventional systems form mixed micelles due to attractive interactions.
2. The cmc values of mixtures lie in between the cmc's of pure components.
3. The contribution of conventional surfactant is more compared to that in the ideal mixing state, i.e., $X_1 > X_1^{ideal}$.
4. The fluorescence quenching method also confirms the above results. N_{agg} increases with the increase in mole fraction of conventional surfactants. Values of N_{gem} and N_{CTAB}/N_{TTAB} again indicate that at high α_1 contribution of conventional is more than that of gemini surfactant.

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