Conductometric and Fluorimetric Investigations on the Properties of Mixed Micelles of Two Cationic Gemini Surfactants

Mohd. Akram, Naved Azum, Andleeb Z. Naqvi, and Kabir-ud-Din*

Department of Chemistry, Aligarh Muslim University, Aligarh-202002, UP, India

---

The mixed micellar properties of two cationic gemini surfactants, alkanediyl-α,ω-bis(tetradecyldimethylammonium bromide) and alkanediyl-α,ω-bis(hexadecyldimethylammonium bromide), 14-*s*-14 and 16-*s*-16, in aqueous solution have been investigated by conductivity and fluorescence techniques. The conductivity method has been carried out to evaluate critical micelle concentration (c), degree of counterion binding (g), and other related parameters like ideal mixed critical micelle concentration (c^*), micellar mole fraction (x), interaction parameter (β) from Rubingh's model, and x^{ideal} from Motomura's model. Activity coefficients (f_1 and f_2) and Gibbs excess energy (G^{E}) were also calculated. Fluorescence measurements were used to obtain the values of N_{agg} and Stern–Volmer constant (K_{sv}). The results suggest synergism in the system. The β values are negative, and their magnitudes increase with increasing spacer chain lengths. $x_1 > x_1^{\text{ideal}}$ values suggest that the contribution of the 14-*s*-14 component is greater as compared to that in the ideal state.

Introduction

Surfactants are used in different technological applications, including pharmaceuticals, food and cosmetic industries, detergency, mineral flotation, enhanced oil recovery, and so on, which always need a blend of surfactants. For application purposes, mixtures of different surfactants are employed. Surfactant mixtures are known to have superior chemical and surface active properties over the individual surfactants, thereby requiring smaller amounts.[1] In a study, Somasundran et al.[2] have shown that nonionic surfactant $C_{12}E_8$ does not adsorb onto solids, whereas it does in the presence of an anionic surfactant. To enhance the performance of surfactant mixtures further, it is helpful to understand the interaction among the surfactants. In some cases, two surfactants interact in such a way that the critical micelle concentration (cmc) of the mixture falls in between (or below) the cmc's of individual components. Such a system is said to show synergism—a condition in which the properties of the mixed system are better than the properties of pure surfactants. In other cases, the cmc of the mixture is larger than the cmc of pure components. The system then exhibits antagonism. The synergistic effect in different components in a mixture greatly improves many technological applications; the composition and concentration can be optimized for each practical application. Since different types of surfactants exist, different combinations are possible, with different properties and applications. Therefore, the specific interaction between the two components of a mixture on their physicochemical properties including micellization is of paramount importance.

Binary mixtures of conventional surfactants have been studied extensively, and various theoretical models have been put forward for dealing with the mixed binary systems to evaluate the composition and interaction parameters among the components at the air/water interface and in the micellar phase. The first model, given by Lange[3] and used by Clint,[4] assumes ideal mixing of surfactants in the micellar phase. Rubingh's model is the first model developed for the nonideal mixed system.[5] It is based on a regular solution approach for the treatment of nonideal mixing, and due to its simplicity, it has been mostly used, even after the development of more complex models. Although Rubingh's treatment was found to be reasonably satisfactory in many cases, the theory was criticized on thermodynamic grounds. Rosen et al.[6] have extended the nonideal solution treatment of Rubingh's to estimate, from surface tension data, the surfactant molecular interactions and also the composition in the adsorbed mixed monolayer at the air/water interface. Motomura et al.[7] proposed their model, to calculate excess thermodynamic properties. More recently, Rodenas et al.[8] 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. Blankschtein's[9,10] group proposed a molecular thermodynamic approach as a valuable tool to predict solution properties of mixed surfactant systems. The reasons for the nonideal behavior among surfactant molecules upon mixing are the various types of molecular interactions: (1) electrostatic interactions between ionic hydrophilic groups, (2) ion–dipole interaction between ionic and nonionic groups, (3) steric interaction between bulky head groups, (4) van der Waals interactions between hydrophobic groups, and (5) hydrogen bonding among constituent surfactant molecules.

Gemini surfactants are a special class of surfactants where two hydrophobic tails and two hydrophilic heads are covalently joined via a spacer.[11,12] These surfactants have attracted considerable interest[13−15] for their better performance than the corresponding conventional surfactants. They have much lower cmc values and greater efficiency in reducing the surface tension of water.[16] These surfactants also have better wetting and solubilizing power, unusual micellar structure, and better viscoelasticity. They also show biological activity[17] and have an effect on photosynthesis.[18] As gemini surfactants contain a spacer, which can be hydrophobic, hydrophilic, flexible (eth-

---

* To whom correspondence may be addressed. Tel.: +91-571-2703515. E-mail: kabir7@rediffmail.com.

10.1021/je100347r

ylene group), or rigid (stilbene unit),[11] their hydrophobic/hydrophilic nature can have dramatic effects on their physicochemical properties. Moreover, gemini surfactants offer additional options to tune the solution properties by varying the length of hydrocarbon chains. Encouraged by our earlier findings[19−21] of the presence of synergism in mixed micelles of geminis with conventional (single head, single tail) surfactants, we have extended the work to the case of mixed micelles formed between gemini−gemini surfactants.

The objective of the present work is to investigate the micellization aspects of binary gemini−gemini surfactant systems. More specifically, the focus has been on (i) effect of hydrophobic chain lengths and hydrophilic head groups with tetradecyl-(C_{14}) and hexadecyl-(C_{16}) chain lengths having cationic head groups in their binary mixtures, (ii) correlating the different parameters for mixed micelle formation between different binary systems. The purpose of selection of the surfactants is 2-fold: (a) their similar hydrophobic chain lengths, a factor expected to lead ideal mixing, and (b) a large difference in their cmc values. In view of the above-mentioned scenario, we have carried out studies on the mixed micellization of alkanediyl-α,*ω*-bis(alkyldimethylammonium bromide) in their binary combinations in aqueous medium and then compared the results with gemini-conventional surfactant systems studied earlier.[19−21] This paper thus presents a systematic study of micellar properties of the above-mentioned surfactants using conductometric and fluorometric techniques.

Materials and Methods

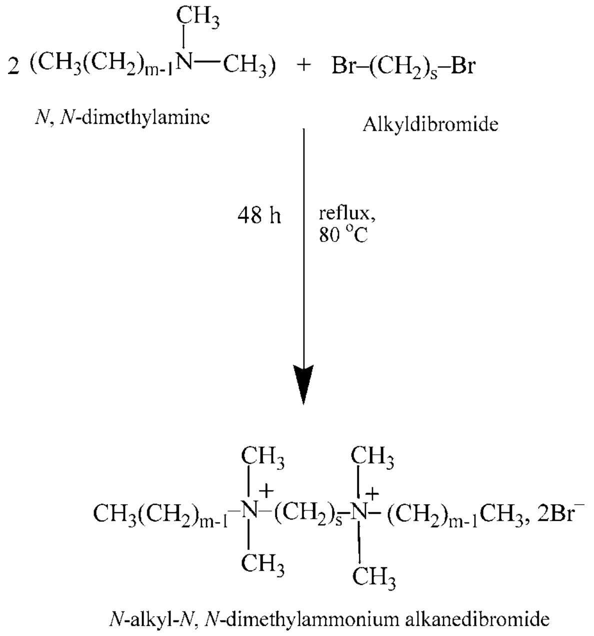
Synthesis of Gemini Surfactants. The reagents *N*,*N*-dimethylhexadecylamine (CASR No. 112-69-6), *N*,*N*-dimethyltetradecylamine (CASR No. 112-75-4), 1,6-dibromohaxane (CASR No. 629-03-8), 1,5-dibromopentane (CASR No. 111-24-0), and 1,4-dibromobutane (CASR No. 110-52-1), used for synthesis, were purchased from Fluka. Compounds in the *m*-*s*-*m* series (m = 14, 16 and s = 4, 5, 6) were synthesized by the action of the corresponding *N*,*N*-dimethylamine on the alkyldibromide, under reflux in absolute ethanol until the alkyl amine was totally consumed. The procedure of synthesis of gemini surfactants (*m*-*s*-*m*) can be presented by the following Scheme 1.

After completion of the reaction (TLC was employed for monitoring the progress), the solvent was removed under vacuum from the reaction mixture, and the solid thus obtained was crystallized five times from a hexane and ethyl acetate mixture to obtain the compound in pure form. The overall yield was (70 to 80) %. All products were checked by ^{1}H NMR spectrum using $CDCl_3$ as a solvent. For example, nine peaks were assigned for protons for 16-4-16, and the integrated spectra gave the expected proton contents: δ:0.88 (t, 6H, alkyl chain 2·1 C**H**$_3$), 1.257 to 1.344 (br m, 44H, alkyl chain 2·11 C**H**$_2$), 1.754 (m, 12H, alkyl chain 2·3 C**H**$_2$), 2.084 (br s, 4H, spacer chain 1·2 C**H**$_2$CH$_2$N$^+$), 3.308 (s, 12H, 2·2 N$^+$C**H**$_3$), 3.431 (m, 4H, alkyl chain 2·1 C**H**$_2$N$^+$), 3.811 (br s, 4H, spacer chain 2·1 C**H**2 N$^+$). The assignments matched well with the literature data.[22] The purity of the gemini surfactants (> 99 %) was checked by C, H, N elemental analyses.

Conductometric Measurements. A series of mixed surfactant systems of different mole fractions were prepared from equimolar stock solutions of 14-*s*-14 and 16-*s*-16 gemini surfactants (1 mM each). 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}. 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 the surfactant mixture in pure water. A representative example is given in Figure 1. The degree of counterion binding (g) was evaluated using the slopes above and below the cmc of the conductivity versus surfactant concentration plots. The uncertainties on the cmc were estimated to be less than ± 0.5·10^{-5}.

Spectrofluorimetric Measurements. A 0.003 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 μmol·dm^{-3}, which was kept constant in all experiments. The total surfactant concentration was 0.002 mol·dm^{-3}. Cetylpyridinium chloride (CPC) was used as quencher, and its concentration was varied from (0 to 60) μmol·dm^{-3}, confirming full solubilization of probe in the micelles and the Poisson distribution for quencher. It was

Scheme 1. Protocol for the Synthesis of *m*-*s*-*m* Compounds, *s* = 4, 5, 6 and *m* = 14, 16



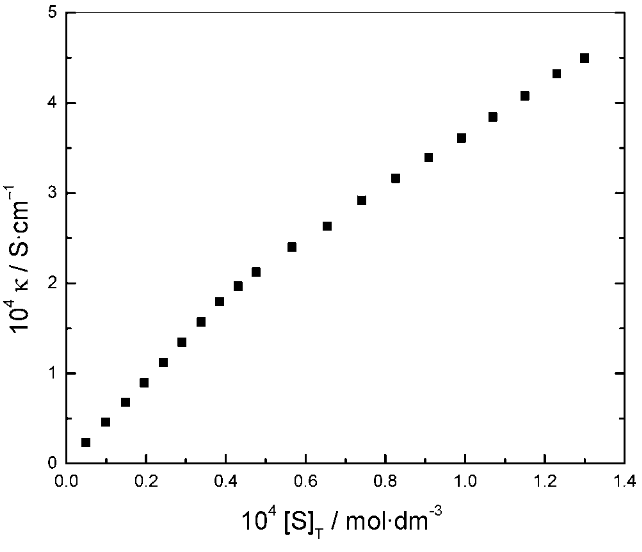


Figure 1. Representative plots of conductivity (κ) of 14-4-14 + 16-4-16 versus total surfactant concentration $[S]_T$ at α_1 = 0.6 mol fraction.

Table 1. Various Physicochemical Parameters for 14-*s*-14 + 16-*s*-16 Mixed Systems at 303 K Evaluated on the Basis of Conductivity Measurements[a]

α_1	$c\cdot10^3$ / $\mathrm{mol\cdot dm^{-3}}$	$c^*\cdot10^3$ / $\mathrm{mol\cdot dm^{-3}}$	g	x_1	x_1^{ideal}	$-\beta$	f_1	f_2	$-G^{\mathrm{E}}$ / $\mathrm{J\cdot mol^{-1}}$
				16-*4*-16 + 14-*4*-14					
0.0	0.026 (0.020)[22]	0.026	0.41						
0.2	0.027	0.031	0.45	0.128	0.041	1.639	0.287	0.973	461
0.4	0.038	0.039	0.16	0.120	0.103	0.223	0.842	0.996	59
0.6	0.042	0.052	0.37	0.288	0.206	1.039	0.590	0.917	537
0.8	0.054	0.077	0.53	0.446	0.409	1.371	0.656	0.761	853
1.0	1.500 (1.500)[21]	1.500	0.68						
				16-*5*-16 + 14-*5*-14					
0.0	0.036 (0.036)[22]	0.036	0.54						
0.2	0.032	0.043	0.22	0.204	0.053	2.561	0.197	0.898	1048
0.4	0.047	0.052	0.34	0.188	0.130	0.693	0.632	0.975	267
0.6	0.054	0.067	0.32	0.326	0.252	1.023	0.628	0.896	567
0.8	0.056	0.095	0.38	0.488	0.474	2.098	0.576	0.606	1321
1.0	1.600 (1.600)[21]	1.600	0.68						
				16-*6*-16 + 14-*6*-14					
0.0	0.041 (0.043)[22]	0.041	0.48						
0.2	0.042	0.048	0.43	0.147	0.057	1.485	0.339	0.968	469
0.4	0.043	0.059	0.37	0.272	0.138	1.835	0.378	0.873	916
0.6	0.054	0.075	0.36	0.359	0.266	1.532	0.532	0.820	888
0.8	0.061	0.104	0.57	0.496	0.491	2.120	0.583	0.593	1336
1.0	1.700 (1.700)[21]	1.700	0.63						

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

ensured that the fluorescence lifetime of pyrene was longer than the residence time of quencher in the micelle. A Hitachi F-2500 Fluorescence spectrometer at an excitation wavelength of 337 nm was used for fluorescence measurements. Excitation and emission slit widths were fixed at 2.5 nm, and emission spectra were recorded in the range (350 to 450) nm at 303 K. All spectra had one to five vibronic peaks. The fluorescence intensities of the peaks decreased with increase in the quencher concentration without appearance of any new peak.

Results and Discussion

The changes in the measurement of physical properties of the surfactants above a certain concentration are recognized as the cmc of the surfactants. For selected systems (14-*4*-14 + 16-*4*-16, 14-*5*-14 + 16-*5*-16, and 14-*6*-14 + 16-*6*-16), the specific conductivity was measured for each system at four bulk mole fractions (α) (Tables S1 to S3 of Supporting Informations). A depiction of a typical conductivity vs concentration plot for the 14-*4*-14 + 16-*4*-16 system at $\alpha_1 = 0.6$ is shown in Figure 1. Similar plots were obtained for other systems at different mole fractions. From these plots, cmc and counterion binding were obtained, and their values are given in Table 1 for the three systems.

c and c*. Like single surfactants, an aqueous solution containing surfactant mixtures also forms aggregates, but in the latter case, the tendency to form micelles can be different from that of the pure surfactants. In single-component systems of the geminis, the cmc increases with the increase in spacer chain length and decreases with the increase in the hydrophobic chain length (i.e., cmcs of 14-*s*-14 geminis are greater than the cmcs of 16-*s*-16). An increase in the length of the tail disrupts water structure and releases more water molecules resulting in an increase in entropy. (Similar cmc increases were reported for both cationic[23] and anionic[24] geminis.) The results also indicate that the gemini molecules are in *cis* conformation, and the spacer is in contact with water. Cmc values for all systems lie between the cmc values of individual components. As the mole fraction of 14-*s*-14 gemini surfactant increases, the cmc of the mixture increases. This indicates that 16-*s*-16 components assist 14-*s*-14 geminis to form micelles and penetrate in 16-*s*-16 micelles. Similar types of results were obtained for conventional-gemini mixtures by us as well as by others.[19−21,25]

The phase separation model is a very important and useful tool to describe micelle formation. In this model, the surfactant monomers in the bulk phase, the micelles, and the monomers at the interface are supposed to be in equilibrium. The micelles are treated as a separate phase, and the condition of equality of the chemical potential of different phases is applied. For two surfactants 1 and 2 with cmc values c_1 and c_2, Clint's[4] equation can be used to relate their cmc values as

$$\frac{1}{c^*} = \frac{\alpha_1}{c_1} + \frac{\alpha_2}{c_2} \qquad (1)$$

where α_1 and α_2 are the bulk mole fractions of the respective surfactants and c^* is the ideal cmc value of the mixture. Equation 1 makes the difference between ideal and nonideal mixtures. A lower observed cmc for the mixture, i.e., negative deviation from eq 1, means a synergistic interaction among the mixing components. The results are in tune with those obtained for 16-*s*-16/14-*s*-14 and conventional surfactant systems.[19−21]

Nonhomologous surfactant mixtures do not behave ideally as interactions between the two components of the mixture would be different from that of two homologous components. Variations of c and c^* values with mole fraction of surfactant 1 (14-*s*-14 gemini in our system) are shown in Figure 2 and presented in Table 1. The cmc (c) values are always found to be lower than the ideal values (c^*), and the difference in two values increases with an increase in α_1. As the spacer length is the same for both components in each system, the difference in chain lengths of the surfactants causes nonideality in the system. Transfer of hydrophobic tails from the monomer phase to the micellar phase increases hydrophobic

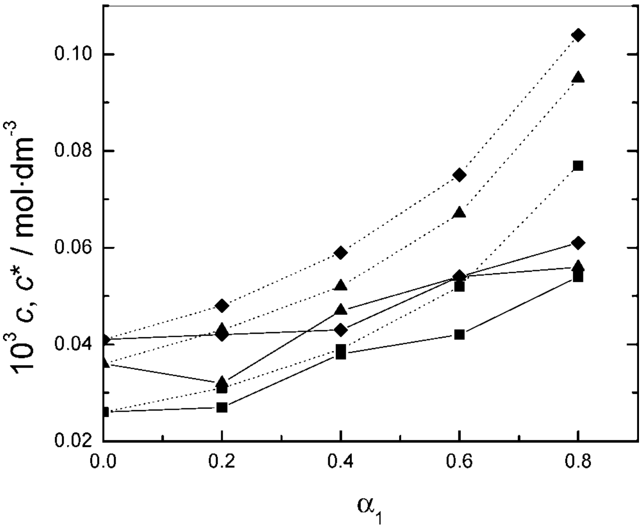


Figure 2. Critical micelle concentration for binary mixtures of 14-*s*-14 + 16-*s*-16. Solid lines represent experimental data (c), and dashed lines were calculated from Clint's model (c^*): ■, $s = 4$; ▲, $s = 5$; and ◆, $s = 6$.

interactions among micelles, and hence c values come out to be lower than c^* values.

Counterion Binding (g). The layer just adjacent to the surface of the micelles, i.e., the Stern layer, binds counterions. The binding of counterions to the micelles causes reduction in the effective charge on the micelles. The fraction of the counterions bound to the micelles was determined conductometrically, using the ratio of pre- and postmicellar slopes (S_1 and S_2). The ratio of S_2/S_1 is considered as the fraction of counterions dissociated from the micelles, so that the fraction bound $g = (1 - S_2/S_1)$. The increased counterion association depicts high charge density of the mixed micelles. The surface charge density of mixed micelles is dependent on the head groups as well as on the chain lengths. The increased counterion associations reduce cmc. Counterion binding increases in all three systems on increasing α_1, suggesting compact micellar aggregates.

Micellar Composition. Clint's model is an oversimplification as it neglects the interaction among different components of the mixture, and it assumes that the cmc values of the individual components can explain their micellization tendency in the mixture also. As our systems are nonideal, we have used Rubingh's regular solution theory. Although several molecular-thermodynamic models have been developed,[9,10,26−28] Rubingh's semiempirical approach remains a very convenient method for analyzing cmc of the mixed micellar systems. The model is simple and straightforward. This model is basically an optimization program toward the cmc values of pure and mixed systems. Corresponding mole fraction of one component in the micellar phase (x_1) is the optimization parameter, which can be calculated by solving eq 2 iteratively

$$\frac{[x_1^2 \ln(c\alpha_1/c_1x_1)]}{(1 - x_1)^2 \ln[c(1 - \alpha_1)/c_2(1 - x_1)]} = 1 \qquad (2)$$

It can be seen that with an increase in α_1, x_1 also increases (Table 1). This indicates that the contribution of 14-*s*-14 is increasing in the mixed system.

Also, the micelle mole fraction in the ideal state (x_1^{ideal}) has been calculated using the equation (Motomura's model[7])

$$x_1^{\text{ideal}} = [(\alpha_1c_2)/(\alpha_1c_2 + (1 - \alpha_1)c_1)] \qquad (3)$$

The data for x_1 and x_1^{ideal}, presented in Table 1, clearly show that the order of $x_1 > x_1^{\text{ideal}}$. Also, as the content of 14-*s*-14 increases in the solution, the difference between x_1^{ideal} and x_1 decreases. Further, as the spacer chain increases from 4 to 6, the difference between x_1 and x_1^{ideal} decreases. This means that, at the same mole fraction, as the spacer chain length increases contribution of 16-*s*-16 decreases. This is also clear from the values of x_1^{ideal} being always less than x_1, indicating that even in the 14-*s*-14 poor region (i.e., low α_1 region) the contribution of 14-*s*-14 is greater than it should be in the ideal state.

Molecular Interaction Parameter (β). The β can be interpreted in terms of a parameter that represents the Gibbs excess energy and can be calculated using x_1 values obtained from eq 2

$$\beta = [\ln(c\alpha_1/c_1x_1)]/(1 - x_1)^2 \qquad (4)$$

A negative β value indicates that the interaction between the two surfactants after mixing is more attractive than before mixing (i.e., synergism between the monomers). While a positive value indicates antagonism in the micellar system, a zero value means that the interactions among monomers after mixing are equal to those before mixing, i.e., ideal mixing. The larger the magnitude of β, the greater the interaction should be. In the present case, the β values are negative throughout for each system (Table 1). This indicates synergism in the system which is also supported by negative deviation of the c from the c^*. The average β values for the three systems are −1.068 ($s = 4$), −1.594 ($s = 5$), and −1.743 ($s = 6$). For dimeric surfactants, the spacer group significantly affects the electrostatic interaction at micellar surface along with size and shape of the micellar aggregate, which, in turn, can affect the hydrophobic interactions within the micellar core.[29,30] Interactions between surfactants in binary mixtures are the result of two contributions:[31] (i) electrostatic interactions in the micellar core and (ii) electrostatic interactions between head groups of both surfactants

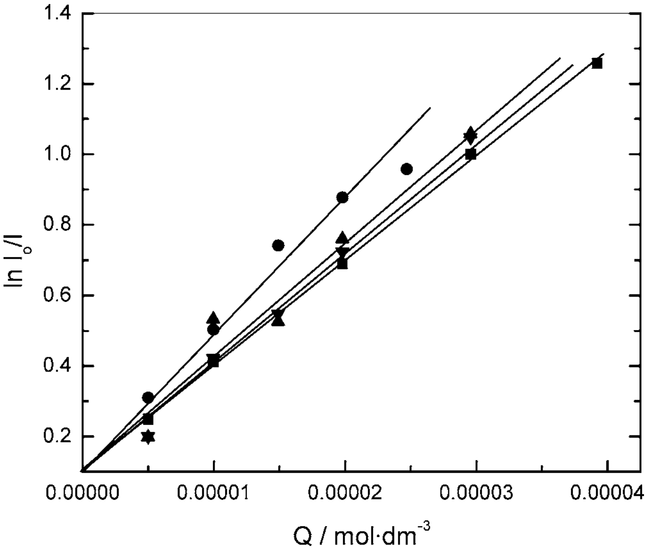


Figure 3. Plots for determination of aggregation number of the 14-4-14 + 16-4-16 system at varying mole fractions (α_1), which were: ■, 0.2; ●, 0.4; ▲, 0.6; and ▼, 0.8.

Table 2. Average Aggregation Numbers (N_{agg}), Aggregation Numbers of First (N_1) and Second (N_2) Components, and Stern−Volmer Constants (K_{sv}) for the 14-*s*-14 + 16-*s*-16 Mixed Systems Evaluated on the Basis of Steady-State Fluorescence Quenching Technique

	14-*4*-14 + 16-*4*-16				14-*5*-14 + 16-*5*-16				14-*6*-14 + 16-*6*-16			
α_1	N_{agg}	N_1	N_2	$\frac{K_{sv}\cdot 10^{-4}}{\text{mol}^{-1}\cdot\text{dm}^3}$	N_{agg}	N_1	N_2	$\frac{K_{sv}\cdot 10^{-4}}{\text{mol}^{-1}\cdot\text{dm}^3}$	N_{agg}	N_1	N_2	$\frac{K_{sv}\cdot 10^{-4}}{\text{mol}^{-1}\cdot\text{dm}^3}$
0	44	-	44	3.8	27	-	27	2.5	28	-	28	2.6
0.2	66	6	60	6.0	56	5	51	4.7	58	6	52	4.2
0.4	84	18	66	7.8	66	13	53	6.1	59	11	48	4.4
0.6	73	21	52	6.0	63	18	45	4.9	55	16	39	3.9
0.8	52	20	32	4.3	64	25	39	5.0	69	27	42	5.5
1	42	42	-	4.1	29	29	-	2.3	31	31	-	2.6

at the interface. Since there are two long chains in the geminis, too small a linkage (less hydrophobicity) between two head groups is not suitable for their packing and inhibits their interaction with itself or other surfactants at the surface of the convex micelle and results in a low average value of β. The x_1 and β values can be used to calculate the activity coefficients (f_1 and f_2) by using the equations

$$f_1 = \exp[\beta(1 - x_1)^2] \tag{5}$$

$$f_2 = \exp(\beta x_1^2) \tag{6}$$

Ideal mixing gives activity coefficients a value equal to 1. In our case, f_1 and f_2 come out to be less than unity (given in Table 1) showing nonideality in the mixtures.

Gibbs Excess Energy of Mixing (G^E). G^E is related to f_1, f_2, and x_1 by

$$G^E = RT[x_1 \ln f_1 + (1 - x_1) \ln f_2] \tag{7}$$

where R and T have their usual meanings. The negative G^E (Table 1) for all mixtures indicates that the mixed micelle formation is thermodynamically favorable, again confirming our earlier explanations.

Aggregation Number (N_{agg}) and Stern−Volmer Constant (K_{sv}). The above results can be further explained on the basis of quenching of pyrene (probe) fluorescence by a suitable quencher such as CPC under steady state conditions. If the probe molecule is luminescent only when it occupies an empty micelle, then based on Poisson statistics, the measured ratio of intensities in the presence (I) and absence (I_o) of quencher is related as[32]

$$\ln\left(\frac{I}{I_o}\right) = -\frac{[Q]}{[M]} \tag{8}$$

where [M] is the concentration of single and mixed micelles, and can be written as

$$[M] = \frac{[S]_T - c}{N_{agg}} \tag{9}$$

($[S]_T$ and N_{agg} represent total surfactant concentration and aggregation number, respectively).

Combining the above two equation yields

$$\ln\left(\frac{I_o}{I}\right) = \frac{N_{agg}[Q]}{[S]_T - c} \tag{10}$$

Accordingly, a linear plot between $\ln(I/I_o)$ and [Q] (Figure 3) allowed us to evaluate N_{agg}. The aggregation number of 16-*s*-16 was then obtained from N_{agg} using the equation

$$N_2 = \{[16\text{-}s\text{-}16] - \alpha_2 c\}\{N_{agg}/([S]_T - c)\} \tag{11}$$

The values of N_{agg} (Table 2) are higher than for pure gemini components. In general, with α_1 the values of aggregation number (N_{agg} and N_2) show peaked behavior, while N_1 increases for all the sets.

The strength of the hydrophobic environment can be evaluated by the Stern−Volmer binding constant (K_{sv}) (also known as the first-order quenching rate constant), given by

$$\frac{I_o}{I} = 1 + K_{sv}[Q] \tag{12}$$

K_{sv} values for all the mixtures are greater than for pure surfactants. This suggests that the quencher and probe are both in stronger hydrophobic environment. As a result, the first-order quenching increases. However, as s increases, K_{sv} values decrease indicating that the micelles are less compact for $s = 6$ (which is also supported by slightly lower g values for $s = 6$), and hence the hydrophobicity of the micelle is lower for $s = 6$.

Conclusions

The results of the present study conclude that 14-*s*-14 + 16-*s*-16 binary mixtures undergo mixed micelle formation due to synergistic interactions. cmc values of the binary mixtures are lower than the ideal ones with negative β values. Micellar compositions evaluated by Rubingh's model show that the contribution of 14-*s*-14 is greater as compared to that in ideal state, i.e., $x_1^{\text{ideal}} < x_1$. Fluorescence results indicate that both N_{agg} and K_{sv} are higher for mixtures than for pure components.

Supporting Information Available:

Concentration and specific conductivity data at all mole fractions (Tables S1 to S3) are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Hill, R. M. *Mixed Surfactant Systems*; Ogino, K., Abe, M., Eds.; Marcel Dekker: New York, 1993.

(2) Somasundaran, P.; Fu, E.; Xu, Q. Co-adsorption of Anionic and Nonionic Surfactant Mixtures at the Alumina-Water Interface. *Langmuir* **1992**, *8*, 1065–1069.

(3) Lange, H. Uber Die Mizellenbildung in Mischlosunggen Homologer Paraffinkettensalze. *Kolloid Z.* **1953**, *131*, 96–103.

(4) Clint, J. H. Micellization of Mixed Nonionic Surface Active Agents. *J. Chem. Soc., Faraday Trans.* **1975**, *71*, 1327–1334.

(5) Rubingh, D. N. *Solution Chemistry of Surfactants*; Mittal, K. L., Ed.; Plenum: New York, 1979.

(6) Rosen, M. J. *Surfactants and Interfacial Phenomena*, 3rd ed.; Wiley: New York, 2004.

(7) Motomura, K.; Yamanaka, M.; Aratono, M. Thermodynamic Consideration of Mixed Micelle of Surfactants. *Colloid Polym. Sci.* **1984**, *262*, 948–955.

(8) Rodenas, E.; Valiente, M.; Villafruela, M. S. Different Theoretical Approaches for the Study of Mixed Tetraethylene Glycol Mono-n-dodecyl Ether/Hexadecyltrimethylammonium Bromide Micelles. *J. Phys. Chem. B* **1999**, *103*, 4549–4554.

(9) Puvada, S.; Blankschtein, D. J. Theoretical and Experimental Investigations of Micellar Properties of Aqueous Solutions Containing Binary Mixtures of Nonionic Surfactants. *J. Phys. Chem.* **1992**, *96*, 5579–5592.

(10) Schiloach, A.; Blankschtein, D. Prediction of Critical Micelle Concentrations and Synergism of Binary Surfactant Mixtures Containing Zwitterionic Surfactants. *Langmuir* **1997**, *13*, 3968–3981.

(11) Menger, F. M.; Littau, C. A. Gemini Surfactants: Synthesis and Properties. *J. Am. Chem. Soc.* **1991**, *113*, 1451–1452.

(12) Karaborni, S.; Esselink, K.; Hilbers, P. A. J.; Smit, B.; Karthauser, J.; van Os, N. M.; Zana, R. Simulating the Self-Assembly of Gemini (Dimeric) Surfactants. *Science* **1994**, *266*, 254–256.

(13) Zana, R.; Talmon, Y. Dependence of Aggregate Morphology on Structure of Dimeric Surfactants. *Nature* **1993**, *362*, 228–230.

(14) Rosen, M. J.; Song, L. D. Dynamic Surface Tension of Aqueous Surfactant Solutions: 8. Effect of Spacer on Dynamic Properties of Gemini Surfactant Solutions. *J. Colloid Interface Sci.* **1996**, *179*, 261–268.

(15) Ghosh, S.; Chakraborty, T. Mixed Micelle Formation Among Anionic Gemini Surfactant (212) and its Monomer (SDMA) with Conventional Surfactants ($C_{12}E_5$ and $C_{12}E_8$) in Brine Solution at pH 11. *J. Phys. Chem. B* **2007**, *111*, 8080–8088.

(16) Rosen, M. J. A New Generation of Surfactants. *CHEMTECH.* **1993**, *23*, 30–33.

(17) Devinsky, F.; Lacko, I.; Mlynarcik, D.; Racasky, V.; Krasnec, L. Relationship Between Critical Micelle Concentrations and Minimum Inhibitory Concentrations for Some Non-Aromatic Quaternary Ammonium Salts and Amine Oxides. *Tenside Deterg.* **1985**, *22*, 10–15.

(18) Perez, L.; Torres, J. L.; Manresa, A.; Solans, C.; Infante, M. R. Synthesis, Aggregation, and Biological Properties of a New Class of Gemini Cationic Amphiphilic Compounds from Arginine, bis(Args). *Langmuir* **1996**, *12*, 5296–5301.

(19) Azum, N.; Naqvi, A. Z.; Akram, M.; Kabir-ud-Din. Mixing Behavior of Conventional and Gemini Cationic Surfactants. *J. Dispersion Sci. Technol.* **2008**, *29*, 711–717.

(20) Azum, N.; Naqvi, A. Z.; Akram, M.; Kabir-ud-Din. Studies of Mixed Micelle Formation Between Cationic Gemini and Cationic Conventional Surfactants. *J. Colloid Interface Sci.* **2008**, *328*, 429–435.

(21) Azum, N.; Naqvi, A. Z.; Akram, M.; Kabir-ud-Din. Properties of Mixed Aqueous Micellar Solutions Formed by Cationic Alkanediyl-α,ω-bis(tetradecyldimethylammonium Bromide) and Alkyltrimethylammonium Bromide: Fluorescence and Conductivity Studies. *J. Chem. Eng. Data* **2009**, *54*, 1518–1523.

(22) De, S.; Aswal, V. K.; Goyal, P. S.; Bhattacharya, S. Role of Spacer Length in Dimeric Micellar Organization. Small-Angle Neutron Scattering and Fluorescence Studies. *J. Phys. Chem.* **1996**, *100*, 11664–11671.

(23) Zana, R.; Benrraou, M.; Rueff, R. Alkanediyl-α,ω-bis(dimethylalkylammonium bromide) Surfactants. 1- Effect of Spacer Chain Length on the Critical Micelle Concentration and Micellar Ionization Degree. *Langmuir* **1991**, *7*, 1072–1075.

(24) Tsubone, K.; Arakawa, Y.; Rosen, M. J. Structural Effects on Surface and Micellar Properties of Alkanediyl-α,ω-bis(sodium *N*-acyl-β-alaninate)gemini surfactants. *J. Colloid Interface Sci.* **2003**, *262*, 516–524.

(25) Zhao, J.; Christian, S. D.; Fung, B. M. Mixtures of Monomeric and Dimeric Cationic Surfactants. *J. Phys. Chem. B* **1998**, *102*, 7613–7618.

(26) Nagarajan, R. Micellization, Mixed Micellization and Solubilization: the Role of Interfacial Interactions. *Adv. Colloid Interface Sci.* **1986**, *26*, 205–264.

(27) Nagarajan, R.; Ruckenstien, E. Theory of Surfactant Self-Assembly: A Predictive Molecular Thermodynamic Approach. *Langmuir* **1991**, *7*, 2934–2969.

(28) Shiloach, A.; Blankschtein, B. Measurement and Prediction of Ionic/Nonionic Mixed Micelle Formation and Growth. *Langmuir* **1998**, *14*, 7166–7182.

(29) Alami, E. G.; Beinert, G.; Marie, P.; Zana, R. Alkanediyl-α,ω-bis(Dimethylalkylammonium Bromide) Surfactants. 3. Behavior at the Air-Water Interface. *Langmuir* **1993**, *9*, 1465–1467.

(30) Rodriguez, A.; Graciani, M. M.; Munoz, M.; Robina, I.; Moya, M. L. Effects of Ethylene Glycol Addition on the Aggregation and Micellar Growth of Gemini Surfactants. *Langmuir* **2006**, *22*, 9519–9525.

(31) Rodriguez, A.; Graciani, M. M.; Moreno-Vargas, A. J.; Moya, M. L. Mixtures of Monomeric and Dimeric Surfactants:Hydrophobic Chain Length and Spacer Group Length Effects on Non-ideality. *J. Phys. Chem. B* **2008**, *112*, 11942–11949.

(32) Turro, N. J.; Yekta, A. Luminescent Probes for Detergent Solutions. A Simple Procedure for Determination of the Mean Aggregation Number of Micelles. *J. Am. Chem. Soc.* **1978**, *100*, 5951–5952.

Received for review April 18, 2010. Accepted July 10, 2010. N. A. is pleased to acknowledge financial support from the Council of Scientific and Industrial Research, New Delhi, India, for providing a Senior Research Fellowship to perform this work.

JE100347R