Surface and Solution Properties of Alkanediyl-α,ω-bis(dimethylcetylammonium bromide) Gemini Surfactants in the Presence of Additives

Kabir-ud-Din,* Waseefa Fatma, Suraiya Khatoon, Ziya Ahmad Khan, and Andleeb Z. Naqvi

Department of Chemistry, Aligarh Muslim University, Aligarh - 202 002, India

Herein, we report the results of a study of surface and micellar properties of alkanediyl-α,ω-bis(dimethylcetylammonium bromide) gemini surfactants in pure aqueous solutions and also in the presence of alcohols (butanol, hexanol) and amines (butylamine, hexylamine). Parameters studied include cmc (critical micelle concentration), C_{20} (concentration required to reduce the surface tension of the solvent by 20 $\mathrm{mN \cdot m^{-1}}$), $\Gamma_{\max}$ (maximum surface excess concentration at the air/solution interface), and $A_{\min}$ (minimum area per surfactant molecule). These parameters indicate mixed micellization between the surfactants and alcohols/amines; therefore, surfactant−additive interactions in mixed micelles and mixed monolayers, as well as activity coefficients, are also calculated. All the results show that high additive concentrations destabilize micelles: ΔG_{ex} (excess free energy of micellization) becomes more negative at low additive concentrations (i.e., micelles stabilize) and less negative at high concentrations (i.e., micelles destabilize).

Introduction

Among natural forces, the hydrophobic−lipophilic effect is one of the most important and necessary forces for the formation of ordered assemblies of amphiphilic molecules, e.g., association colloids, vesicles, biological membranes, etc.[1,2] Upon dispersion in water, above a certain concentration known as the critical micelle concentration (cmc), the hydrocarbon segment of the surfactants tends to minimize exposure and thus self-associates to form aggregates (called micelles). The force that drives this association is entropic in origin and enhances the release of "structured" water molecules. But, while the hydrophobic chains (or surfactant tails) pack closely to minimize water contacts, the polar groups (or head groups), due to electrostatic repulsion and extensive headgroup hydration, tend to stay away from each other. In a micellar aggregate, thus, an "equilibrium" distance between the polar heads is maintained as a result of compromise between the two opposite tendencies. These tendencies are found to be dependent upon additives because they can affect either one or both of them by interacting with the micelle or by modifying bulk solution properties.

Since the first report by Bunton et al.,[3] dicationic surfactants are attracting a lot of interest. These surfactants, known as dimeric or gemini surfactants, contain two hydrophobic tails and two hydrophilic groups connected at the level of head groups by a spacer that may be hydrophilic, hydrophobic, flexible, or rigid [4−7] and may be cationic, anionic, or nonionic. All these surfactants showed two important features with respect to the monomeric surfactants, viz., much lower cmc values (10 to 100 times lower than corresponding conventional surfactants) and high efficiency to reduce the surface tension of water.[8] In general, these surfactants possess unusual surface and bulk properties, including better wetting power,[9] unusual micellar structure,[10,11] better solubilizing power,[12] low Krafft point,[8,12,13] unusual viscosity changes with an increase in surfactant concentration,[14] better viscoelasticity, gelification and shear thickening,[12] and superior performance as catalysts.[15,16] Cationic gemini surfactants are also capable of various biological activities.[17,18] Arginine-based gemini surfactants display a broad range of antimicrobial activity.[19] *N*-Acylamino acid derivatives are used in many cosmetic products because of their environmental acceptability and their mildness to skin.

In most of their applications, surfactants are used in the presence of additives. Among various additives, alcohols hold a special place because alcohols are the most common cosurfactants used with surfactant + oil systems to generate a microemulsion. Use of microemulsions in enhanced oil recovery has made it essential to study every aspect of the physicochemistry of surfactant + alcohol systems. Though the studies using amines as the cosurfactants in microemulsions are few, it has been proved that they are also potential candidates for such formulations.[20,21]

In this paper, we report a systematic study of surface and micellar properties of cationic gemini surfactants bis(quaternary ammonium halides) with linear chain length alcohols and amines. Parameters studied/evaluated are cmc, C_{20}, $\Gamma_{\max}$, $A_{\min}$, X_1^{m}, β^{m}, f_1^{m}, f_2^{m}, X_1^{σ}, β^{σ}, f_1^{σ}, f_2^{σ}, and $\Delta G_{\mathrm{m}}^{\circ}$. Although there are many reports on surface properties of cationic[4,19,22] as well as anionic[23−25] geminis, only the effect of salts, especially NaCl, has been studied. To the best of our knowledge, this is the first detailed report on gemini−alcohol/amine systems.

Materials and Methods

Three members of the series alkanediyl-α,ω-bis(dimethyl cetylammonium bromide), viz., butanediyl-1,4-bis(dimethylcetylammonium bromide), pentanediyl-1,5-bis(dimethylcetylammonium bromide), and hexanediyl-1,6-bis(dimethylcetylammonium bromide) (referred to as 16−4−16, 16−5−16, and 16−6−16 in this paper), were synthesized in the laboratory by adopting the following procedure[26,27]

---

* To whom correspondence may be addressed. E-mail: kabir7@rediffmail.com.

10.1021/je800032e CCC: $40.75

$$\mathrm{Br(CH_2)_{\mathit{m}}Br} \xrightarrow[\text{reflux}]{a} \mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{(Me)_2N^+} - \mathrm{(CH_2)}_m - {}^{+}\mathrm{N(Me)_2C}_n\mathrm{H}_{2n+1}, 2\mathrm{Br}^- \qquad (n = 16, m = 4 - 6)\ a = \mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{N(Me)_2}\ (3.0\ \text{equiv})$$

All compounds were obtained by refluxing the corresponding α,ω-dibromoalkane (with different *m*) with long chain *N*,*N*-dimethylalkylamine in dry ethanol (at ~ 80 °C) for 48 h. The solvent was then removed under vacuum, and the solids thus obtained were recrystallized from a hexane/ethylacetate mixture to obtain pure surfactants. ^{1}H NMR, CHN analysis, mass, and IR spectroscopy were used for product characterization.

All the chemicals used during the synthesis and additives (butanol, C_4OH, BDH (England), ≥ 99.0 %; hexanol, C_6OH, BDH (England), ≥ 99.0 %; butylamine, C_4NH_2, Fluka (Switzerland), ≥ 98.0 %; hexylamine, C_6NH_2, Fluka (Switzerland), 99.0 %) were used as received. Aqueous solutions of additives, with fixed additive concentration prepared in double distilled water of surface tension, $\gamma = 72\ \mathrm{mN \cdot m^{-1}}$, and specific conductivity, $\kappa = 2 \cdot 10^{-6}\ \mathrm{S \cdot cm^{-1}}$, were used as solvent throughout. Stock solutions of surfactants were prepared by dissolving the surfactant in aqueous + additive solutions. The different concentrations of surfactants were prepared by successive dilution of stock solution (of 50 mM) by solvent (with or without additives) using a Hamilton microsyringe.

The surface tension was measured by the ring method using the Du Nouy tensiometer at ~308 K. The instrument was calibrated against double distilled water at the time of measurement. The uncertainties on cmc are estimated to be less than ± $(0.1\ \text{to}\ 0.3) \cdot 10^{-5}$.

Results and Discussion

(A) Surface and Micellar Properties. (i) cmc. Figures 1 and 2 show the variation of surface tension of pure gemini surfactants and in the presence of different fixed concentrations of additives (concentration range (0 to 200.0) mM for C_4OH, (0 to 20.0) mM for C_6OH, (0 to 100.0) mM for C_4NH_2, and (0 to 10.0) mM for C_6NH_2) with surfactant concentration. cmc values of the geminis in water are in fair agreement with the published data in the literature.[4,26] Clearly, the surface tension decreases as the concentration of surfactant increases. Surfactant molecules at low concentrations adsorb at the liquid/air interface until the surface of the solution is completely occupied. Then, the excess molecules tend to self-associate in the solution to form micelles, and surface tension becomes constant.

From the intersection points in γ−log (concentration) curves, the cmc is determined for each additive concentration and is given in Tables 1 and 2. Two opposite effects control micellization: the effect of the hydrophobic group as an important driving force in micellization and the effect of the hydrophilic group opposing it.

Variation of cmc of gemini surfactants with the addition of C_4OH is presented in Figure 3. The values show a similar pattern for all the three geminis: a sharp decrease at low alcohol concentrations and an increase at high concentrations.

Compared to cetyltrimethylammonium bromide, the geminis have remarkably low cmc values which arise mainly because of the two hydrophobic chains which transfer at the same time from the aqueous to micellar phase.[28] In conventional surfactants of homologous series, cmc varies as

$$\log(\mathrm{cmc}) = A - Bn_{\mathrm{c}} \qquad (1)$$

where n_{c} is the number of carbon atoms in the hydrocarbon chain and A and B are constants, specific to a series under constant conditions of temperature, pressure, etc. However, in gemini surfactants, cmc depends on another factor: the spacer, which can affect the cmc in an unusual way.

In the absence of C_4OH, cmc increases with the increase in spacer chain length. A similar trend of cmc increase for short spacers was observed for both cationic[4,19] as well as anionic[24] gemini surfactants. The results were discussed in terms of a change in conformation of the surfactants as the spacer chain length increases. Monte Carlo simulations of gemini surfactant solutions predicted the presence of a maximum in the cmc vs spacer chain length plot for surfactants with a hydrophobic spacer.[29,30]

As the concentration of C_4OH increases in the solution, the cmc values first decrease steeply and then increase again after attaining a minimum value at 3 mM C_4OH. The behavior can be explained by taking into consideration the distribution of alcohols between the micellar and aqueous phase. Due to the presence of the nonpolar hydrocarbon part together with the strongly hydrophilic hydroxyl group in an alcohol molecule, it may be imagined that when the alcohol molecule is brought in contact with the aqueous environment the hydrophobic hydrocarbon group resists the pull into solution exerted by the hydrophilic hydroxyl group. The influence of alcohols on the thermodynamics and on the structure of micelles has been studied using different techniques[31−33] which suggests that the alcohol induces structural changes in the micelles. It has been shown that short chain length alcohols (C_1 to C_3) prefer the aqueous phase; medium chain length alcohols (C_4 and C_5) distribute between the two phases; and long chain length ones (C_6 and above) prefer the micellar phase.[32,34,35] Medium to long chain length alcohols, hence, form mixed micelles with surfactants. Usually the cmc's of mixed systems fall in between the cmc's of the individual components. However, they may sometimes fall above or below this concentration range.[36,37]

Solubilization of C_4OH molecules in the micellar palisade layer decreases the repulsive forces between the head groups of similar charge. Also, reduction of the dielectric constant of the palisade layer, when C_4OH molecules replace water molecules, decreases the degree of dissociation of the surfactant molecules, thus decreasing the charge density.[38] As a result, cmc values should decrease which is observed in our case.

However, above 3.0 mM the opposite trend is observed. The cmc starts increasing with an increase in C_4OH concentration. It is well-known that alcohols, when added in large amount, decrease the aggregation number, increase the cmc, and cause micellar breakdown. Caponetti et al.[33] studied the effect of alcohols on the size of SDS micelles. They observed that at high alcohol concentrations the distribution coefficient of the alcohol as well as the number of alcohol molecules/micelle increases and the number of surfactant molecules/micelle decreases with an increase in alcohol concentration. Our results of cmc as well as of X_{m} and β also support this. At high alcohol concentration, the mole fraction of the alcohol in the micelles increases to a value of 0.5256 (see Table 3), and hence the mole fraction of surfactant in the micelles decreases. This decreases the surfactant aggregation number, or in other words, micellar breakdown increases the cmc.

Results of cmc variation of geminis in the presence of C_6OH are plotted in Figure 4. The behavior is similar to that of C_4OH with the difference that the cmc increasing region is absent. cmc decreases up to 5.0 mM and then becomes constant. C_6OH solubilizes in the headgroup region and enhances the process of micellization. Due to low aqueous solubility of C_6OH, we

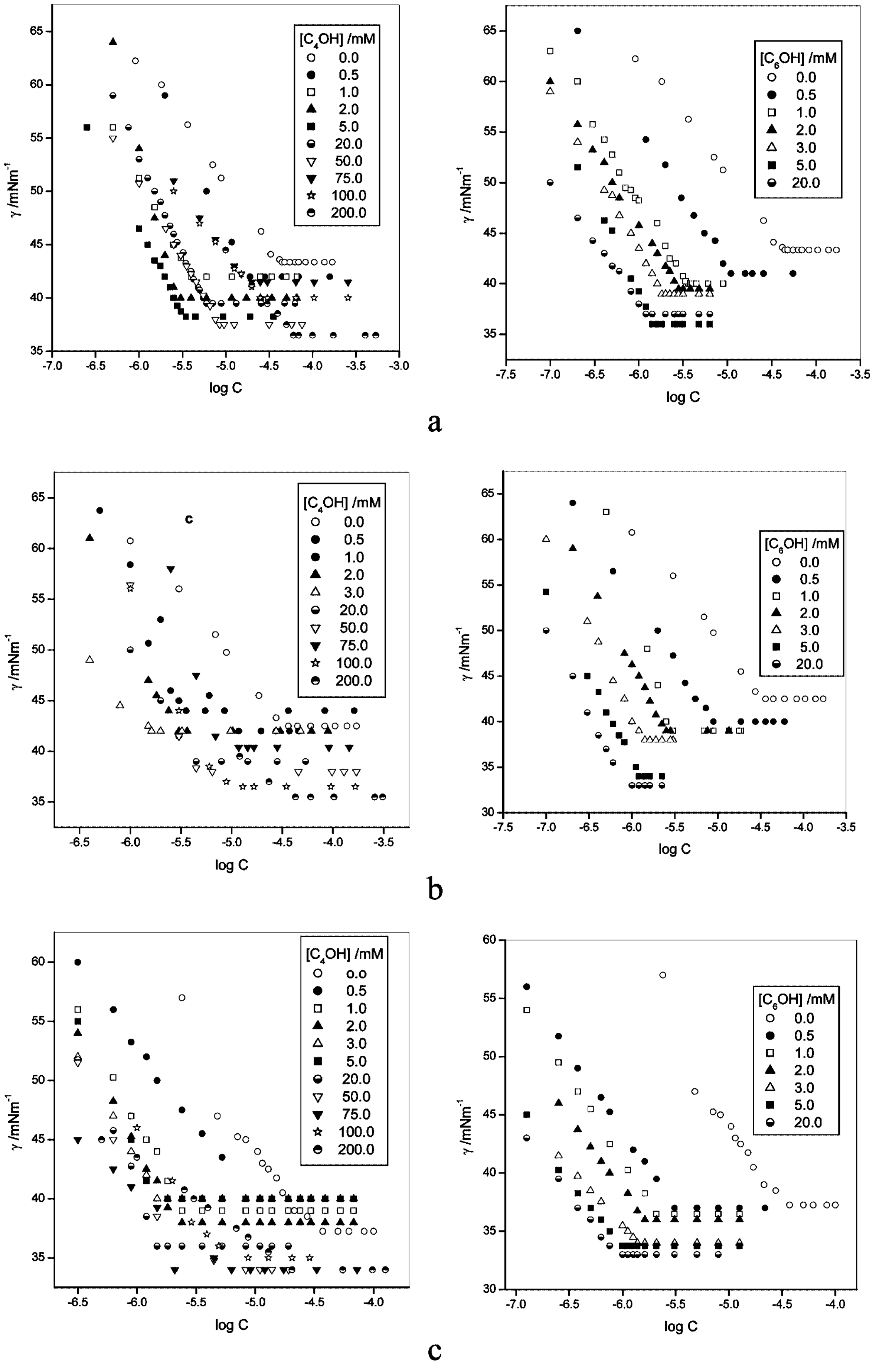

Figure 1. Variation of surface tension (γ) with concentration of gemini surfactants at different fixed concentrations of alcohols. (a) 16−4−16; (b) 16−5−16; (c) 16−6−16.

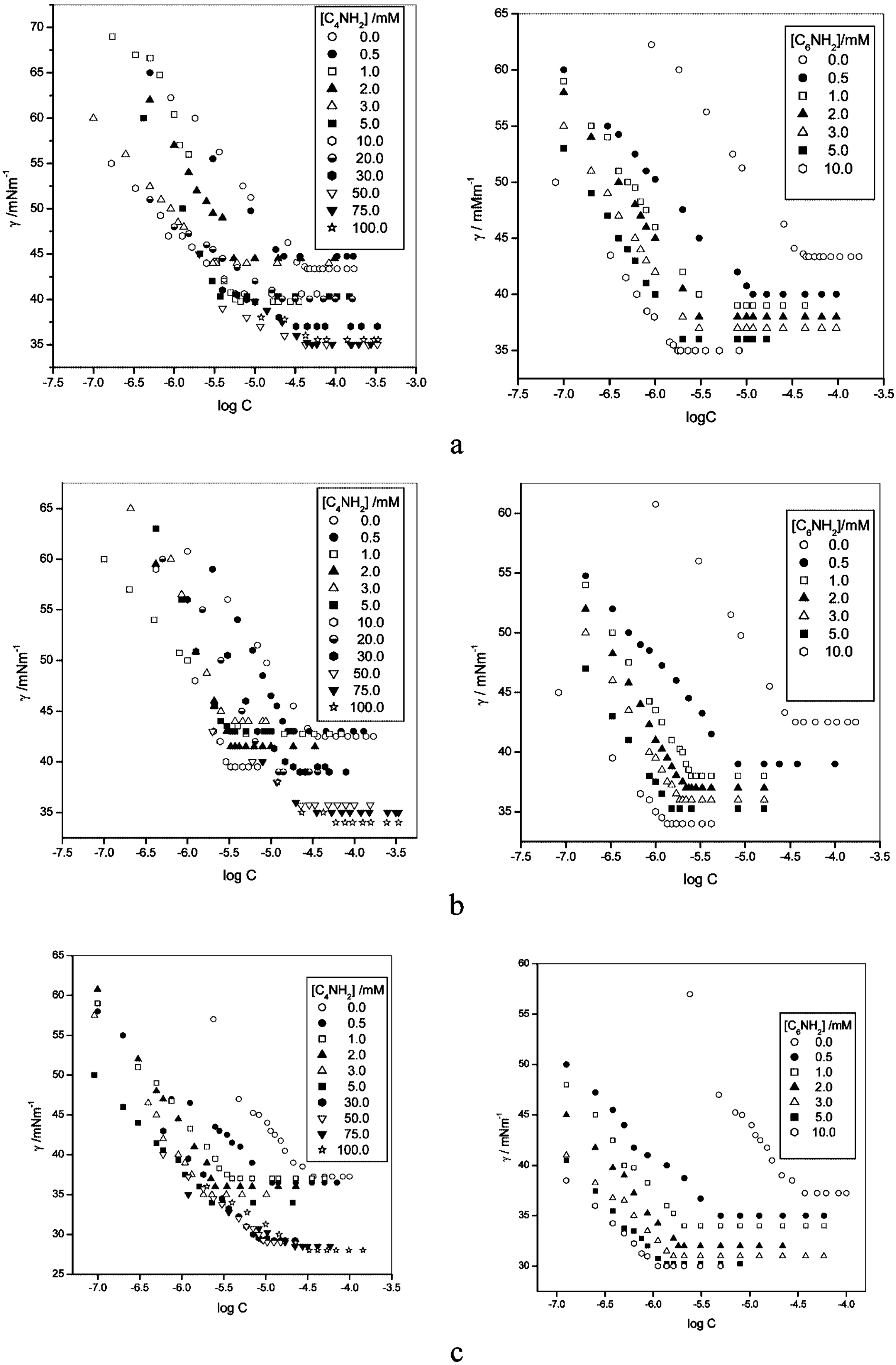

Figure 2. Variation of surface tension (γ) with concentration of gemini surfactants at different fixed concentrations of amines. (a) 16−4−16; (b) 16−5−16; (c) 16−6−16.

Table 1. cmc, C_{20}, Γ_{max}, and A_{min} for Gemini Surfactants in the Presence of Alcohols

	16−4−16				16−5−16				16−6−16			
additive	$10^5\cdot$cmc	$10^5\cdot C_{20}$	$10^{11}\cdot\Gamma_{max}$	A_{min}	$10^5\cdot$cmc	$10^5\cdot C_{20}$	$10^{11}\cdot\Gamma_{max}$	A_{min}	$10^5\cdot$cmc	$10^5\cdot C_{20}$	$10^{11}\cdot\Gamma_{max}$	A_{min}
mM	M	M	mol·cm^{-2}	Å^2	M	M	mol·cm^{-2}	Å^2	M	M	mol·cm^{-2}	Å^2
						C_4OH						
0	2.72	0.22	7.55	220.00	3.61	0.72	6.95	239.01	4.46	0.69	6.79	238.62
0.5	1.09	0.14	7.73	214.88	1.17	0.28	8.83	187.93	1.92	0.50	7.01	164.01
1.0	0.23	0.09	10.52	157.84	0.84	0.25	–	–	0.39	0.15	8.87	187.09
2.0	0.20	0.07	10.88	152.67	0.29	0.15	12.77	129.97	0.30	0.17	18.73	88.66
3.0	0.14	0.07	9.85	168.62	0.16	0.51	6.36	261.10	–	–	–	–
5.0	0.17	0.08	13.47	123.27	–	–	–	–	0.35	0.12	8.99	184.63
20.0	0.20	0.08	11.19	148.35	0.45	0.03	9.95	166.89	0.59	0.35	10.33	160.78
50.0	0.44	0.10	10.44	159.04	0.64	0.36	16.09	103.16	0.84	0.45	8.04	206.57
75.0	0.61	0.49	8.45	196.48	1.17	0.83	21.31	77.092	1.99	3.47	6.37	260.64
100.0	0.88	–	–	–	1.27	0.83	11.59	143.29	2.48	6.31	5.69	291.99
200.0	2.92	10.90	3.88	428.19	4.21	25.12	4.87	340.77	5.92	28.84	5.61	295.81
						C_6OH						
0	2.72	0.22	7.55	220.00	3.61	0.72	6.95	239.01	4.46	0.69	6.79	238.62
0.5	0.31	0.07	7.36	217.75	0.88	0.34	8.26	201.06	1.07	0.46	7.79	212.86
1.0	0.21	0.06	8.07	205.85	0.3	0.17	8.30	90.72	0.36	0.18	8.53	194.53
2.0	0.16	0.04	6.95	238.81	0.25	0.15	10.51	157.93	0.28	0.16	7.95	208.77
3.0	0.13	0.02	5.67	292.86	0.14	0.08	11.19	148.35	0.18	0.11	8.81	188.54
5.0	0.10	0.08	6.20	267.77	0.12	0.11	10.32	160.87	0.14	0.17	10.22	162.47
20.0	0.09	0.09	6.76	245.60	0.10	0.01	10.71	155.01	0.12	0.27	6.76	245.60

Table 2. cmc, C_{20}, Γ_{max}, and A_{min} for Gemini Surfactants in the Presence of Amines

	16−4−16				16−5−16				16−6−16			
additive	$10^5\cdot$cmc	$10^5\cdot C_{20}$	$10^{11}\cdot\Gamma_{max}$	A_{min}	$10^5\cdot$cmc	$10^5\cdot C_{20}$	$10^{11}\cdot\Gamma_{max}$	A_{min}	$10^5\cdot$cmc	$10^5\cdot C_{20}$	$10^{11}\cdot\Gamma_{max}$	A_{min}
mM	M	M	mol·cm^{-2}	Å^2	M	M	mol·cm^{-2}	Å^2	M	M	mol·cm^{-2}	Å^2
						C_4NH_2						
0	2.72	0.22	7.55	220.00	3.61	0.72	6.95	239.01	4.46	0.69	6.79	238.62
0.5	1.20	0.06	5.66	293.16	1.55	0.65	10.13	163.92	2.29	0.81	7.03	236.32
1.0	0.39	0.04	7.76	213.94	0.33	0.12	5.85	283.80	0.66	0.26	12.56	132.20
2.0	0.24	0.07	9.59	173.19	0.33	0.21	10.98	151.26	0.55	0.49	9.11	182.22
3.0	0.18	0.05	9.77	169.99	0.37	0.21	6.05	274.52	0.30	0.23	6.13	270.98
5.0	0.22	0.03	6.35	261.34	0.33	0.25	13.51	122.90	0.37	0.25	12.04	137.91
10.0	0.29	0.04	–	–	0.32	0.28	12.70	130.73	0.56	0.41	5.19	319.63
20.0	–	–	–	–	1.22	1.06	9.37	177.17	2.20	2.20	3.54	467.74
30.0	0.81	0.16	6.95	239.01	2.19	2.63	6.22	267.04	3.19	0.39	2.49	667.59
50.0	1.04	0.17	5.05	328.94	2.29	2.19	3.87	429.45	4.21	0.79	2.26	734.35
75.0	2.22	0.11	2.86	580.52	3.47	2.19	5.65	293.74	5.12	4.39	4.13	402.39
100.0	3.27	0.40	3.75	442.38	5.66	7.69	3.11	534.08	6.01	0.15	5.11	324.94
						C_6NH_2						
0	2.72	0.22	7.55	220.00	3.61		6.95		4.46	0.70	6.79	238.62
0.5	0.50	0.08	5.37	309.20	0.98	0.39	5.08	326.74	1.17	0.80	5.39	307.60
1.0	0.21	0.50	6.59	251.77	0.25	0.15	7.52	220.86	0.35	0.33	1.94	85.39
2.0	0.18	0.03	6.38	260.18	0.21	0.50	7.86	211.32	0.30	0.21	7.46	222.53
3.0	0.16	0.02	5.09	326.17	0.18	0.11	11.01	150.79	0.25	0.18	7.40	224.29
5.0	0.13	0.02	5.64	294.33	0.13	0.19	6.84	327.11	0.20	0.13	7.65	216.94
10.0	0.11	0.06	5.16	321.73	0.15	0.08	5.08	242.76	0.18	0.28	6.43	258.35

were unable to study the effect of high C_6OH concentration on micellization.

(ii) Γ_{max}. It is well-known that the air/solution interface of an amphiphile solution is well populated by the adsorbed molecules.[39] Accordingly, it has been shown that the concentration of the surfactant is always more at the surface due to adsorption over and above the concentration of surfactant in the bulk.

On the basis of the plot of the surface tension as a function of the equilibrium concentration of these surfactants in water, the maximum surface excess concentration at the air/water interface, Γ_{max}, was evaluated by the Gibbs adsorption equation[40,41] as

$$\Gamma_{max} = (-1/2.303nRT)(d\gamma/d \log C)_{T,P} \tag{2}$$

where R is the gas constant and T the temperature in Kelvin. n is introduced to allow for the simultaneous adsorption of cations and anions. The value of n was calculated using the equation given by Matejevic and Pethica[42]

$$n = 1 + C/(C + C_s) \tag{3}$$

where C_s is the concentration of added electrolytes. Thus, $n = 2$ in water and approaches 1 in the presence of excess electrolyte. For ionic surfactants in the absence of electrolyte, the value of n decreases with an increase in surfactant concentration as that changes the counterion concentration. For divalent geminis, n is taken as 3 (the divalent amphiphile and two counterions).[19,24] The values of Γ_{max} (and also of A_{min}) given in Tables 1 and 2 are based upon $n = 3$ with the understanding that they merely indicate changes within the two additives.

In the absence of any alcohol, Γ_{max} values are in the order: 16−4−16 < 16−5−16 < 16−6−16. This may be due to intramolecular headgroup distances. In this case, the spacer chain could be in contact with water. On adding alcohols (both C_4OH and C_6OH) into the gemini surfactant solutions, Γ_{max} values

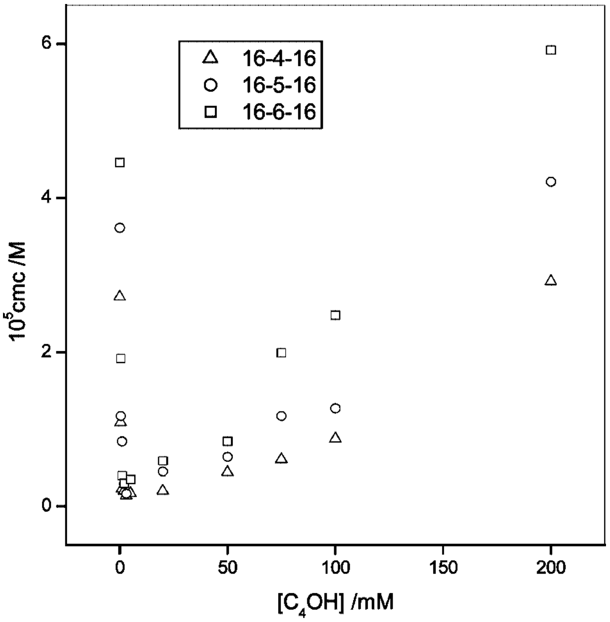

Figure 3. Variation of cmc of gemini surfactants at different fixed concentrations of C_4OH (alcohol was added up to the solubility limit).

increase up to a certain concentration, which is different for different surfactants, and then decrease. The presence of low alcohol concentrations decreases the repulsion among head groups, and more surfactant molecules can adsorb at the interface. However, after saturation of the interface, the surfactant molecules start solubilizing into the solution decreasing the Γ_{max}.

(iii) A_{min}. Using Γ_{max} values, the minimum area per headgroup, A_{min}, can be evaluated by the equation[41,43]

$$A_{min} = 1/N_A\Gamma_{max} \cdot 10^{16} \tag{4}$$

The A_{min} values in water are smaller for the gemini of smaller spacer chain length, which is further evidence that chains are lying at the air/water interface. A_{min} values show a U-shaped behavior in the presence of alcohols: A_{min} first decreases and then at high alcohol concentrations it increases again. The A_{min} decreasing trend is expected as electrostatic repulsions between the head groups are reduced by the addition of alcohols, and surfactant molecules are more tightly packed in the presence of alcohols.

(iv) pC_{20}. It is a measure of surface tension reduction efficiency.

$$pC_{20} = -\log C_{20} \tag{5}$$

C_{20} is the molar concentration of surfactant required to reduce the surface tension of the solvent by 20 mN·m^{-1}. As noted for Γ_{max} values, because of the repulsion in charged head groups in the presence of alcohols, pC_{20} values are greater than that of pure surfactants, and with increasing alcohol concentration, the values show inverted U-shaped curves. Thus, the presence of alcohols appears to cause a more efficient adsorption at the interface.

Figures 5 and 6 show the effect of butylamine and hexylamine on the cmc values of the three geminis. The behavior is by and large similar to alcohols, the reason being the same as that given for alcohols. The cmc values are, however, higher with amines in comparison to the values with alcohols. This can be understood in light of the hydrophobic ranking of the two types of additives. Amines are more hydrophilic than alcohols in the cationic systems.[44] It is known that C_4 to C_{10} alkylamines are solubilized in ionic micelles by electrostatic and hydrophobic effects with the amine group left on the micellar surface.[45] Their

Table 3. Micellar Compositions (X_1^m, X_1^σ), Interaction Parameters (β^m, β^σ), and Activity Coefficients (f_1^m, f_2^m, f_1^σ, f_2^σ) of Binary Mixtures of Gemini Surfactants and C_4OH at Different Mole Fractions of C_4OH (α_1)

α_1	X_1^m	β^m	f_1^m	f_2^m	ΔG_{ex}/ kJ·mol^{-1}	X_1^σ	β^σ	f_1^σ	f_2^σ
					16−4−16				
0.625	0.335	−12.050	0.005	0.259	−6.8	0.234	−8.058	0.009	0.642
0.769	0.377	−14.326	0.004	0.131	−8.5	0.289	−9.614	0.008	0.447
0.870	0.401	−18.265	0.001	0.053	−11.1	0.342	−11.570	0.007	0.258
0.909	0.428	−21.946	0.001	0.018	−13.5	0.388	−13.822	0.006	0.125
0.943	0.452	−22.656	0.001	0.010	−14.2	0.415	−15.539	0.005	0.069
0.985	0.473	−22.213	0.002	0.007	−13.9	0.432	−16.721	0.005	0.044
0.994	0.500	−23.463	0.003	0.003	−14.8	0.459	−19.262	0.004	0.017
0.995	0.503	−21.542	0.005	0.004	−13.6	0.473	−21.185	0.003	0.009
0.996	0.513	−21.944	0.006	0.003	−13.8	0.489	−23.473	0.002	0.004
0.998	0.526	−17.909	0.018	0.007	−11.3	0.502	−26.345	0.002	0.001
					16−5−16				
0.500	0.335	−12.554	0.004	0.244	−7.0	0.232	−8.377	0.007	0.636
0.667	0.377	−14.693	0.003	0.125	−8.5	0.283	−9.615	0.007	0.464
0.833	0.412	−19.174	0.001	0.038	−11.7	0.364	−12.593	0.006	0.188
0.882	0.445	−23.553	0.001	0.009	−14.7	0.393	−14.167	0.005	0.112
0.976	0.479	−22.798	0.002	0.005	−14.4	0.422	−16.359	0.004	0.054
0.990	0.493	−22.771	0.003	0.004	−14.3	0.440	−17.798	0.004	0.032
0.993	0.512	−22.417	0.005	0.003	−11.3	0.455	−19.386	0.003	0.018
0.995	0.530	−23.701	0.005	0.001	−14.9	0.463	−20.653	0.003	0.012
0.996	0.548	−19.923	0.017	0.003	−12. 5	0.477	−22.525	0.002	0.006
					16−6−16				
0.500	0.323	−10.961	0.007	0.318	−6.0	0.223	−7.958	0.008	0.673
0.667	0.379	−16.766	0.002	0.090	−9. 9	0.283	−9.552	0.007	0.467
0.800	0.402	−18.552	0.001	0.050	−11.3	0.325	−10.788	0.007	0.320
0.909	0.440	−20.526	0.002	0.019	−12.7	0.401	−14.386	0.006	0.099
0.977	0.454	−19.712	0.003	0.017	−12.6	0.419	−15.434	0.005	0.067
0.980	0.485	−21.031	0.004	0.007	−13.2	0.427	−16.275	0.005	0.051
0.993	0.503	−19.177	0.009	0.008	−12.1	0.435	−17.141	0.004	0.039
0.995	0.525	−20.218	0.010	0.004	−12.7	0.442	−17.932	0.004	0.030
0.998	0.542	−17.693	0.024	0.006	−11.1	0.450	−19.267	0.003	0.020

Table 4. Micellar Compositions (X_1^{m}, X_1^{σ}), Interaction Parameters (β^{m}, β^{σ}), and Activity Coefficients (f_1^{m}, f_2^{m}, f_1^{σ}, f_2^{σ}) of Binary Mixtures of Gemini Surfactants and C_6OH at Different Mole Fractions of C_6OH (α_1)

α_1	X_1^{m}	β^{m}	f_1^{m}	f_2^{m}	ΔG_{ex}/kJ·mol^{-1}	X_1^{σ}	β^{σ}	f_1^{σ}	f_2^{σ}
16−4−16									
0.625	0.393	−17.181	0.002	0.071	−10.3	0.288	−8.593	0.013	0.491
0.769	0.421	−19.636	0.001	0.031	−12.0	0.332	−10.079	0.011	0.329
0.869	0.443	−21.854	0.001	0.014	−13.6	0.374	−11.879	0.009	0.191
0.909	0.452	−23.249	0.001	0.009	−14. 6	0.402	−14.024	0.007	0.104
0.943	0.463	−25.093	0.001	0.005	−15.8	0.423	−16.367	0.004	0.053
0.985	0.489	−28.202	0.001	0.001	−17.8	0.440	−18.947	0.003	0.026
16−5−16									
0.500	0.356	−13.070	0.004	0.191	−7.6	0.276	−8.467	0.012	0.526
0.667	0.410	−18.809	0.001	0.042	−11.5	0.312	−9.645	0.010	0.391
0.800	0.441	−20.592	0.002	0.018	−12.8	0.353	−11.171	0.009	0.248
0.857	0.454	−23.540	0.001	0.008	−14.7	0.394	−13.487	0.007	0.124
0.909	0.472	−25.465	0.001	0.004	−16.0	0.415	−15.808	0.005	0.065
0.976	0.489	−27.770	0.001	0.001	−17.5	0.433	−19.333	0.002	0.027
16−6−16									
0.500	0.361	−12.808	0.005	0.189	−7.4	0.275	−8.650	0.011	0.520
0.667	0.412	−16.486	0.003	0.061	−10.1	0.311	−9.667	0.010	0.394
0.800	0.438	−19.947	0.002	0.022	−12.4	0.347	−11.185	0.009	0.259
0.857	0.449	−22.071	0.001	0.012	−13. 8	0.380	−13.038	0.007	0.153
0.909	0.467	−24.456	0.001	0.005	−15.3	0.401	−15.653	0.004	0.081

partial dissociation into NH_3^+ and OH^- may affect the electrostatic interaction with the cationic headgroup, which may hinder the micellization.

(B) Surfactant−Additive Interactions. All the above results indicate that the additives form mixed micelles with the gemini surfactants; hence, to investigate the nature of interaction between the constituents in the mixed micelles, we calculated the interaction parameters for mixed micelles and mixed monolayer, β^{m} and β^{σ}, which are presented in Tables 3 to 6.

(v) X_1. The interaction parameter for mixed micelle formation is calculated using Rubingh's theory.[46] According to this theory, if two components form mixed micelles, the mole fraction of component 1, X_1, in the micelle is related to α_1 and the cmc's of pure components (cmc_1, cmc_2) and mixture (cmc) by the following relation

$$\frac{[(X_1^{m})^2 \cdot \ln(\text{cmc} \cdot \alpha_1/\text{cmc}_1 \cdot X_1^{m})]}{[(1 - X_1^{m})^2 \cdot \ln\{\text{cmc} \cdot (1 - \alpha_1)/\text{cmc}_2 \cdot (1 - X_1^{m})\}]} = 1 \quad (6)$$

$$\beta^{m} = \ln(\text{cmc} \cdot \alpha_1/\text{cmc}_1 \cdot X_1^{m})/(1 - X_1^{m})^2 \quad (7)$$

The composition of the adsorbed mixed monolayer of binary component systems in equilibrium with the singly dispersed components can be evaluated using Rosen's equations.[47,48] From analogy with the derivation of Rubingh's equations for mixed micelles, the mole fraction of component 1, X_1^{σ}, in the mixed monolayer is related to α_1 as

$$\frac{[(X_1^{\sigma})^2 \cdot \ln(C \cdot \alpha_1/C_1 \cdot X_1^{\sigma})]}{[(1 - X_1^{\sigma})^2 \cdot \ln\{C \cdot (1 - \alpha_1)/C_2 \cdot (1 - X_1^{\sigma})\}]} = 1 \quad (8)$$

$$\beta^{\sigma} = \ln(C \cdot \alpha_1/C_1 \cdot X_1^{\sigma})/(1 - X_1^{\sigma})^2 \quad (9)$$

C_1, C_2, and C are the molar concentrations of components 1 and 2 and their mixture at α_1, required to produce a given surface tension reduction. Equations 6 and 8 are solved iteratively for X_1, and β values are obtained by substituting X_1 in eqs 7 and 9.

The values of X_1^{m} and X_1^{σ}, given in Tables 3 to 6, reveal that the contribution of X_1^{m}/X_1^{σ} increases continuously with the increase in alcohol concentration. The contribution of surfactant is significant at low alcohol mole fractions, whereas at higher mole fractions, mixed micelles become rich in alcohol content. Above $\alpha_1 = 0.994$, mixed micelles contain more than 50 % of the total molecules as alcohol molecules. In other words, the aggregation numbers of surfactants are decreasing at higher mole fraction of alcohol resulting in micellar breakdown (which is evidenced in a cmc increase in the presence of high alcohol contents). Results with amines are similar to that of alcohols with the exception that values of X_1 are smaller with amines than with alcohols. Due to a charge similar to the charge of surfactants, less amine partitions in the headgroup region.

(vi) β^{m}/β^{σ}. β not only indicates the degree of interaction between the two components but also accounts for the deviation from ideality. β assumes a value of zero for ideal mixing of two components. A positive β-value means repulsion among mixed species. A negative β-value implies an attractive interaction: the more negative its value, the greater the interaction. The β^{m} values are negative at all mole fractions of the mixed system, suggesting that the interaction between the two components is more attractive in the mixed

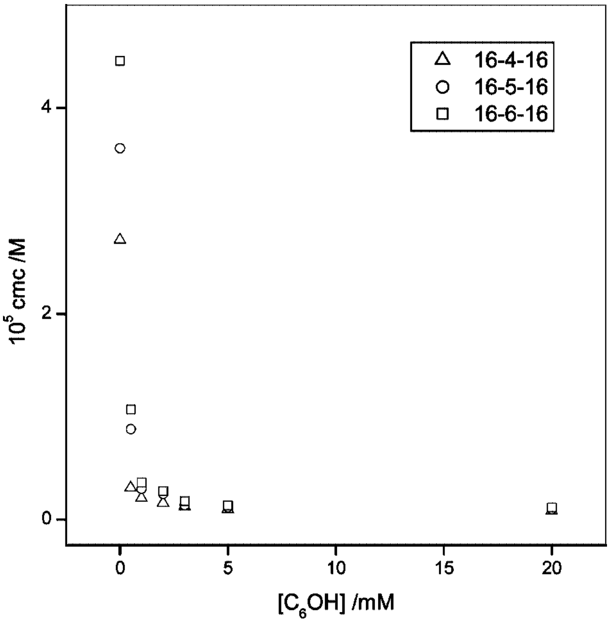

Figure 4. Variation of the cmc of gemini surfactants at different fixed concentrations of C_6OH (alcohol was added up to the solubility limit).

Table 5. Micellar Compositions (X_1^m, X_1^σ), Interaction Parameters (β^m, β^σ), and Activity Coefficients (f_1^m, f_2^m, f_1^σ, f_2^σ) of Binary Mixtures of Gemini Surfactants and C_4NH_2 at Different Mole Fractions of C_4NH_2 (α_1)

α_1	X_1^m	β^m	f_1^m	f_2^m	ΔG_{ex}/kJ·mol^{-1}	X_1^σ	β^σ	f_1^σ	f_2^σ
					16−4−16				
0.500	0.310	−12.867	0.002	0.290	−6.9	0.268	−13.765	0.001	0.373
0.667	0.322	−10.208	0.009	0.347	−5.6	0.302	−14.922	0.001	0.256
0.800	0.351	−17.535	0.001	0.115	−10.1	0.338	−16.521	0.001	0.152
0.857	0.362	−18.759	0.001	0.086	−10.9	0.362	−18.046	0.001	0.094
0.909	0.379	−19.225	0.001	0.063	−11.4	0.372	−18.712	0.001	0.075
0.952	0.399	−19.783	0.001	0.043	−11.9	0.381	−19.443	0.001	0.059
0.978	0.422	−18.423	0.002	0.038	−11.3	0.399	−20.999	0.001	0.035
0.980	0.434	−18.513	0.003	0.031	−11. 5	0.410	−22.146	0.0004	0.024
0.987	0.449	−17.083	0.007	0.032	−10.6	0.418	−23.054	0.0004	0.018
0.990	0.457	−16.328	0.008	0.033	−10.2	0.429	−24.634	0.0003	0.011
					16−5−16				
0.500	0.312	−12.410	0.003	0.298	−6.7	0.272	−13.958	0.001	0.356
0.667	0.328	−15.875	0.001	0.182	−8. 8	0.312	−15.542	0.001	0.220
0.800	0.342	−16.257	0.001	0.149	−9.2	0.338	−16.713	0.001	0.148
0.857	0.365	−17.151	0.001	0.102	−10.0	0.368	−18.461	0.001	0.083
0.909	0.390	−18.912	0.001	0.057	−11.3	0.380	−19.259	0.001	0.062
0.952	0.402	−19.749	0.001	0.041	−11.9	0.387	−19.889	0.001	0.051
0.976	0.417	−16.835	0.003	0.054	−10.3	0.397	−20.742	0.001	0.038
0.978	0.422	−15.444	0.006	0.064	−9.5	0.402	−21.394	0.001	0.031
0.980	0.438	−16.280	0.006	0.044	−10.1	0.411	−22.333	0.0004	0.023
0.987	0.452	−15.840	0.009	0.039	−9.9	0.419	−23.391	0.0004	0.017
0.990	0.469	−15.235	0.014	0.035	−9.6	0.431	−24.962	0.0003	0.009
					16−6−16				
0.500	0.313	−11.605	0.004	0.322	−6.3	0.277	−13.820	0.001	0.347
0.667	0.332	−14.567	0.002	0.201	−8.2	0.312	−15.450	0.001	0.222
0.800	0.353	−15.676	0.001	0.142	−9.0	0.340	−16.916	0.001	0.142
0.857	0.371	−18.031	0.001	0.084	−10.6	0.368	−18.795	0.001	0.079
0.909	0.391	−18.694	0.001	0.057	−11.2	0.388	−20.438	0.001	0.046
0.952	0.410	−18.729	0.002	0.043	−11.4	0.392	−21.149	0.0004	0.039
0.976	0.428	−15.780	0.006	0.056	−9.7	0.403	−22.367	0.0003	0.026
0.978	0.434	−14.403	0.010	0.066	−8.9	0.410	−23.291	0.0003	0.020
0.980	0.441	−14.617	0.010	0.058	−9.1	0.420	−24.842	0.0002	0.013
0.987	0.452	−14.544	0.013	0.051	−9.1	0.423	−25.809	0.0002	0.010
0.990	0.463	−14.669	0.015	0.043	−9.2	0.434	−27.484	0.0002	0.006

Table 6. Micellar Compositions (X_1^m, X_1^σ), Interaction Parameters (β^m, β^σ), and Activity Coefficients (f_1^m, f_2^m, f_1^σ, f_2^σ) of Binary Mixtures of Gemini Surfactants and C_6NH_2 at Different Mole Fractions of C_6NH_2 (α_1)

α_1	X_1^m	β^m	f_1^m	f_2^m	ΔG_{ex}/kJ·mol^{-1}	X_1^σ	β^σ	f_1^σ	f_2^σ
					16−4−16				
0.625	0.323	−13.042	0.003	0.256	−7.2	0.272	−12.780	0.001	0.388
0.769	0.362	−16.588	0.001	0.114	−9.6	0.303	−13.934	0.001	0.278
0.869	0.398	−18.940	0.001	0.050	−11.5	0.324	−14.934	0.001	0.208
0.909	0.416	−20.514	0.001	0.029	−12.6	0.345	−16.223	0.001	0.144
0.943	0.440	−22.999	0.001	0.012	−14.3	0.368	−17.793	0.001	0.090
0.943	0.452	−13.042	0.003	0.256	−8.7	0.383	−19.205	0.001	0.059
					16−5−16				
0.500	0.313	−11.649	0.004	0.319	−6.3	0.279	−13.491	0.001	0.350
0.667	0.357	−16.226	0.001	0.126	−9.4	0.308	−14.534	0.001	0.252
0.800	0.394	−18.524	0.001	0.056	−11.2	0.331	−15.470	0.001	0.183
0.857	0.424	−20.968	0.001	0.023	−12.9	0.357	−17.024	0.001	0.115
0.909	0.444	−23.497	0.001	0.010	−14.6	0.379	−19.006	0.001	0.065
0.952	0.471	−25.502	0.001	0.004	−16.0	0.398	−20.712	0.001	0.038
					16−6−16				
0.500	0.323	−11.673	0.005	0.295	−6.4	0.277	−13.576	0.001	0.354
0.667	0.354	−15.254	0.002	0.147	−8.8	0.310	−15.014	0.001	0.237
0.800	0.388	−17.117	0.002	0.076	−10.3	0.339	−16.443	0.001	0.152
0.857	0.412	−19.079	0.001	0.039	−11.6	0.362	−18.052	0.001	0.094
0.909	0.435	−21.374	0.001	0.017	−13.2	0.389	−20.774	0.0004	0.043
0.962	0.459	−11.673	0.005	0.295	−7.8	0.401	−22.375	0.0003	0.027

micelle than the self-interaction of two components before mixing. As the mole fraction of alcohols increases, β^m values become more negative. This indicates an increase in attractive interaction with the increase in additive concentration which is also evident from the cmc values which decrease with the additive concentration.

The trend followed by β^σ is similar. The surfactant−alcohol mixtures show stronger attractive interaction at the air/water interface. These interactions are stronger than in mixed micelles as evidenced by the fact that β^σ values are more negative than β^m values. This is due to the steric factor which is more important in micelle formation than in monolayer formation at a planar interface. Increased bulkiness in the hydrophobic group (alkyl chain) of alcohol causes greater difficulty in getting it incorporated into the curved mixed micelle compared to that of accommodating at the planar air/water interface.[49]

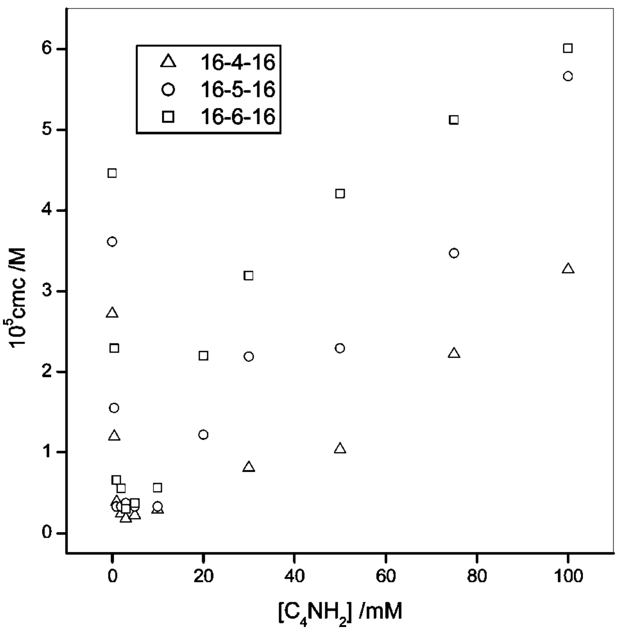

Figure 5. Variation of cmc of gemini surfactants at different fixed concentrations of C_4NH_2 (amine was added up to the solubility limit).

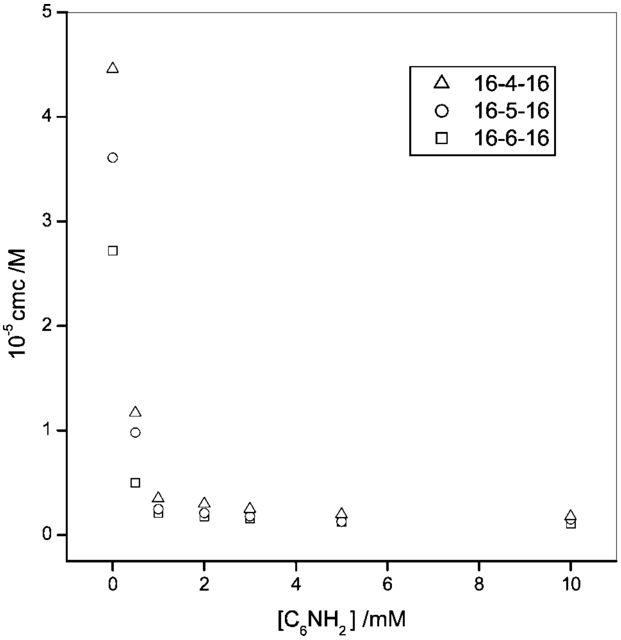

Figure 6. Variation of cmc of gemini surfactants at different fixed concentrations of C_6NH_2 (amine was added up to the solubility limit).

However, $|\beta|$ decreases at high mole fractions of alcohol. The trend of β values is understandable in light of all the above discussions. As the micelle aggregation number decreases and micelles become less stable at high alcohol content, the interaction among alcohol−surfactant also decreases.

(vii) f_1 and f_2. The activity coefficients f_1 and f_2 can be calculated as defined by Rosen et al.[49,50]

$$f_1 = \exp \beta \cdot (1 - X_1)^2 \qquad (10)$$

$$f_2 = \exp \beta \cdot (X_1)^2 \qquad (11)$$

For mixed micelles, $\beta = \beta^{\mathrm{m}}$ and $X_1 = X_1^{\mathrm{m}}$, whereas for a mixed monolayer, $\beta = \beta^{\sigma}$ and $X_1 = X_1^{\sigma}$. It is clear from eqs 10 and 11 that the activity coefficients are directly related to both β and X_1. As the attractive or repulsive forces between various molecules in the mixed systems increase, the activity coefficients deviate from ideality (where activity coefficients should be unity). The values obtained in the above systems are less than unity owing to attractive interactions in the systems.

(viii) ΔG_{ex}. The above discussion is confirmed by the values of excess free energy of micellization, ΔG_{ex}, calculated by the equation

$$\Delta G_{\mathrm{ex}} = [X_1 \cdot \ln f_1 + (1 - X_1) \cdot \ln f_2]RT \qquad (12)$$

The values of ΔG_{ex} are negative for all alcohol concentrations. The magnitude increases (or ΔG_{ex} becomes more negative) with increasing alcohol content in the solution indicating stability of the micelles. However, when the alcohol concentration increases beyond a certain concentration, the $|\Delta G_{\mathrm{ex}}|$ starts decreasing. This means that when a large amount of alcohols are introduced in the system, surfactant−alcohol micelles become less stable.

The results of amines fall in line with alcohol results. The behavior is self-explanatory in light of the discussion given for surface properties of alcohols and amines.

Conclusions

Micellar and interfacial properties of gemini surfactants 16−*m*−16 (m = 4, 5, 6) in the presence of alcohols (butanol, hexanol) and amines (butylamine, hexylamine) have been studied by surface tension measurements. The results show mixed micellization. cmc and headgroup area values decrease with increasing additive concentration, and at high additive concentration, these values again increase. Activity coefficients show nonideality in the solution. The mole fraction of additives in the micelles increases (only with short chain length additives) continuously, and therefore, at high additive concentration, micelles start to break, causing an increase in cmc and decrease in interaction. ΔG_{ex} values also confirm that at high additive concentrations micelles become relatively unstable.

Literature Cited

(1) Tanford, C. *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*, 2nd ed.; Wiley: New York, 1980.

(2) Fendler, J. H. *Membrane Mimetic Chemistry*; Wiley Interscience: New York, 1982.

(3) Bunton, C. A.; Robinson, L.; Schaak, J.; Stam, M. F. Catalysis of Nucleophilic Substitutions by Micelles of Dicationic Detergents. *J. Org. Chem.* **1971**, *36*, 2346–2350.

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

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

(6) Menger, F. M.; Littau, C. A. Gemini Surfactants: a New Class of Self-Assembling Molecules. *J. Am. Chem. Soc.* **1993**, *115*, 10083–10090.

(7) Song, L. D.; Rosen, M. J. Surface Properties, Micellization, and Premicellar Aggregation of Gemini Surfactants with Rigid and Flexible Spacers. *Langmuir* **1996**, *12*, 1149–1153.

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

(9) Zana, R. In *Structure−Performance Relationships in Surfactants*; Esumi, K., Ueno, M., Eds.; Marcel Dekker: New York, 1997.

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

(11) 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.

(12) Devinsky, F.; Lacko, I.; Imam, T. Relationship Between Structure and Solubilization Properties of Some Bisquaternary Ammonium Amphiphiles. *J. Colloid Interface Sci.* **1993**, *143*, 336–342.

(13) Bai, G.; Wang, J.; Yan, H.; Li, Z.; Thomas, R. K. Thermodynamics of Molecular Self-Assembly of Cationic Gemini and Related Double Chain Surfactants in Aqueous Solution. *J. Phys. Chem.* **2001**, *105*, 3105–3108.

(14) Kern, F.; Lequex, F.; Zana, R.; Candau, S. J. Dynamic Properties of Salt-Free Viscoelastic Micellar Solutions. *Langmuir* **1994**, *10*, 1714–1723.

(15) Kabir-ud-Din; Fatma, W. Role of Cationic Gemini Surfactants Toward Enhanced Ninhydrin-Tryptophan Reaction. *J. Phys. Org. Chem.* **2007**, *20*, 440–447.

(16) Brinchi, L.; Germani, R.; Goracci, L.; Savelli, G.; Bunton, C. A. Decarboxylation and Dephosphorylation in New Gemini Surfactants. Changes in Aggregate Structures. *Langmuir* **2002**, *18*, 7821–7825.

(17) Imam, T.; Devinsky, F.; Lacko, I.; Mlynarcik, D.; Krasnec, L. Preparation and Antimicrobial Activity of Some New Bisquaternary Ammonium Salts. *Pharmazie* **1983**, *38*, 308–310.

(18) 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.

(19) 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.

(20) Wormuth, K. R.; Kaler, E. W. Amines as Microemulsion Cosurfactants. *J. Phys. Chem.* **1987**, *91*, 611–617.

(21) Singh, H. N.; Prasad, Ch. D.; Kumar, S. Water Solubilization in Microemulsions Containing Amines as Cosurfactant. *J. Am. Oil Chem. Soc.* **1993**, *70*, 69–73.

(22) Perez, L.; Pinazo, A.; Rosen, M. J.; Infante, M. R. Surface Activity Properties at Equilibrium of Novel Gemini Cationic Amphiphilic Compounds from Arginine, Bis(Args). *Langmuir* **1998**, *14*, 2307–2315.

(23) Tsubone, K.; Ogawa, T.; Mimura, K. Surface and Aqueous Properties of Anionic Gemini Surfactants having Dialkyl Amide, Carboxyl, and Carboxylate Groups. *J. Surf. Deterg.* **2003**, *6*, 39–46.

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

(25) Tsubone, K. The Interaction of an Anionic Gemini Surfactant with Conventional Anionic Surfactants. *J. Colloid Interface Sci.* **2003**, *261*, 524–528.

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

(27) Kabir-ud-Din; Fatma, W.; Khan, Z. A. A ^{1}H NMR Study of 1,4-bis(*N*-Hexadecyl-*N*,*N*-Dimethylammonium)Butane Dibromide/Sodium Anthranilate System: Spherical to Rod-Shaped Transition. *Colloid Polym. Sci.* **2006**, *284*, 1339–1344.

(28) Camesano, T. A.; Nagarajan, R. Micelle Formation and CMC of Gemini Surfactants: a Thermodynamic Model. *Colloids Surf. A* **2000**, *167*, 165–177.

(29) Maiti, P. K.; Choudhary, D. Micellar Aggregates of Gemini Surfactants: Monte Carlo Simulation of a Microscopic Model. *Europhys. Lett.* **1998**, *41*, 183–188.

(30) Maiti, P. K.; Choudhary, D A microscopic model of gemini surfactants: Self-assemblies in water and at air-water interface. *J. Chem. Phys.* **1998**, *109*, 5126–5133.

(31) Forland, G. M.; Samseth, J.; Hoiland, H.; Mortensen, K. The Effect of Medium Chain Length Alcohols on the Micellar Properties of Sodium Dodecyl Sulfate in Sodium Chloride Solutions. *J. Colloid Interface Sci.* **1994**, *164*, 163–167.

(32) Zana, R. Aqueous Surfactant-Alcohol Systems: A Review. *Adv. Colloid Interface Sci.* **1995**, *57*, 1–64.

(33) Caponetti, E.; Chillura-Martino, D.; Floriano, M. A.; Triolo, R. Localization of n-Alcohols and Structural Effects in Aqueous Solutions of Sodium Dodecyl Sulfate. *Langmuir* **1997**, *13*, 3277–3283.

(34) Backlund, S.; Rundt, K.; Birdi, K. S.; Dalsagar, S. Aggregation Behavior of Ionic Surfactant Micelles in Aqueous Alcoholic Solutions at Different Temperatures. *J. Colloid Interface Sci.* **1981**, *79*, 578–580.

(35) Almgren, M.; Swarup, S. Size of Sodium Dodecyl Sulfate Micelles in the Presence of Additives I. Alcohols and Other Polar Compounds. *J. Colloid Interface Sci.* **1983**, *91*, 256–266.

(36) Nguyen, C. M.; Rathman, J. F.; Scamehorn, J. F. Thermodynamics of Mixed Micelle Formation. *J. Colloid Interface Sci.* **1986**, *112*, 438–446.

(37) Sugihara, G.; Yamamoto, M.; Wada, Y.; Murata, Y.; Ikawa, Y. Mixed Micelle Formation in Aqueous Solutions of Nonyl-N-Methylglucamine with Sodium Perfluorooctanoate at Different Pressures. *J. Solution Chem.* **1988**, *17*, 225–235.

(38) Rao, I. V.; Ruckenstein, E. Micellization Behavior in the Presence of Alcohols. *J. Colloid Interface Sci.* **1986**, *113*, 375–387.

(39) Clint, J. H. *Surfactant Aggregation*; Blackie: London, 1992.

(40) Chattoraj, D. K.; Birdi, S. *Adsorption and the Gibbs Surface Excess*; Plenum: New York, 1984.

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

(42) Matejevic, E.; Pethica, B. The Properties of Ionized Monolayers. Part 1.—Sodium Dodecyl Sulphate at the Air/Water Interface. *Trans. Faraday Soc.* **1958**, *54*, 1382–1399.

(43) Anand, K.; Yadav, O. P.; Singh, P. P. Studies on the Surface and Thermodynamic Properties of Some Surfactants in Aqueous and water+1,4-Dioxane Solutions. *Colloids Surf.* **1991**, *55*, 345–358.

(44) Lindemuth, P. M.; Bertrand, G. L. Calorimetric Observations of the Transition of Spherical to Rodlike Micelles with Solubilized Organic Additives. *J. Phys. Chem.* **1993**, *97*, 7769–7773.

(45) Yamashita, T.; Yano, H.; Harada, S.; Yasunaga, T. Kinetic Studies of the Hydrolysis of n-Octylamine on the Surface of a Sodium Dodecyl Sulfate Micelle by the Ultrasonic Absorption Method. *J. Phys. Chem.* **1983**, *87*, 5482–5485.

(46) Rubingh, D. N. In *Solution Chemistry of Surfactants*; Mittal, K. L. Ed.; Plenum: New York, 1979; *Vol. 1*.

(47) Li, F.; Rosen, M. J.; Sulthana, S. B. Surface Properties of Cationic Gemini Surfactants and Their Interaction with Alkylglucoside or -maltoside Surfactants. *Langmuir* **2001**, *17*, 1037–1042.

(48) Zhou, Q.; Rosen, M. J. Molecular Interactions of Surfactants in Mixed Monolayers at the Air/Aqueous Solution Interface and in Mixed Micelles in Aqueous Media: The Regular Solution Approach. *Langmuir* **2003**, *19*, 4555–4562.

(49) Rosen, M. J.; Gao, T.; Nakatsuji, Y.; Masuyama, A. Synergism in Binary Mixtures of Surfactants 12. Mixtures Containing Surfactants with Two Hydrophilic and Two or Three Hydrophobic Groups. *Colloids Surf. A* **1994**, *88*, 1–11.

(50) Rosen, M. J.; Hua, X. Y. Surface Concentrations and Molecular Interactions in Binary Mixtures of Surfactants. *J. Colloid Interface Sci.* **1982**, *86*, 164–172.

Received for review January 13, 2008. Accepted July 5, 2008.

JE800032E