Mixed Micellization Properties of Cationic Monomeric and Gemini Surfactants†

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Mixed micellization properties of the cationic monomeric surfactants hexadecyltrimethylammonium bromide (CTAB), hexadecyltriphenylphosphonium bromide (CTPB), hexadecyltributylphosphonium bromide (CT-BuPB), and tetradecyltriphenylphosphonium bromide (TTPB) with gemini surfactant $C_{16}H_{33}(CH_2)_2N^+$-$(CH_2)_{10}N^+(CH_2)_2C_{16}H_{33}\cdot 2Br^-$ (C_{16}-10-$C_{16}\cdot 2Br^-$) have been investigated by performing conductivity measurements in aqueous solution. The conductance data were used to obtain the values of the critical micelle concentration (cmc) of mixed surfactant systems having different compositions. The mixed cmc values determined from the experimental data were used to calculate the interaction parameter (β) using regular solution theory for the mixed surfactant system. The cmc values show nonideality, and the negative values of β indicate an overall attractive force in the mixed state. Also, the measured values of the excess free energy of mixing have negative values for all of the systems.

Introduction

Mixed micelles that contain more than one type of surfactant are of great importance from the viewpoints of fundamental, technological, pharmaceutical, and biological considerations.[1,2] In practical fields, mixed surfactants often perform better than single surfactants when used in industrial preparations, pharmaceutical and medicinal formulations, and enhanced oil recovery processes for the purpose of solubilization, suspension, dispersion, catalyzing functions, etc. When two (or more) types of surfactants are in solution, a complex balance of intermolecular forces is responsible for the formation of mixed micelles as opposed to the formation of micelles by one type of surfactant.[3]

The interactions between ionic surfactants are generally governed by the electrostatic forces between their head groups,[4] and it is expected that such interactions are always stronger for surfactants having two ionic groups. The nature and strength of the interactions between two surfactants in binary systems can be determined by calculating the values of their parameters.[5] Mixed surfactants[6–10] generally have better surface properties and thus have attracted even more attention. When a gemini surfactant is mixed with a conventional surfactant, it usually exhibits even better surface properties.[11–14] This phenomenon is called synergism. Mixtures of surfactants often exhibit nonideal behavior that can also be influenced by differences in the surfactant structures such as the sizes of the surfactants' heads or tails. The interactions leading to nonideality in solutions may be either favorable or unfavorable. In such mixtures, favorable or synergistic interactions may be found, making these systems even more attractive and useful. In many cases, the mixed surfactant system shows synergistic behavior, resulting in a reduction of the total amount of surfactant used in a particular application, which in turn reduces both the cost and the environmental impact.[15] Recently, Kabir-ud-Din and co-workers[16,17] studied the surface properties and mixed micellization of cationic gemini surfactants with ethyleneamines as well as with conventional surfactants in aqueous media. Azum et al.[18,19] studied the properties of mixed aqueous micellar solutions formed by cationic gemini surfactants as well as the mixing behavior of conventional and gemini cationic surfactants. These studies obtained some important results about the aggregation behavior of mixtures of gemini and single-chain surfactants. Similarly, Moya and co-workers[9] studied mixtures of monomeric and dimeric surfactants C_mTAB + 12-*s*-12 ($m = 10, 12, 14, 16$; $s = 3, 4, 5$) using conductivity and fluorescence measurements.

A new class of surfactants known as gemini surfactants 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.[20–25] Hence, the spacer represents a new structural parameter that can be used to tune the behavior and properties of the amphiphile in addition to the classical variation of the nature of the hydrophilic head group and the hydrophobic tail. All of the gemini surfactants show two important features, namely, much lower critical micelle concentration (cmc) val-

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Table 1. Critical Micelle Concentrations (C_{mix}, cmc_{ideal}), Micellar Mole Fractions (X_1, X_{ideal}), Interaction Parameters (β), Activity Coefficients (f_1, f_2), and Excess Gibbs Free Energies (ΔG^E) for CTAB + C_{16}-10-C_{16} Mixtures (T = 303 K)

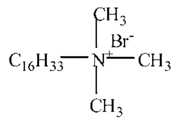
α_{CTAB}	$10^3 \cdot C_{mix}$ / $mol \cdot dm^{-3}$	$10^3 \cdot cmc_{ideal}$ / $mol \cdot dm^{-3}$	X_1	X_{ideal}	β	f_1	f_2	ΔG^E / $J \cdot mol^{-1}$
0.000	0.028	0.028						
0.203	0.036	0.034		0.006				
0.406	0.048	0.046		0.018				
0.502	0.060	0.054		0.027				
0.598	0.068	0.066	0.024	0.039	0.552	1.692	1.000	31
0.698	0.080	0.087	0.123	0.060	−1.033	0.452	0.984	−281
0.799	0.102	0.125	0.214	0.099	−1.560	0.381	0.931	−661
0.899	0.148	0.212	0.332	0.199	−2.044	0.402	0.798	−1142
1.000	1.000	1.000						

Table 2. Critical Micelle Concentrations (C_{mix}, cmc_{ideal}), Micellar Mole Fractions (X_1, X_{ideal}), Interaction Parameters (β), Activity Coefficients (f_1, f_2), and Excess Gibbs Free Energies (ΔG^E) for CTPB + C_{16}-10-C_{16} Mixtures (T = 303 K)

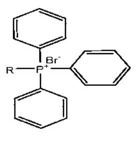
α_{CTPB}	$10^3 \cdot C_{mix}$ / $mol \cdot dm^{-3}$	$10^3 \cdot cmc_{ideal}$ / $mol \cdot dm^{-3}$	X_1	X_{ideal}	β	f_1	f_2	ΔG^E / $J \cdot mol^{-1}$
0.000	0.028	0.028						
0.198	0.032	0.033	0.078	0.039	−0.877	0.973	0.995	−17
0.398	0.036	0.041	0.190	0.098	−1.243	0.442	0.956	−482
0.498	0.048	0.047	0.139	0.140	0.010	1.007	1.000	2
0.598	0.056	0.055	0.196	0.196	0.006	1.004	1.000	1
0.698	0.063	0.067	0.301	0.276	−0.311	0.859	0.802	−503
0.799	0.083	0.084	0.398	0.385	−0.059	0.979	0.991	−34
0.897	0.096	0.111	0.568	0.589	−0.620	0.891	0.819	−382
1.000	0.170	0.170						

ues[26] and high efficiency with respect to reducing the surface tension of water.

In the present study, the mixed micellar behavior of the cationic monomeric surfactants hexadecyltrimethylammonium bromide (CTAB), hexadecyltriphenylphosphonium bromide (CTPB), hexadecyltributylphosphonium bromide (CTBuPB), and tetradecyltriphenylphosphonium bromide (TTPB) and the gemini surfactant $C_{16}H_{33}(CH_2)_2N^+(CH_2)_{10}N^+(CH_2)_2C_{16}H_{33} \cdot 2Br^-$ (C_{16}-10-$C_{16} \cdot 2Br^-$) (**I**) in mixed states has been investigated by performing conductivity measurements in aqueous solutions at 303 K.

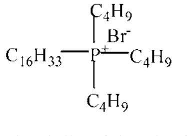


Hexadecyltrimethylammonium bromide

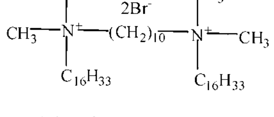


R = $C_{16}H_{33}$, $C_{14}H_{29}$

Alkyltriphenylphosphonium bromide



Hexadecyltributylphosphonium bromide



Gemini surfactant [C_{16}-10-C_{16}], $2Br^-$

(**I**)

Experimental Section

Materials. The gemini surfactant was synthesized by refluxing the corresponding decanediyl-1,10-bis(cetyldimethylammonium bromide) in dry ethanol for 48 h followed by recrystallization from hexane/ethyl acetate mixtures.[27] CTAB was obtained from Sigma, and CTBuPB, CTPB, and TTPB were obtained from Caledon Chemicals (Georgetown, ON; distributors of Lancaster Synthesis of England). All of the surfactants obtained were of high purity (99.0 %) and used without any further purification. All solutions were prepared in triply distilled water.

Method. Conductance measurements were carried out with a Systronics direct-reading conductivity meter (type 306). The conductivity cell was calibrated with KCl solutions in the appropriate concentration range. The accuracy of the measured conductance was within ± 0.5 %. The cmc values for single and mixed surfactants were determined from conductivity measurements at 303 K.[28] Pure surfactant solutions were prepared by diluting concentrated stock solutions. The mixed solutions were prepared by mixing two pure solutions and were stored for at least 12 h to equilibrate. The conductivity at each mole fraction was measured by successive additions of a concentrated solution of the surfactant mixture in pure water.

Results and Discussion

Tables 1 to 4 summarize the cmc values obtained for different monomeric and dimeric surfactant binary mixtures. The cmc values of various surfactant solutions were determined by the break in the plots of specific conductance (κ) versus surfactant concentration. The experimental conductivity data are given in the Supporting Information. Representative illustrations are presented in Figures 1 and 2.

Formation of mixed micelles due to the mixing of surfactants can be ideal and nonideal. The formation of a mixed micelle can be represented by the relation[4,6–8,13,14,28]

$$\frac{1}{cmc_{ideal}} = \sum_{i=1}^{n} \left(\frac{\alpha_i}{cmc_i f_i} \right) \tag{1}$$

where cmc_i and cmc_{ideal} are the critical micelle concentrations of the ith component and the mixture, respectively, α_i is the mole fraction of component i in the surfactant mixture in solution, and f_i is its activity coefficient in the mixed micelle. In the ideal case, $f_i = 1$, and eq 1 reduces to the Clint equation:[29]

$$\frac{1}{cmc_{ideal}} = \sum_{i=1}^{n} \left(\frac{\alpha_i}{cmc_i} \right) \tag{2}$$

Table 3. Critical Micelle Concentrations (C_{mix}, cmc_{ideal}), Micellar Mole Fractions (X_1, X_{ideal}), Interaction Parameters (β), Activity Coefficients (f_1, f_2), and Excess Gibbs Free Energies (ΔG^E) for CTBuPB + C_{16}-10-C_{16} Mixtures (T = 303 K)

α_{CTBuPB}	$10^3 \cdot C_{mix}$ / $mol \cdot dm^{-3}$	$10^3 \cdot cmc_{ideal}$ / $mol \cdot dm^{-3}$	X_1	X_{ideal}	β	f_1	f_2	ΔG^E / $J \cdot mol^{-1}$
0.000	0.028	0.028						
0.198	0.032	0.033	0.077	0.033	−1.050	0.409	0.994	−187
0.398	0.040	0.042	0.130	0.084	−0.653	0.610	0.986	−186
0.498	0.045	0.048	0.176	0.121	−0.668	0.635	0.979	−245
0.598	0.051	0.057	0.236	0.172	−0.752	0.645	0.959	−341
0.698	0.065	0.070	0.278	0.244	−0.387	0.817	0.970	−196
0.799	0.080	0.089	0.384	0.356	−0.481	0.833	0.931	−287
0.899	0.098	0.123	0.537	0.554	−0.930	0.819	0.765	−582
1.000	0.200	0.200						

Table 4. Critical Micelle Concentrations (C_{mix}, cmc_{ideal}), Micellar Mole Fractions (X_1, X_{ideal}), Interaction Parameters (β), Activity Coefficients (f_1, f_2), and Excess Gibbs Free Energies (ΔG^E) for TTPB + C_{16}-10-C_{16} Mixtures (T = 303 K)

α_{TTPB}	$10^3 \cdot C_{mix}$ / $mol \cdot dm^{-3}$	$10^3 \cdot cmc_{ideal}$ / $mol \cdot dm^{-3}$	X_1	X_{ideal}	β	f_1	f_2	ΔG^E / $J \cdot mol^{-1}$
0.000	0.028	0.028						
0.198	0.031	0.034	0.091	0.010	−2.738	0.105	0.978	−567
0.397	0.046	0.045	0.009	0.027	1.125	3.016	1.000	26
0.497	0.050	0.053	0.093	0.041	−1.071	0.415	0.991	−226
0.597	0.061	0.065	0.112	0.060	−0.864	0.506	0.989	−216
0.698	0.080	0.084	0.129	0.091	−0.522	0.673	0.991	−148
0.798	0.093	0.118	0.259	0.147	−1.468	0.447	0.906	−709
0.900	0.130	0.200	0.383	0.282	−1.941	0.478	0.752	−1155
1.000	0.640	0.640						

In eq 1, the value of f_i is required in order to obtain the cmc, but use of eq 2 to predict the cmc is straightforward. In spite of inherent limitations, eq 2 is useful for comparison between ideal and nonideal mixtures. A difference between the cmc of the mixture (C_{mix}) and cmc_{ideal} indicates nonideality. C_{mix} and cmc_{ideal} values for various combinations of C_{16}-10-C_{16} and conventional surfactants are given in Tables 1 to 4. The ideal-behavior mixed cmc values calculated using eq 2 were also plotted against the mole fractions of the monomeric surfactants (CTAB, CTPB, CTBuPB, and TTPB) (Figure 3). It was observed that the experimental mixed cmc values were always lower than the cmc_{ideal} values for CTBuPB and TTPB, but in the case of the CTAB and CTPB, some of the experimental mixed cmc values were higher than the cmc_{ideal} values. The lower experimental mixed cmc values relative to the corresponding cmc_{ideal} values indicate the nonideality of the mixed systems. The experimental cmc values increase slowly with increasing mole fraction for all the systems in a nonlinear manner. As the mole fraction of the conventional surfactant in the mixture increases, the deviation from ideal behavior in the system increases.

To investigate the nature of the interactions among the components, we calculated various other parameters using Rubingh's model.[30] This model is based on regular solution theory for nonideal mixed systems. The micellar mole fraction of surfactant 1 in the mixed micelle (X_1) and the micellar interaction parameter (β) are the optimization parameters, which can be calculated iteratively using eqs 3 and 4:

$$\frac{X_1^{\,2} \ln(\alpha_1 C_{mix}/X_1 C_1)}{(1 - X_1)^2 \ln[(1 - \alpha_1) C_{mix}/(1 - X_1) C_2]} = 1 \qquad (3)$$

and

$$\beta = \frac{\ln(\alpha_1 C_{mix}/X_1 C_1)}{(1 - X_1)^2} \qquad (4)$$

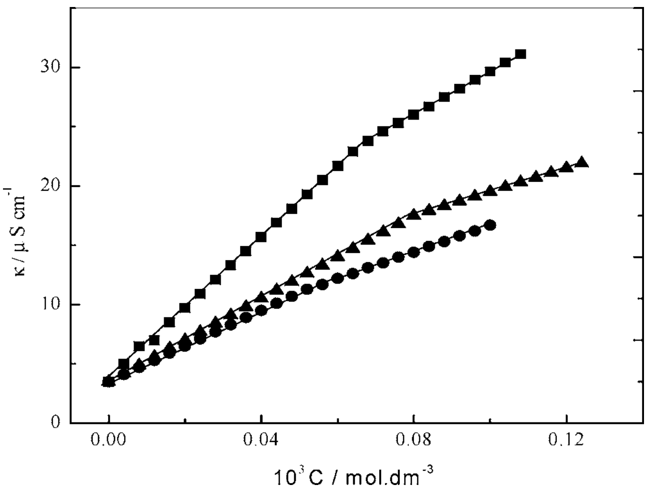


Figure 1. Dependence of the specific conductivity (κ) on surfactant concentration (C) for the CTBuPB + C_{16}-10-C_{16} system as a function of CTBuPB mole fraction: ▲, 0.598; ■, 0.698; ●, 0.798.

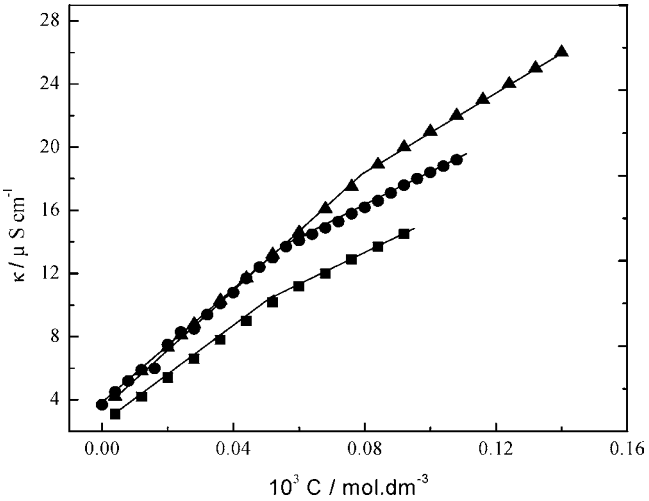


Figure 2. Dependence of the specific conductivity (κ) on surfactant concentration (C) for the CTPB + C_{16}-10-C_{16} system as a function of CTPB mole fraction: ●, 0.398; ■, 0.598; ▲, 0.799.

where C_1, C_2, and C_{mix} are the cmc's for surfactants 1 and 2 and their mixture, respectively, at mole fraction α_1. The β value indicates the magnitude of the interaction between the two unlike components in the mixed micelle state and thus demonstrates the extent of the interactions between the two surfactants that lead to the deviation from ideality. β values computed from eq 4 in aqueous solution are listed in Tables 1 to 4. Negative β values for these binary surfactant systems suggest that a strong attractive interaction (synergism) between the two surfactants exists, while positive values indicate a repulsive interaction of the surfactants (antagonism). Our results show that although the β values do not exhibit a trend, they are negative throughout the concentration range with average values of -1.54, -0.622, -0.703, and -1.38 for the mixtures of C_{16}-10-C_{16} with CTAB, CTPB, CTBuPB, and TTPB, respectively. The interaction parameter of CTAB + C_{16}-10-C_{16} is more negative than those for the CTPB and CTBuPB systems, as shown in Tables 1 to 3. There is an effect of chain length on β, as it can be seen from Tables 2 and 4 that the values of β decrease with increasing chain length. Interactions between the surfactants in binary mixtures are usually considered to be the result of two contributions,[31] one associated with the interactions between the hydrophobic moieties of the two surfactants in the micellar core and the other with the electrostatic interactions between the head groups of the two surfactants at the interface.

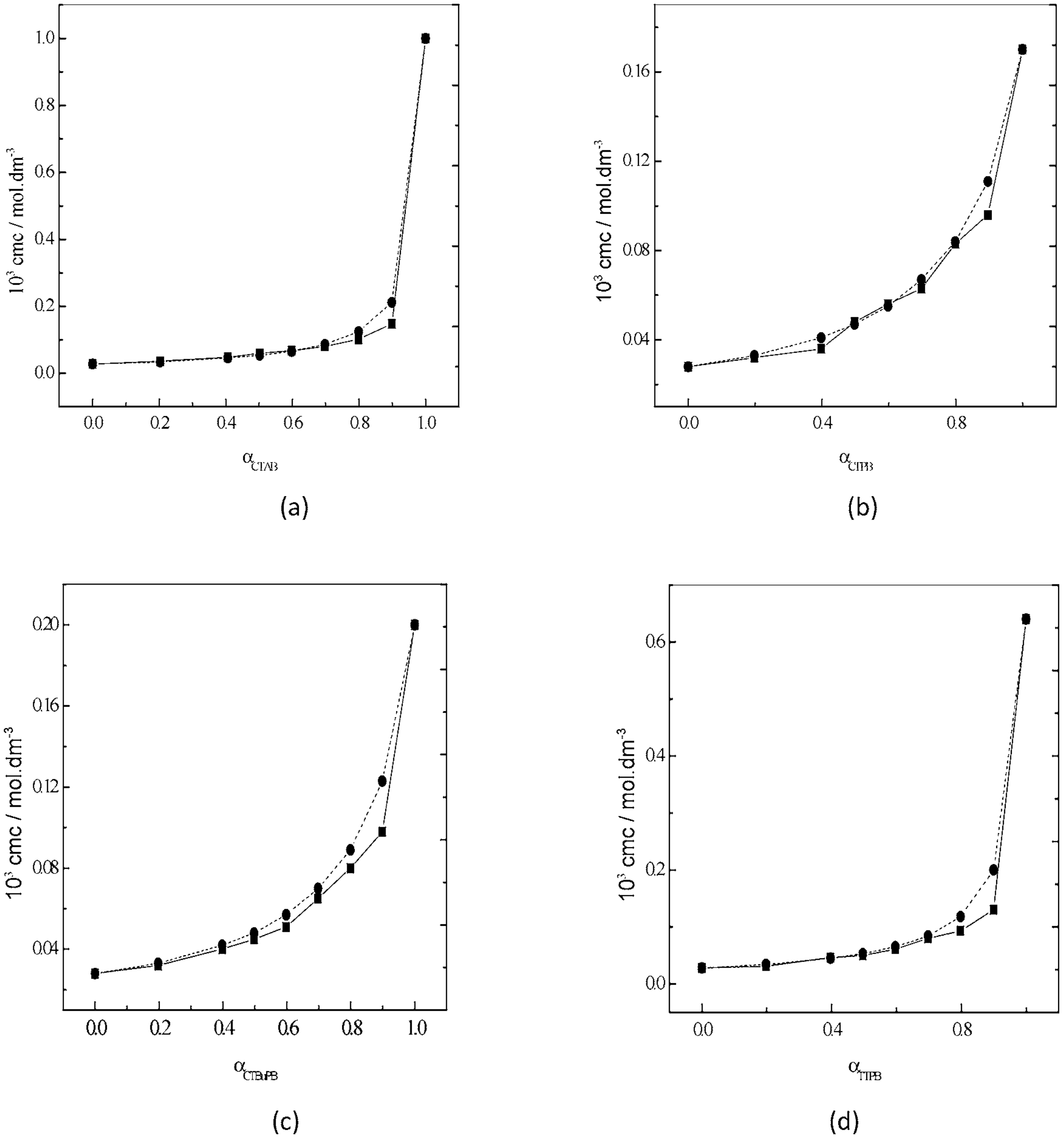
The micellar mole fractions of surfactant 1 (X_1) are significantly smaller than the corresponding stoichiometric mole fractions (α_1).

The interaction parameter β is related to the activity coefficients (f_1 and f_2) of the surfactants within the micelles as follows:

$$f_1 = \exp[\beta(1 - X_1)^2] \tag{5}$$

$$f_2 = \exp(\beta X_1^{\,2}) \tag{6}$$

The values of the activity coefficients f_1 and f_2 calculated from eqs 5 and 6 are less than unity, indicating the nonideal behavior of the mixed systems.



(a) (b)

(c) (d)

Figure 3. Variation of the cmc with mole fraction (α) for binary mixtures of C_{16}-10-C_{16} with (a) CTAB, (b) CTPB, (c) CTBuPB, and (d) TTPB. Solid lines indicate $\mathrm{cmc}_{\mathrm{exptl}}$ and dotted lines $\mathrm{cmc}_{\mathrm{ideal}}$.

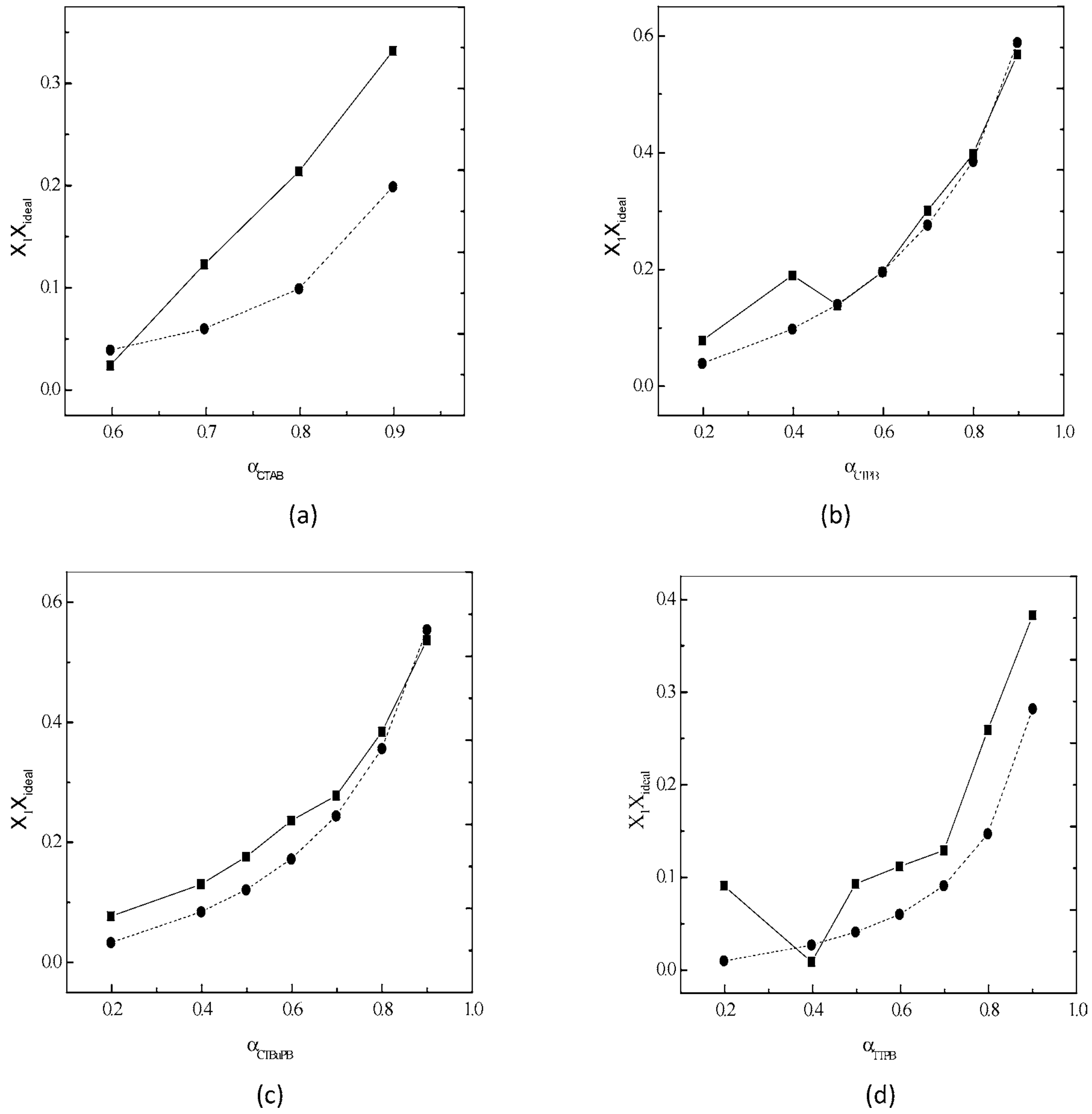


Figure 4. Micellar mole fractions X_1 and X_{ideal} as functions of mole fraction (α) for binary mixtures of C_{16}-10-C_{16} with (a) CTAB, (b) CTPB, (c) CTBuPB, and (d) TTPB. Solid lines indicate X_1 and dotted lines X_{ideal}.

The activity coefficients can also be used to calculate the excess free energy of mixing (ΔG^E) from the relation[32]

$$\Delta G^E = RT[X_1 \ln f_1 + (1 - X_1) \ln f_2] \qquad (7)$$

where R and T have their usual meanings. Table 1 shows that the ΔG^E value decreases with increasing α_{CTAB}. Other tables do not show such behavior. A negative value of ΔG^E indicates relatively more stable mixed micelles, whereas positive values of ΔG^E denote unstable mixed micelles.

The micelle mole fraction in the ideal state was computed by applying Motomura's approximation:[33]

$$X_{ideal} = \frac{\alpha_1 \mathrm{cmc}_2}{\alpha_1 \mathrm{cmc}_2 + (1 - \alpha_1)\mathrm{cmc}_1} \qquad (8)$$

The values of X_{ideal} and X_1 are plotted against α_1 in Figure 4. It is clear from the figure that the X_1 value is greater than the X_{ideal} value at almost every mole fraction. Larger X_1 values indicate that the mixed micelles of gemini and conventional surfactants contain more conventional surfactant than in the ideal mixing state, with less transfer of the gemini surfactant from the solution to the micellar phase.

Conclusions

The mixed critical micelle concentration values determined from the experimental data were used to calculate the interaction parameters β using regular solution theory. From these values, the following conclusions can be drawn:

1. The mixed systems in water exhibit synergism in the formation of mixed micelles.
2. The micellar stability of the mixed micelle decreases linearly with increasing mole fraction of the ionic surfactant in the mixed micelle.
3. The contribution of conventional surfactant to the micelle is greater than that in the ideal-mixing state (i.e., $X_1 > X_{ideal}$).

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Supporting Information Available:

Tables of experimental conductivity data. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Rosen, M. J. In *Phenomena in Mixed Surfactant Systems*; Scamehorn, J. F., Ed.; ACS Symposium Series *311*; American Chemical Society: Washington, DC, 1989; p 144.
(2) De, S.; Aswal, V. K.; Goyal, P. S.; Bhattacharya, S. Small-Angle Neutron Scattering Studies of Different Mixed Micelles Composed of Dimeric and Monomeric Cationic Surfactants. *J. Phys. Chem. B* **1997**, *101*, 5639–5945.
(3) Hill, R. M. In *Mixed Surfactant Systems*; Ogino, K., Abe, M., Eds.; Surfactant Science Series *46*; Marcel Dekker: New York, 1993; Chapter 11.
(4) Ray, G. B.; Chakraborty, I.; Ghosh, S.; Moulik, S. P.; Palepu, R. Self-Aggregation of Alkyltrimethylammonium Bromides (C_{10}-, C_{12}-, C_{14}-, and C_{16}TAB) and Their Binary Mixtures in Aqueous Medium: A Critical and Comprehensive Assessment of Interfacial Behavior and Bulk Properties with Reference to Two Types of Micelle Formation. *Langmuir* **2005**, *21*, 10958–10967.
(5) Rosen, M. J.; Zhou, Q. Surfactant−Surfactant Interaction in Mixed Monolayer and Mixed Micelle Formation. *Langmuir* **2001**, *17*, 3532–3537.
(6) Moulik, S. P.; Ghosh, S. Surface chemical and micellization behaviors of binary and ternary mixtures of amphiphiles (Triton X-100, Tween-80 and CTAB) in aqueous medium. *J. Mol. Liq.* **1997**, *72*, 145–161.
(7) Ghosh, S.; Moulik, S. P. Interfacial and Micellization Behaviors of Binary and Ternary Mixtures of Amphiphiles (Tween-20, Brij-35, and Sodium Dodecyl Sulphate) in Aqueous Medium. *J. Colloid Interface Sci.* **1998**, *208*, 357–366.
(8) Ghosh, S. Surface Chemical and Micellar Properties of Binary and Ternary Surfactant Mixtures (CetylPyridinium Chloride, Tween-40, and Brij-56) in an Aqueous Medium. *J. Colloid Interface Sci.* **2001**, *244*, 128–138.
(9) Rodriguez, A.; Graciani, M. d. M.; Moreno-Vargas, A. J.; Moyá, M. L. Mixture of Monomeric and Dimeric Surfactants: Hydrophobic Chain Length and Spacer Group Length Effects on Non Ideality. *J. Phys. Chem. B* **2008**, *112*, 11942–11949.
(10) Alargova, R. G.; Kochijashky, I. I.; Sierra, M. L.; Kwetkat, K.; Zana, R. Mixtures of Monomeric and Dimeric (Gemini) Surfactants and Conventional Surfactants, II. CMC and Micelle Aggregation Numbers for Various Mixtures. *J. Colloid Interface Sci.* **2001**, *235*, 119–129.
(11) Tsubone, K.; Ghosh, S. Micelle Ionization Degree of Anionic Gemini Surfactant Having *N*,*N*-Dialkylamide and Carboxylate Groups. *J. Surfactants Deterg.* **2003**, *6*, 225–229.
(12) Tsubone, K.; Ghosh, S. Micellization of an Anionic Gemini Surfactant Having *N*,*N*-Dialkylamide, Carboxyl, and Carboxylate Groups in Aqueous NaCl Solutions. *J. Surfactants Deterg.* **2004**, *7*, 47–52.
(13) 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.
(14) Chakraborty, T.; Ghosh, S. Mixed Micellization of an Anionic Gemini Surfactant (GA) with Conventional Polyethoxylated Nonionic Surfactants in Brine Solution at pH 5 and 298 K. *Colloid Polym. Sci.* **2007**, *285*, 1665–1673.
(15) Paria, S. The Mixing Behavior of *n*-Alkylpyridinium Bromide NP-9 Mixed Surfactant Systems. *Colloids Surf., A* **2006**, *281*, 113–118.
(16) Khan, I. A.; Mohammad, R.; Alam, M. S.; Kabir-ud-Din. Surface Properties and Mixed Micellization of Cationic Gemini Surafactants with Ethyleneamines. *J. Chem. Eng. Data* **2010**, *55*, 370–380.
(17) Kabir-ud-Din; Shekh, M. S.; Dar, A. A. Interaction of a Cationic Gemini Surfactant with Conventional Surfactants in the Mixed Micelle and Monolayer Formation in Aqueous Medium. *J. Colloid Interface Sci.* **2009**, *333*, 605–612.
(18) 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.
(19) 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.
(20) Menger, F. M.; Littau, C. A. Gemini Surfactants: A New Class of Self-Assembling Molecules. *J. Am. Chem. Soc.* **1993**, *115*, 10083–10090.
(21) Han, L.; Ye, Z.; Chen, H.; Luo, P. The Interfacial Tension Between Cationic Gemini Surfactant Solution and Crude Oil. *J. Surfactants Deterg.* **2009**, *12*, 185–190.
(22) Sharma, P.; Sachar, S.; Kaur, G.; Thakur, P.; Bakshi, M. S.; Banipal, T. S. Mixed Micelle Behavior of Dodecyl-β-D-glucopyranoside with Cationic Gemini Surfactants: A Fluorescence Study. *J. Surf. Sci. Technol.* **2007**, *23*, 131–147.
(23) Prez, L.; Pinazo, A.; Infant, M. R.; Pons, R. Investigation of the Micellization Process of Single and Gemini Surfactants from Arginine by SAXS, NMR Self Diffusion, and Light Scattering. *J. Phys. Chem. B* **2007**, *111*, 11379–11387.
(24) Wattebled, L.; Note, C.; Laschewsky, A. Structure−Property Relationships of "Gemini" Surfactants and Synergism with Hydrotropes. *Tenside, Surfactants, Deterg.* **2007**, *44*, 24–33.
(25) Lu, T.; Li, Z.; Huang, J.; Fu, H. Aqueous Surfactant Two-Phase System in a Mixture of Cationic Gemini and Anionic Surfactants. *Langmuir* **2008**, *24*, 10723–10728.
(26) Zana, R.; Levy, H.; Danino, D.; Talman, Y.; Kwetkat, K. Mixed Micellization of Cetyltrimethylammonium Bromide and an Anionic Dimeric (Gemini) Surfactant in Aqueous Solution. *Langmuir* **1997**, *13*, 402–408.
(27) Kuwamoto, K.; Asakawa, T.; Ohta, A.; Miyagishi, S. Degree of Micelle Ionization and Micellar Growth for Gemini Surfactants Detected by 6-Methoxy-*N*-(3-sulfopropyl)quinolinium Fluorescence Quenching. *Langmuir* **2005**, *21*, 7691–7695.
(28) Chakraborty, T.; Ghosh, S.; Moulik, S. P. Micellization and Related Behavior of Binary and Ternary Surfactant Mixtures in Aqueous Medium: Cetyl Pyridinium Chloride (CPC), Cetyl Trimethyl Ammonium Bromide (CTAB), and Polyoxyethylene (10) Cetyl Ether (Brij-56) Derived System. *J. Phys. Chem. B* **2005**, *109*, 14813–14823.
(29) Clint, J. H. *Surfactant Aggregation*; Blackie/Chapman and Hall: New York, 1992.
(30) Rubingh, D. N. Mixed Micelle Solutions. In *Solution Chemistry of Surfactants*; Mittal, K. L., Ed.; Plenum Press: New York, 1979; Vol. 1, p 337.
(31) Haque, M.; Das, A. R.; Rakshit, A. K.; Moulik, S. P. Properties of Mixed Micelles of Binary Surfactant Combinations. *Langmuir* **1996**, *12*, 4084–4089.
(32) 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.
(33) Motomura, K.; Aratono, M. In *Mixed Surfactant Systems*; Ogino, K., Abe, M., Eds.; Surfactant Science Series *46*; Marcel Dekker: New York, 1993; p 99.

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