Mixtures of Monomeric and Dimeric Cationic Surfactants

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Compounds with the formula $C_mH_{2m+1}(CH_3)_2N^+(C_sH_{2s})N^+(CH_3)_2C_mH_{2m+1} \cdot 2Br^-$, abbreviated as *m-s-m* according to a previous convention, are considered to be dimeric cationic surfactants. The Krafft temperatures of five of these dimeric surfactants (12-2-12, 14-2-14, 16-2-16, 16-4-16, and 16-6-16) and that of a monomeric surfactant, $C_{16}H_{33}(CH_3)_3N^+ \cdot Br^-$ (hexadecyltrimethylammonium bromide, CTAB, where C stands for cetyl), have been determined from conductivity measurements. The values are 14.4, 32.8, 45.0, 34.0, 41.0, and 24.0 °C, respectively. The conductivities of these surfactants and the binary mixtures of the dimeric surfactants with CTAB were studied at 46.5 °C. A new mathematical treatment has been used to analyze the conductivity data to obtain the critical micelle concentration (cmc) of each binary mixture. Through the study of the cmc's, the nonideality of the binary mixtures was determined, and the trends are 16-2-16 ≫ 14-2-14 > 12-2-12, and 16-2-16 > 16-4-16 ≈ 16-6-16. It is suggested that the nonideality is due to the tendency of the dimeric surfactants to form ropelike micelles, especially with the increase in the length of the terminal chains and the decrease in the length of the spacer, whereas the monomeric surfactant CTAB prefers to form spherical micelles.

Introduction

Double-chain surfactants with two hydrophilic headgroups are a special type of compound that has attracted a considerable amount of attention in the area of surfactant research.[1−3] Compounds with symmetric structures are sometimes called gemini or dimeric surfactants. Among the various types of dimeric surfactants, alkanediyl-α,ω-bis(alkyldimethylammonium) salts having the structure
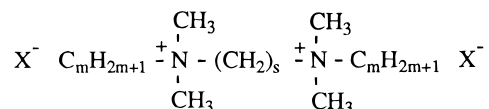
are probably the most widely studied.[3−11] They are abbreviated as *m-s-m*, where the X^- anion is often bromide. Compared with the corresponding conventional monomeric surfactants, many dimeric surfactants have lower critical micelle concentrations and are more efficient in lowering the surface tension of water.

Many fundamental properties of the *m-s-m* dimeric surfactants, such as the critical micelle concentration (cmc), degree of micelle ionization, and aggregation number have been studied extensively by Zana and co-workers[3,6] and by several other groups.[4,5,7−12] Most of these properties are strongly affected by the number of ethylene groups (*s*) in the spacer. Zana and co-workers have also studied the comicellization of the *m-s-m* surfactants with the corresponding single-chain quaternary ammonium surfactants and other surfactants and obtained some interesting results.[6c] For example, when 12-2-12 is mixed with dodecyltrimethylammonium bromide (DTAB), the shape of the micelles changes progressively from ropelike to spheroidal with the increase in the fraction of DTAB.

The Krafft point is the temperature at which the solubility of hydrated surfactant crystals increases sharply with increasing temperature.[13] The increase in solubility is so sharp that the Krafft temperature is essentially independent of the concentration of the surfactant when the solution is above the cmc. Below the Krafft temperature, the surfactant concentration is not high enough to form micelles. However, if the solution is cooled slowly from above the Krafft temperature to room temperature, it may become supersaturated before reaching true equilibrium. Therefore, for the determination of the cmc of a surfactant, it is essential to perform the experiment above the Krafft temperature. Unfortunately, the cmc's reported for several *m-s-m* dimeric surfactants were determined at 25 °C,[6a] without considering their Krafft temperatures. We have carried out a systematic determination of the Krafft temperatures of five dimeric surfactants and found that four of the five values are above 25 °C. Consequently, their cmc's were redetermined at 46.5 °C, which is slightly above the highest Krafft temperature of the compounds studied. The cmc's of binary mixtures of each of the five dimeric surfactants with a monomeric surfactant, hexadecyltrimethylammonium bromide (CTAB, where C stands for cetyl), were also determined at this temperature. The results are analyzed in terms of the nonideal mixing behavior of these systems.

Experimental Section

CTAB was purchased from Fisher Scientific and was used without further purification. Bromoalkanes (1-bromododecane, 1-bromotetradecane, 1-bromohexadecane) and *N,N,N′,N′*-tetramethylethylenediamine were purchased from Sigma Chemicals. *N,N,N′,N′*-tetramethyl-1,4-butanediamine and *N,N,N′,N′*-tetramethyl-1,6-hexanediamine were purchased from ACROS Organics.

Compounds in the *m-s-m* series (12-2-12, 14-2-14, 16-2-16, 16-4-16, and 16-6-16) were synthesized by reacting an alkyl bromide with alkanediyl-α,ω-bis(dimethylamine).[6] The reactions were performed in dry ethanol under reflux for 48 h in
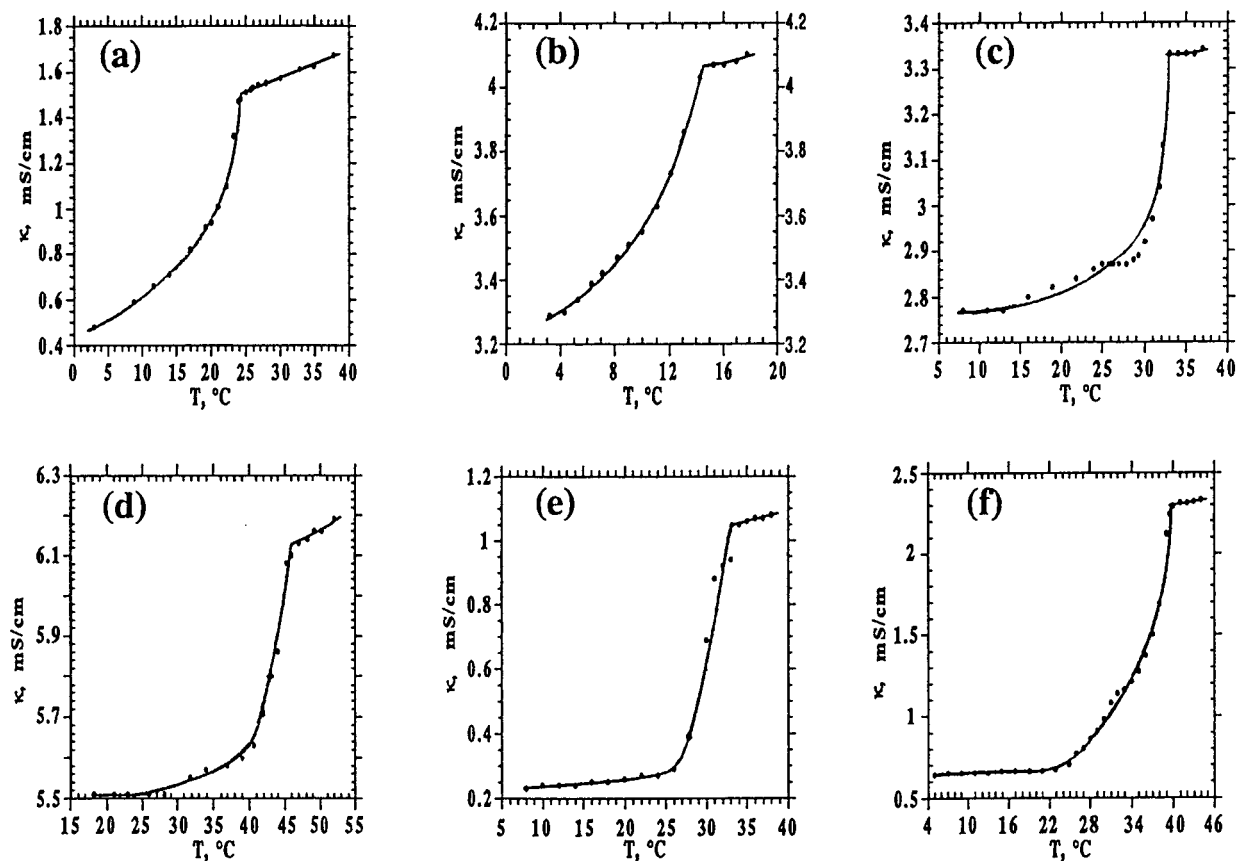
Figure 1. Conductivity of several cationic surfactants as a function of temperature: (a) CTAB; (b) 12-2-12; (c) 14-2-14; (d) 16-2-16; (e) 16-4-16; (f) 16-6-16. The lines are drawn to guide the eye only.

the presence of a 5−10% excess of 1-bromoalkane to ensure complete bis-quaternization. The products were recrystallized in various solvent mixtures (ethanol−ethyl acetate and/or acetone−ethyl acetate for the dodecyl and tetradecyl compounds and chloroform−ethyl acetate for the hexadecyl series). The recrystallization was normally repeated three times.

All products were checked by ^{1}H NMR spectroscopy at 500 MHz, using CDCl$_3$ as solvent. For example, nine peaks were assigned for the protons for 16-4-16, and the integrated spectra gave the expected proton contents: δ (ppm) = 0.87 (t, 6H, ω-CH$_3$), 1.22−1.26 (m, 44H, CH$_2$ in the middle of the chains), 1.35 (m, 4H, δ-CH$_2$), 1.50−1.55 (m, 4H, γ-CH$_2$), 1.75−1.78 (m, 4H, β-CH$_2$), 2.20−2.22 (m, 4H, spacer β'-CH$_2$), 3.23 (s, 12H, headgroup N−CH$_3$), 3.26−3.28 (m, 4H, α-CH$_2$), 4.05−4.08 (m, 4H, spacer α'-CH$_2$).

A VWR Scientific conductivity meter, model 2052, and a VWR 515 conductivity dip cell were employed to perform the conductivity measurements. A Fisher Scientific isotemp refrigerated circulator, model 901, was used as a water bath for the temperature control. To prepare samples for the conductivity measurements, a surfactant was dissolved in hot water and the solution was cooled to 0 °C for at least overnight until the surfactant precipitated. During the determination of Krafft temperature, the temperature of the water bath was raised gradually. At each temperature, the conductance reading was checked every 2−5 min until it reached a steady value. Then, the temperature was raised by 1−2 °C again for another conductance measurement. Every time the reading was checked, the conductivity probe was moved up and down to stir the sample. All the cmc measurements were carried out at 46.5 °C, at which no precipitate was present. To minimize the effect of sample evaporation during the experiments, a small sample

cell (1 cm in diameter) was used. The samples were prepared by successive dilution while keeping the total volume constant in the cell. The conductance of the distilled water used to prepare the solutions was subtracted from each experimental data point for all plots.

Results and Discussion

Krafft Temperature and the cmc of Pure *m-s-m* Dimeric Surfactants. For the determination of the Krafft temperatures, 3 mM samples of CTAB and each of the five dimeric surfactants, 12-2-12, 14-2-14, 16-2-16, 16-4-16, and 16-6-16, were made and the conductivity of each sample was measured as described in the previous section. The results are plotted in Figure 1. The plots show that the conductivity increases rapidly with the increase in temperature due to gradual dissolution of the surfactant, until the Krafft temperature is reached. Then, the conductivity increases slowly due to the increase in ionic mobility with increasing temperature. The determination of the Krafft temperature by conductivity measurement is superior to the commonly used method of visual observation, which is dependent on the judgment of the observer. For three of the dimeric surfactants (14-2-14, 16-4-16, and 16-6-16), the changes in the conductivity before reaching the Krafft temperatures are less smooth (Figure 1, parts c, e, and f, respectively), but the reason for this is not clear to us.

The Krafft temperatures determined from the conductance measurements are listed in Table 1. The value of 24 °C for CTAB is comparable to that obtained from visual observation (26 °C).[14] In our experience, visual observation usually gives a slightly higher Krafft temperature than conductance measurement. For the three *m*-2-*m* surfactants (*m* = 12, 14, and 16), the Krafft temperature increases with the chain length, which

TABLE 1: Krafft Temperatures (T_k) and Critical Micelle Concentrations (cmc) of Several Cationic Surfactants

		CTAB	12-2-12	14-2-14	16-2-16	16-4-16	16-6-16
T_k, °C[a]		24.0	14.4	32.8	45.0	33.6	41.0
cmc (mM)	at 46.5 °C[b]	1.15 ± 0.01	1.38 ± 0.02	0.20 ± 0.01	0.034 ± 0.003	0.044 ± 0.001	0.047 ± 0.004
	at 46.5 °C[c]	1.12 ± 0.02	1.31 ± 0.02	0.21 ± 0.02	0.032 ± 0.002	0.042 ± 0.002	0.048 ± 0.002
	at 25.0 °C	$0.90-0.97^d$	$0.84+0.04^e$		0.021 ± 0.001^e	0.027 ± 0.015^e	0.043 ± 0.005^e

[a] Estimated error = ± 0.5 °C. [b] This work obtained by fitting the data to eq 2. [c] This work obtained from a model-independent method of fitting the data described in the text. [d] References 15 and 16. [e] Reference 6a.
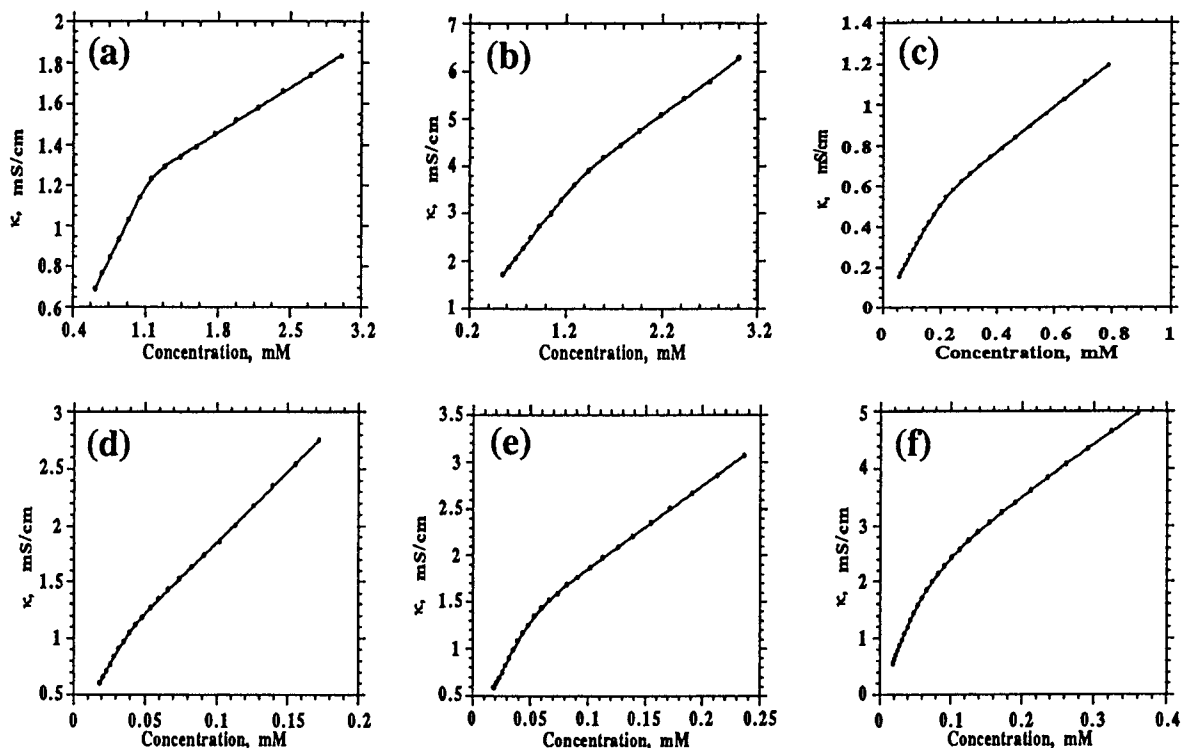

Figure 2. Conductivity of several cationic surfactants at 46.5 °C as a function of concentration: (a) CTAB; (b) 12-2-12; (c) 14-2-14; (d) 16-2-16; (e) 16-4-16; (f) 16-6-16. The solid lines were caluculated by fitting the experimental data to eq 2.

is expected. For the three 16-s-16 surfactants ($s = 2$, 4, and 6), the Krafft temperatures do not change regularly with the length of the spacer. This may be related to the fact that lengthening of the spacer not only increases the hydrophobicity of the surfactant but also decreases the Coulombic interactions between the positive charges in the headgroup as well as their interactions with the bromide ions, and the two effects counteract each other to a large extent. Overall, except for 12-2-12, the Krafft temperatures of the dimeric surfactants are higher than 25 °C.

New Mathematical Procedure To Find the cmc from the Conductance Data. The cmc's of CTAB and the five dimeric surfactants were determined at 46.5 °C using conductivity measurements. The reason for choosing this temperature is that it is slightly above the Krafft temperature of 16-2-16 (45 °C), which is the highest among all six compounds. Furthermore, to compare the cmc of various compounds, all conductivity measurements should be performed at the same temperature. The plots of conductivity versus concentration (c) are shown in Figure 2.

A common practice in obtaining the cmc from the conductivity plot is to draw two linear segments and determine the intersection point. This procedure is also used for determining the cmc from some other physical quantities, such as surface tension versus ln c and chemical shift versus $1/c$. For example, the data in Figure 2, parts a–c, can be treated this way to obtain the cmc. However, the transition between the two "linear"

portions in Figure 2, parts d–f, is very gradual, and this approach does not yield very reliable cmc values. This is also the case for most of the conductivity plots of the binary mixtures of dimeric surfactants and CTAB. Therefore, to obtain unbiased and reliable cmc values from the conductivity data, a more logical mathematical approach was used.

When the derivative of a function consisting of two nearly linear segments is plotted, it would be a step function. The second derivative of the original function would show a positive or negative peak, the position of which would correspond to the intersection point of the two nearly linear segments of the original function. If we assume that the second derivative is a Lorentzian function

$$\frac{\mathrm{d}^2 y}{\mathrm{d}x^2} = -\frac{k_1}{k_2{}^2 + (x - x_0)^2} \tag{1}$$

then the functional form of the original curve can be obtained from integrating it twice:

$$y = -\frac{k_1(x - x_0)}{k_2} \tan^{-1}\left[\frac{(x - x_0)}{k_2}\right] + \frac{k_1}{2} \log[k_2{}^2 + (x - x_0)^2] + k_3 x + k_4 \tag{2}$$

where x_0, k_1, k_2, k_3, and k_4 are constants, and x_0 is the x coordinate of the intersection point. By use of least-squares
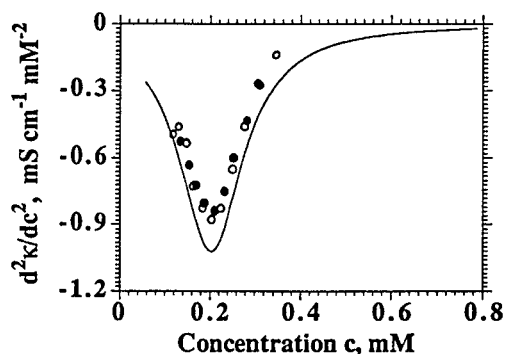
Figure 3. Second derivative of the conductivity of 14-2-14 with respect to the surfactant concentration. The solid line was caluculated from eq 1, using parameters obtained from fitting the experimental data to eq 2; the open circles are direct least-squares fits in groups of five as described in the text; the closed circles are direct least-squares fits in groups of six.

analysis to fit the experimental data to eq 2, the value of x_0 can be determined and is taken as the value of the cmc. The results for the pure surfactants are listed in Table 1.

The assumption made in eq 1, namely that the second derivative of the conductivity data is a Lorentzian function, is an arbitrary one for the sake of mathematical convenience; a Gaussian function cannot be integrated in closed form. One can, of course, make other assumptions for the functional form in eq 2, such as a polynomial or a hyperbola. However, a polynomial containing only a few terms would only fit the data in the given range; it often cannot be extrapolated outside this range and does not give the cmc value directly. The experimental data do resemble one branch of a hyperbola, but it is often difficult to use least-squares procedures to obtain the relevant parameters because one of them is part of a square root, which easily becomes an imaginary number to spoil the iteration procedure.

To examine the validity of the assumption expressed by eq 1, we treated the data with a model-independent least-squares method of data analysis for comparison. The experimental data represented in plots such as those in Figure 2 were put into groups containing N points at a time, where N is typically 4−7. For example, for 20 data sets with $N = 5$, the groups contain data points 1−5, 2−6, 3−7, ..., 16−20. Each group was fitted by linear least-squares analysis to obtain the slope of the curve, applicable at the average abscissa value for each group. Next, the slope values were fitted as functions of the same abscissa (again N data sets at a time) to obtain estimates of the second derivative at the average abscissa values. Finally, the second derivatives were plotted versus the abscissa variable to determine the maximum in the absolute value of the second derivative. The results of a typical plot are given in Figure 3, and the cmc values thus obtained are listed in the third row in Table 1. It can be seen that the shapes of the second derivative curves obtained from the two methods of data analyses are essentially the same, and the cmc values agree with each other very well. It is to be emphasized that the method of taking "second derivatives" from a discrete set of data, as represented by the individual symbols in Figure 3, is not necessarily the best way to obtain the cmc values. The method is used only to compare with the results obtained from eq 1 to establish that it is a valid assumption so that the analytical expression of eq 2 can be used to determine the cmc from the conductivity data of other systems, including those of binary mixtures to be discussed in the next section.

Zana and co-workers also determined cmc values for the dimeric surfactants *m-s-m* by conductivity measurements,[6a] but

the experiments were carried out at 25 °C. In comparing the two sets of cmc data listed in Table 1, one might conclude that the cmc values at the two temperatures are similar and the difference could be due to different temperatures. This would be a reasonable conclusion for CTAB[15,16] and 12-2-12. However, the data in the first row in Table 1 show that the Krafft temperatures for the other four dimeric surfactants are above 25 °C. From our experience, the solutions of these dimeric surfactants can stay clear at room temperature for a long time before they become cloudy and eventually precipitate. During the oversaturation period, conductance measurements can be made to determine the apparent cmc's at 25 °C, but they are not equilibrium values. In fact, we found that it was difficult to obtain reproducible results when the experiments were performed below the Krafft temperature.

From the cmc values listed in Table 1, it can be seen that the chain length has a much more pronounced effect on the cmc value than does the length of the spacer. The cmc of 12-2-12, which has the shortest chain length among the five dimeric surfactants studied, is much larger than those of the other four dimeric surfactants and that of the monomeric surfactant CTAB, which has 16 carbons in the chain. When the number of carbons in the hydrocarbon chain increases from 12 to 14 and 16 while the spacer is kept same, the cmc decreases from 1.38 to 0.21 and 0.034 mM, respectively. On the other hand, when the spacer increases from 2 to 4 to 6, the cmc increases slightly (Table 1). The reason for this is that the long alkyl chain is located in the micelle interior and becomes the major factor in determining the cmc's of the dimeric surfactants, whereas the spacer is located in the outer part of the micelles and has only a small effect in determining the aggregation of the surfactants.

Finally, we would like to point out that eq 2 not only is applicable to the treatment of the conductivity data but also can be used to analyze other physical properties, such as surface tension, chemical shifts, relaxation times, etc., to obtain the cmc of surfactant systems. In addition, it can also be used to fit the experimental data of many physical studies, such as thermo-chemical measurements as a function of time, pH titration, and conductrimetric titration.

Mixed cmc of Binary Systems. A cationic surfactant *m-2-m* can be considered as a genuine dimer of the corresponding monomeric alkyltrimethylammonium surfactant, which contains an alkyl chain with *m* carbons. For example, the surfactant 16-2-16 is a dimer of CTAB, with a C−C bond replacing one hydrogen atom in the headgroup of each of the two CTAB molecules. Therefore, it is of interest to study the micellar behavior of the binary system CTAB + 16-2-16. For comparison, the lengths of the alkyl chains and the spacer in 16-2-16 can be varied separately. Thus, we have studied the cmc values of five binary systems (CTAB + 12-2-12, CTAB + 14-2-14, CTAB + 16-2-16, CTAB + 16-4-16, and CTAB + 16-6-16) using conductivity measurements. For each system, the cmc's of nine binary mixtures with mole fractions ranging from 0.10 to 0.90 were determined. As discussed above, all the conductivity measurements were made at 46.5 °C.

The value of x_0 obtained from fitting each set of data to eq 2 was assigned to be the mixed cmc. The results are listed in Table 2 and plotted in Figure 4. For the binary systems CTAB + 12-2-12 and CTAB + 14-2-14, the mixed cmc values spread rather evenly between the cmc's of the two pure components. However, for the binary systems CTAB + 16-2-16, CTAB + 16-4-16, and CTAB + 16-6-16, most of the mixed cmc values are close to the cmc value of the pure 16-*s*-16 surfactant. The mixed cmc values start to increase rapidly only when the fraction

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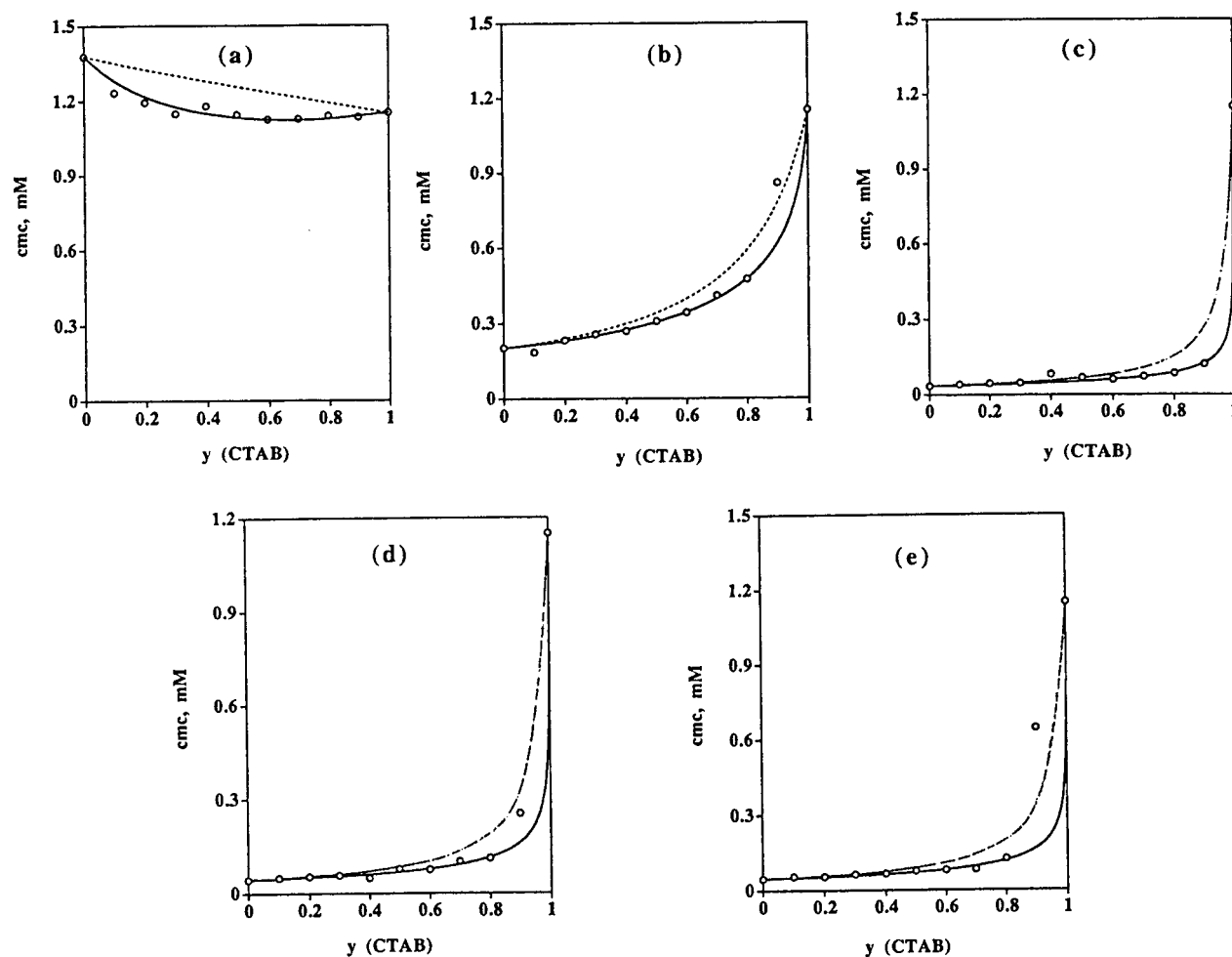*J. Phys. Chem. B, Vol. 102, No. 39, 1998* **7617**

Figure 4. Critical micelle concentrations for binary mixtures of cationic surfactants: (a) CTAB + 12-2-12; (b) CTAB + 14-2-14; (c) CTAB + 14-2-14; (d) CTAB + 16-4-16; (e) CTAB + 16-6-16. The circles are experimental data, the dashed lines were calculated from the ideal mixing model, and the solid lines were calculated from the nonideal mixing model.

TABLE 2: Mixed cmc (mM) of CTAB + *m-s-m* Binary Systems at 46.5 °C (Uncertainty = ±5%)

fraction of CTAB	CTAB + 12-2-12	CTAB + 14-2-14	CTAB + 16-2-16	CTAB + 16-4-16	CTAB + 16-6-16
1.0	1.15	1.15	1.15	1.15	1.15
0.9	1.13	0.86	0.12	0.25	0.65
0.8	1.14	0.47	0.085	0.11	0.13
0.7	1.13	0.41	0.071	0.10	0.082
0.6	1.12	0.34	0.060	0.076	0.080
0.5	1.14	0.31	0.068	0.078	0.076
0.4	1.18	0.27	0.054	0.050	0.067
0.3	1.15	0.26	0.056	0.056	0.063
0.2	1.19	0.23	0.050	0.050	0.055
0.1	1.23	0.19	0.038	0.050	0.054
0.0	1.38	0.20	0.034	0.044	0.047

TABLE 3: Averaged Interaction Parameter (*β*) for CTAB + *m-s-m* Binary Systems at 46.5 °C

CTAB + 12-2-12	CTAB + 14-2-14	CTAB + 16-2-16	CTAB + 16-4-16	CTAB + 16-6-16
−0.38 ± 0.07	−1.04 ± 0.10	−4.19 ± 0.50	−3.57 ± 0.40	−3.69 ± 0.40

of CTAB is close to 0.9. These results indicate that the surfactant 16-*s*-16 can easily partition into the micelles formed by CTAB, but the CTAB molecules do not partition well into the micelles of the dimeric surfactant 16-*s*-16.

In a binary surfactant system, the mixing of the hydrophobic core from the hydrophobic chains is viewed as an ideal process and the electrostatic interactions between "head" groups can be viewed as a nonideal process. Therefore, even if the monomer phase in a micelle solution is considered to be ideal, the micelle phase may be nonideal. The nonideality can be expressed in terms of an interaction parameter *β*, which

represents the free energy of mixing. For most of the systems where hydrocarbon chains mix inside the hydrophobic micelle core, *β* is negative. This means that the free energy is lowered when a hydrocarbon chain moves from the monomer phase to the micelle phase.

The principles of the quantitative treatment of the data have been discussed rather extensively in the literature[13,17−29] and will not be repeated here. By use of the pseudo-phase-separation approach,[22−25] all five binary surfactant systems studied in this work were treated with both ideal and nonideal models. The results are plotted as dashed and solid lines, respectively, in

Figure 4. In consideration of the counterion effect in the nonideal model, the dimeric surfactants are treated as a 1:1 type electrolyte. The reason for doing so is that even though there are two ionic groups in a dimeric surfactant molecule, the two groups are separated by a spacer. Therefore, the Coulombic interaction between each ionic group would be similar to a 1:1 type electrolyte. In the modeling, a parameter k_i is used to account for the counterion effect, and we used the value of $k_i = 0.6$ obtained for *n*-alkyltrimethylammonium salts[29] for the calculation of all five binary systems. For systems CTAB + 14-2-14, CTAB + 16-4-16, and CTAB + 16-6-16, the mixed cmc values at a mole fraction of CTAB = 0.9 were discarded due to their discordance with other data. The interaction parameters for all five systems are listed in Table 3; the errors in β were calculated by using a method described previously.[30]

The nonideality of the binary systems studied in this work, as judged by the value of represented by $-\beta$, has the trend CTAB + 12-2-12 < CTAB + 14-2-14 < CTAB + 16-4-16 ≈ CTAB + 16-6-16 < CTAB + 16-2-16. In other words, the nonideality of binary CTAB + *m-s-m* systems increases significantly with the carbon chain length of the dimeric surfactant. On the other hand, when the spacer of the dimeric surfactant increases from two to four carbons while the chain length is kept unchanged, the nonideality only decreases slightly; further increase of the spacer from four to six carbons has practically no effect on the nonideality of the binary system formed with CTAB, as the nonideality of the systems 16-4-16 and 16-6-16 can be considered to be the same within experimental error.

Although 16-2-16 can be regarded as the true dimer of CTAB, its binary mixtures with CTAB deviate most from ideal behavior. This indicates that in a micelle, the headgroups of CTAB are likely to be much farther apart from each other than those in the dimeric surfactant 16-2-16. As a result of its short spacer, 16-2-16 is expected to have the most compact microstructure. As a result, CTAB prefers to form spherical micelles but 16-2-16 prefers to form ropelike micelles,[6] and this difference can account for the large deviation from ideality when the two surfactants are mixed. Among the five dimeric surfactants studied, 16-2-16 has the highest Krafft temperature and lowest cmc (Table 1). The tendency to form ropelike micelles decreases in the order 16-2-16 > 16-4-16 ≈ 16-6-16 > 14-2-14 > 12-2-12, and the nonideality of their mixed micelle systems with CTAB changes according to the same trend. Because the interaction parameter represents the extra free energy of mixing, this correspondence is easy to understand. In all cases, even when the spacer has six carbon atoms, the motional freedom of the cationic headgroups in a dimeric surfactant is greatly reduced compared with that of the headgroup in a monomeric surfactant, and the micellar behavior is profoundly affected by this change.

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