Electrostatic Contribution to the Stability and the Synergism of Ionic/Nonionic Mixed Micelles in Salt Solutions

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A phenomenological procedure is presented to analyze the stability and the synergism of ionic/nonionic mixed micelles in salt solutions under three assumptions: (A) The ionic strength is independent of the mole fraction of the ionic species in the micelle, x. (B) The surface charge density varies linearly with x. (C) The nonelectric contribution to the excess free energy per monomer, g^{ex}, is given by the regular solution theory (RST) $g^{ex,non} = \beta^{non}x(1 - x)$, where β^{non} is a constant. When the electrostatic contribution to g^{ex} is written as $g^{ex,el} = \beta^{el}(x)x(1 - x)$, $\beta^{el}(x)$ is negative at all x but becomes less so as x increases. This feature is valid regardless of the shape of the micelles, whether spherical, rodlike, or platelike. The synergism due to the electrostatic contribution is shown to arise from the positive curvature of the electrostatic free energy per monomer, g^{el} (i.e., $d^2g^{el}(x)/dx^2 > 0$). In contrast, the electrostatic free energy per charge, $f(x)$, has a negative curvature: $d^2f(x)/dx^2 \leq 0$. It is found that $f(x)$ can be approximated with a polynomial of the form $A(x) = a_1x + a_2x^2 + a_3x^3$, again regardless of the micellar shape. The total excess free energy, g^{ex}, defined as ($g^{ex,non} + g^{ex,el}$), is found to be $g^{ex}(x) = -\{a_1{}^* + a_2{}^*(1 + x)\}x(1 - x) = \beta(x)x(1 - x)$, where $a_1{}^* = a_1 - \beta^{non}$ and $a_2{}^* = a_2 + a_3$. For 11 mixed micelles, x, $a_1{}^*$, and $a_2{}^*$ were determined experimentally using the reported relations between the critical micelle concentration (cmc) and the overall composition. Under the given assumptions, $a_1{}^*$ and $a_2{}^*$ thus obtained are expected to remain constant even at concentrations higher than the cmc, where the micelle composition is different. For most of the 11 mixed micelles examined, g^{ex} was not symmetric with respect to $x = 0.5$. Instead, the minimum was reached at $x < 0.5$ and was deeper than that estimated from the symmetric RST. A parameter $B_1 = \ln(\text{cmc}_I/\text{cmc}_N) + \beta(x = 0)$, where cmc_I and cmc_N are the cmc values of the pure ionic and nonionic species, is introduced to assess the nonelectric synergism properly.

1. Introduction

Mixtures of surfactants are of practical importance and theoretical interest.[1] In the case of ionic/nonionic mixed micelles, the charge density varies with the micelle composition, and the electrostatic free energy plays a central role in determining their stability. The thermodynamics of charged micelles has been developed,[2−5] and useful and practical procedures to enumerate the electrostatic thermodynamic quantities have been proposed.[4,5] The stability of mixed micelles in general has been extensively studied by molecular thermodynamic approaches,[6−14] phenomenological or thermodynamic approaches,[15−22] and combined approaches.[23,24] Although the molecular thermodynamic approach is more fundamental and of predictive character, it requires a priori information on the structures of both surfactant molecules and mixed micelles, which is not usually available. In the present study, we confine our interest to the phenomenological approach to the ionic/nonionic mixed micelles.

First, we shall discuss several popular approaches in this area. In the phenomenological approach, it would be pertinent to distinguish three regimes depending on the ionic strength of the medium: (I) High ionic strength ($C_s >$ about 0.2 M). The electrostatic interaction in this regime is of short-range nature due to sufficient shielding of the electric repulsion by the ionic atmosphere around each charged site. (II) Medium ionic strength ($C_s <$ about 0.2 M). The ionic strength in this regime is

practically kept constant independent of the micelle composition, whereas the long-range nature of the electric interaction is no longer negligible. (III) Low ionic strength. In this regime, the ionic strength of the medium varies significantly with the micelle composition.

The most popular procedure among the phenomenological approaches is undoubtedly the regular solution theory (RST) developed by Rubingh and Holland.[15−17] It works quite well in regime I where the interaction parameter β can be assumed to be independent of micelle composition x. In regimes II and III, however, the application of RST often provides us a composition-dependent interaction parameter $\beta_{RST}(x)$. Values of β evaluated at the critical micelle concentration (cmc) cannot generally be used at a different total concentration because the micelle composition will be different even at the same total composition.

The Gibbs−Duhem (G−D) relation for the binary ionic (I)−nonionic (N) mixed micelles in regime I can be written in terms of the chemical potential μ_i of the ith species. With the mole fraction of the ionic species in the micelle, x, we have

$$x \, d\mu_I + (1 - x) \, d\mu_N = 0 \qquad (1)$$

Thus, the micelle composition x can be evaluated when the cmc is known as a function of the mole fraction of the monomers in the solution, x_1.[18,19] In regimes II and III, however, the change in the chemical potential of the counterions, μ_C, cannot be ignored, and the G−D relation takes the following form[25]

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$$x\, d\mu_I + (1-x)\, d\mu_N + x\nu\, d\mu_C = 0 \qquad (2)$$

where ν represents the degree of counterion binding. The activities of the ionic surfactants can be determined directly by the use of surfactant-selective electrodes. The activity of the nonionic surfactant in the ionic/nonionic mixed micelles, however, can be evaluated only when the ionic strengths are high enough that the activity coefficient of the surface-active ionic species can be regarded as practically constant.[23,24] This condition is generally not satisfied in regimes II and III, so μ_N cannot be assessed unless ν is known as a function of x.

As seen above, the representative phenomenological procedures that are valid in regime I are not always applicable to regimes II and III. However, the predictive approaches can be applied to any of these three regimes when the required parameters are given.

In regimes II and III, the nonideal behavior is often nonsymmetric with respect to $x = 0.5$. It has been generally noted that the electrostatic contribution always introduces the asymmetric nature of the nonideality if the ionic strength is not high enough. In the phenomenological approach, at least two parameters are required to describe the asymmetric nonideality. Several two-parameter theories have been proposed, but they require that micelle compositions are known in advance.[21,22]

In the present study, we propose a two-parameter phenomenological procedure that is applicable to regimes I and II (but not to regime III). The electrostatic free energy of ionic/nonionic mixed micelles and its contribution to the excess free energy are presented in an approximate but general way that is valid for spherical, rodlike, and platelike micelles. The present approach may be regarded as a counterpart of the predictive approaches of Reif−Somasundaran,[12] Eriksson−Bergström,[13,14] and Peyre,[24] where the electrostatic effect is the only or the major contribution.

2. Electrostatic Free Energy of Ionic/Nonionic Mixed Micelles in a Salt Solution

We consider two-component mixed micelles consisting of one ionic and one nonionic surfactant immersed in a salt solution where the counterion concentration can be regarded as practically constant independent of the micelle composition. For the micelles at the cmc, the Poisson−Boltzmann equation takes the following form in terms of the electric potential ψ, the Boltzmann constant k, the protonic charge e_0, and the absolute temperature T. The reduced potential ϕ is defined as $|e_0\psi/kT|$.

$$\Delta\phi = \kappa^2 \sinh\phi \qquad (3)$$

In eq 3, $\kappa^2 = 8\pi l_B n_S$ where l_B and n_S denote, respectively, the Bjerrum length and the salt concentration. Equation 3 can be solved under proper boundary conditions for a given micellar shape: spherical, rodlike, or platelike. Then, the surface potential ψ_0 is given as a function of κ and the surface charge density σ. In the present analysis, the electrostatic free energy G_{el} is obtained by charging the micelle. The electrostatic free energy per charge of a mixed micelle consisting of m_I ionic and m_N nonionic species (the aggregation number $m = m_I + m_N$) is $G_{el}/(mx)$, where x is the micellar mole fraction of the ionic species (i.e., $x = m_I/m$). We choose x as the micelle composition. We define $f(x)$ as $G_{el}/(mxkT)$, and it is given in eqs 6 and 7 for particular micellar shapes in terms of a charge parameter s defined as follows.

$$s = \frac{4\pi l_B |\sigma/e_0|}{\kappa} \qquad (4)$$

Throughout the present study, we assume the following simple relation about the charge parameter s.

$$s(x) = xs(x = 1) \qquad (5)$$

For an infinite plate,

$$\frac{G_{el}}{mxkT} = f(x) = \frac{4}{s}\left[\frac{s}{2}\ln\left[\frac{s}{2} + \left\{\left(\frac{s}{2}\right)^2 + 1\right\}^{1/2}\right] - \left[\left\{\left(\frac{s}{2}\right)^2 + 1\right\}^{1/2} - 1\right]\right] \qquad (6)$$

For a sphere (radius R), the following approximate equation has been proposed.[26]

$$\frac{G_{el}}{mxkT} = f(x) = 2\ln\{z + (z^2 - 1)^{1/2}\} -$$
$$2(z+1)(z^2-1)^{-1/2} + \frac{8}{s}\left\{1 + \frac{2}{\kappa R}\right\}^{1/2}$$
$$+ \frac{16}{s\kappa R}\left[\ln\left[\left\{z + 1 + \frac{4}{\kappa R}\right\}^{1/2} - (z+1)^{1/2}\right] -$$
$$\ln\left[\left\{2 + \frac{4}{\kappa R}\right\}^{1/2} - 2^{1/2}\right]\right] \qquad (7)$$

where

$$z = \left[\left\{1 + \frac{2}{\kappa R}\right\}^{1/2} + \frac{s^2}{4}\right]^{1/2} - \frac{2}{\kappa R} \qquad (8)$$

We adopt this approximate expression (eq 7) because it is important to have an analytic expression of $f(x)$ in the present analysis. The corresponding approximate expression for the rodlike micelles[26] is similar to eq 7, so we examine only the two cases of the plate and sphere here. In the predictive approach, the values of $f(x)$ are evaluated on the basis of the molecular parameters, but in the present study, they are replaced with a polynomial that turned out to hold for all three shapes considered here. (See section 4.)

3. Electrostatic Contribution to the Excess Free Energy G^{ex} of Mixed Micelles

We define the free energy of a mixed micelle with aggregation number m and composition x as $G(m, x)$ and $g(x)$ as G/mkT. Then, the excess free energy of the mixed micelle can be written as follows.

$$\frac{G^{ex}}{mkT} = g^{ex}(x) = g(x) - xg(x = 1) - (1 - x)\, g(x = 0) -$$
$$\{x \ln x + (1 - x)\ln(1 - x)\} \qquad (9)$$

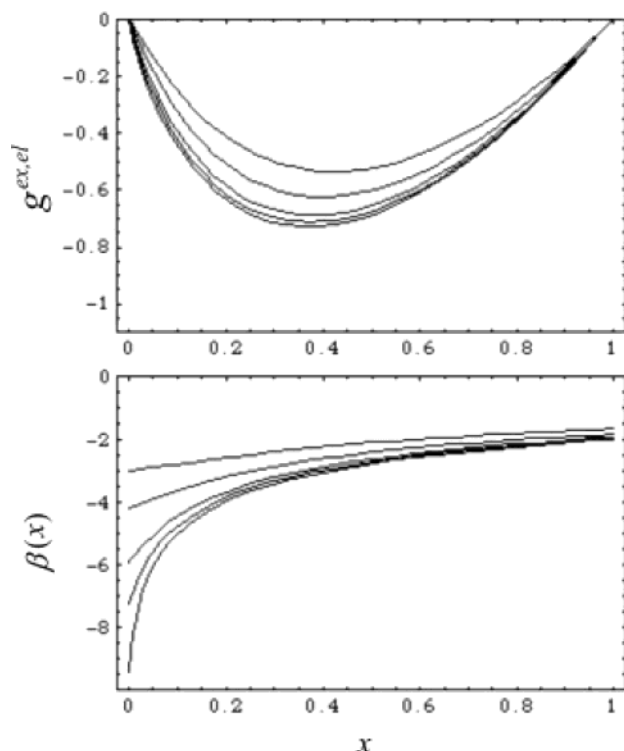We divide g^{ex} into two contributions from the electric and the nonelectric interactions.

$$g^{ex} = g^{ex,non} + g^{ex,el} \qquad (10)$$

We can assume that $g^{ex,non}$ has the form given below in terms of the regular solution parameter β^{non}.

$$g^{ex,non} = \beta^{non}x(1 - x) \qquad (11)$$

However, for $g^{ex,el}$

$$g^{ex,el} = g^{el}(x) - xg^{el}(x = 1) \qquad (12)$$

Figure 1. Electrostatic contribution to the excess free energy $g^{ex,el}$ and the corresponding $\beta(x) = g^{ex,el}/\{x(1-x)\}$ for infinite plates as functions of the mole fraction of the ionic component in the mixed micelle, x. Values of s are (from top to bottom) 10, 20, 50, 100, and 300.

Noted that

$$g^{el}(x) = \frac{G^{el}}{mkT} = x\,f(x) \tag{13}$$

Activity coefficients of the ionic (γ_I) and the nonionic (γ_N) species in mixed micelles can be evaluated from G^{ex} using eq 14, and they should satisfy eq 15.

$$kT \ln \gamma_I = \left(\frac{\partial G^{ex}}{\partial m_I}\right)_{m_N} \quad \text{and} \quad kT \ln \gamma_N = \left(\frac{\partial G^{ex}}{\partial m_N}\right)_{m_I} \tag{14}$$

$$g^{ex} = x \ln \gamma_I + (1-x) \ln \gamma_N \tag{15}$$

From eqs 6, 7, 12, and 13, we can calculate $g^{ex,el}$ as functions of x, and some representative results for platelike and spherical micelles are shown in Figures 1 and 2, respectively.

Now, we examine the range of parameter s. For sodium dodecyl sulfate (SDS) micelles in 0.03 M NaCl solution, the micelles can be well approximated with a sphere of a radius R = 1.81 nm and an area per charge of 0.58 nm².[26] In this example, we have $s = 15.60 \ \kappa^{-1}$/nm. In the case of a univalent salt, the variation in the concentration C_s from 1 to 10^{-4} M results in a change in κ^{-1} from 0.3 to 30 nm and a change in s from 4.68 to 468. For spheres, $g^{ex,el}(x)$ depends on both s and κR. For mixed micelles containing dodecyl sulfate at $C_s = 10^{-2}$ M, κR = 0.60 and s varies from 0 (pure nonionic micelles) to 46.8 (SDS micelle). The parameters chosen in Figures 1 and 2 are consistent with these estimates. For an infinite plate, we observe the effects of both the charge density and ionic strength in a unified manner through the parameter s, as shown in eq 6. For a sphere of radius R, the effect of ionic strength contributes in two different ways, as can be seen in eq 7; one contribution is from the term κR, and the other is from s. The effect of the
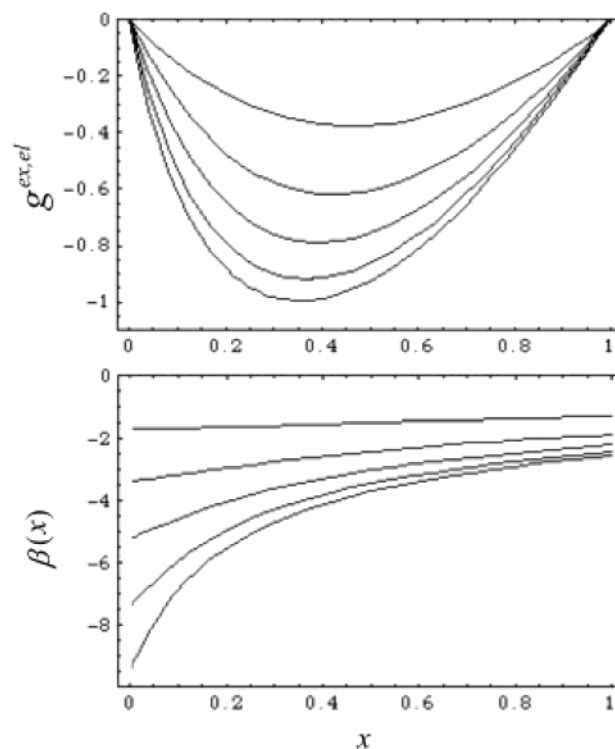
Figure 2. Electrostatic contribution to the excess free energy $g^{ex,el}$ and the corresponding $\beta(x) = g^{ex,el}/\{x(1-x)\}$ for spheres as functions of the mole fraction of the ionic component in the mixed micelle, x. Radius of sphere $R = 1.81$ nm and area per charge = 0.58 nm². Values of the salt concentration (M) of a univalent salt are (from top to bottom) 1, 0.1, 0.01, 1×10^{-3}, and 1×10^{-4}.

charge density at constant ionic strength is determined by the parameter s, and the result is qualitatively similar to that of a plate (Figure 1) (not shown for sphere). The effect of the ionic strength at a constant charge density is shown in Figure 2.

In Figures 1 and 2, we can observe the following general tendency. For small s, $g^{ex,el}(x)$ is symmetric with respect to $x = 0.5$, and RST is valid with a single composition-independent parameter β_{RST}. As s increases, however, the minimum of $g^{ex,el}(x)$ becomes deeper, and the peak shifts away from $x = 0.5$. For infinite plates with $s \gg 1$, $f(x) \approx 2 \ln\{x\,s(x=1)/e\}$, which predicts that $g^{ex,el}$ takes the minimum ($-2/_e \approx -0.736$) at $x = 1/_e$ (~ 0.368). It is clear from the results shown in Figures 1 and 2 that at least two parameters are generally necessary to describe the stability of the ionic/nonionic mixed micelles. When RST in terms of the single parameter β_{RST} is applied, β_{RST} becomes composition-dependent. For any stability analysis on cmc data to be useful, it should provide stability parameters that are independent of micelle composition x. This is crucial because the micelle composition varies with the total surfactant mixture concentration even at a fixed overall composition.

We define $\beta^{el}(x)$ as below. (It is also given in Figures 1 and 2.)

$$\beta^{el}(x) = \frac{g^{ex,el}}{x(1-x)} \tag{16}$$

Experimental cmc data have often been analyzed tentatively by RST, and the following behaviors have been observed for the interaction parameter β_{RST}.

(1) β_{RST} is negative.

(2) β_{RST} increases with micelle composition x. This dependence could be regarded as linear except for low x if s is not
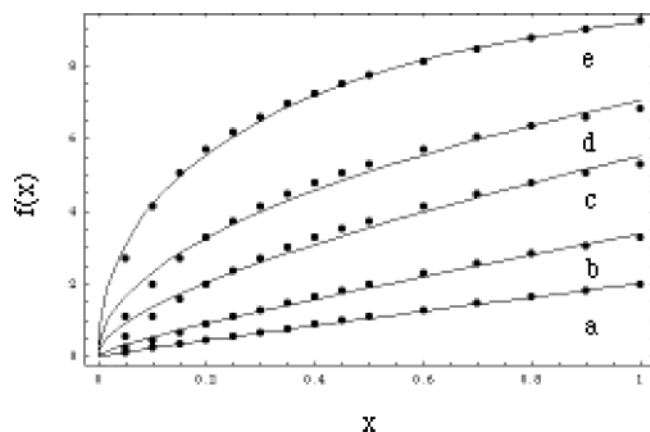
Figure 3. Approximation of the electrostatic free energy per charge $f(x)$ with a series $(a_1 x^{0.5} + a_2 x)$ for a sphere of $R = 1.81$ nm and $\kappa R = 0.5$. Values of s are (from top to bottom) 300, 100, 50, 20, and 10. Curves represent the series that fit best to the values calculated (points) from eq 7.

too high. Such a linear dependence was observed by Reif−Somasundaran[12] and Peyre.[24]

(3) As the ionic strength increases or the charge density decreases, β_{RST} becomes less negative, and RST becomes a better approximation.

All of these behaviors were confirmed to arise mostly from the electrostatic contributions,[12,24] as can also be seen from $\beta^{el}(x)$ in Figures 1 and 2. Qualitatively similar results are obtained for other values of κR for spherical micelles and for rodlike micelles (not shown). When β_{RST} exhibits a behavior different from the above observations (1−3), it is indicative of significant contributions from the nonelectric interactions. Observation 1, the negative β or synergism, will be further discussed in section 6.

It is pertinent to evaluate the limiting values of $\beta^{el}(x)$. As x approaches zero, $\beta^{el}(x = 0) = [g^{ex,el}(x)/x](x \rightarrow 0) = f(x = 0) - f(x = 1) = -f(x = 1) = -g^{el}(x = 1)$. Thus, we obtain a quantitative relation between the electrostatic free energy of pure ionic micelles $g^{el}(x = 1)$ and the magnitude of the electric synergism $[\beta^{el}(x = 0)]$ due to the insertion of nonionic species. In Figure 1, values of $\beta^{el}(x = 0)$ are consistent with values of $f(x = 1)$, which are given in Table 1 as $(a_1 + a_2 + a_3)$. Consistent results were also obtained for the sphere model at constant κR values (not shown). As x approaches 1, on the other hand, $\beta^{el}(x = 1) = [g^{ex,el}(x)/\{x(1 - x)\}](x \rightarrow 1) = \{f(x \rightarrow 1) - f(x = 1)\}/(1 - x) = -\{df(x)/dx\}(x = 1)$. For the plate model with large s values, $f(x) = 2 \ln\{x\, s(x = 1)/e\}$, and we obtain $\beta^{el}(x = 1) = -2$.

4. Approximations of $f(x)$ by Simple Polynomials

Because we need to describe the stability of mixed micelles in terms of at least two parameters, we first try to approximate $f(x)$ given by eqs 6 and 7 with a series of x. A type of series
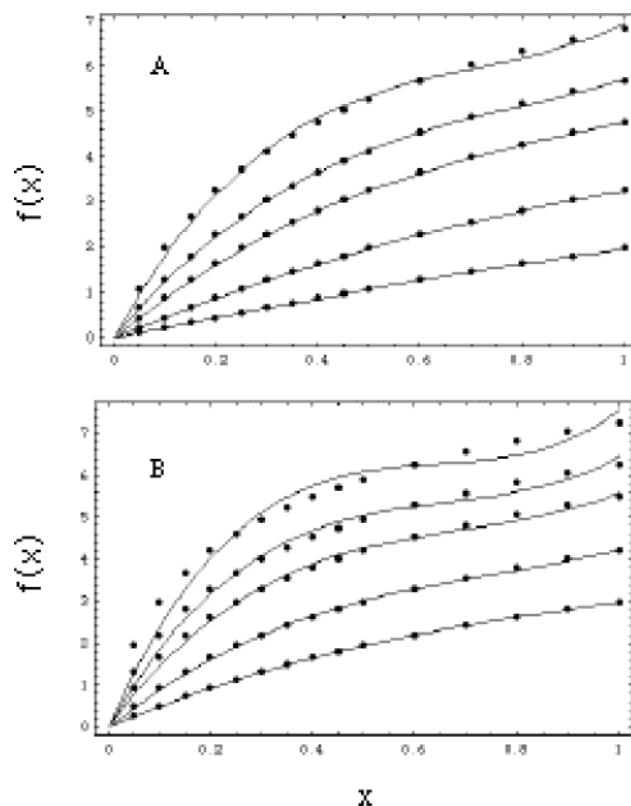
Figure 4. Approximation of the electrostatic free energy per charge $f(x)$ with a series $A(x) = a_1 x + a_2 x^2 + a_3 x^3$. Curves represent $A(x)$ that fit best to the calculated values (points). (A) Sphere of $R = 1.81$ nm and $\kappa R = 0.5$. Values of s are (from top to bottom) 100, 60, 40, 20, and 10. (B) Plate. Values of s are (from top to bottom) 100, 60, 40, 20, and 10.

$a_1 x^{1/2} + a_2 x$ is found to fit $f(x)$ quite well for both platelike and spherical cases. In Figure 3, an example of spherical micelles for $\kappa R = 0.5$ is shown. In the case $f(x) = a_1 x^{1/2} + a_2 x$, we have

$$g^{ex,el}(x) = -\left\{a_2 + \frac{a_1}{1 + x^{1/2}}\right\}x(1 - x) \qquad (17)$$

A linear relation was often found between a_1 and a_2,

$$a_2 = b_0 + b_1 a_1 \qquad \text{with} \qquad b_1 = -0.55 \approx -0.65, \ b_0 = 2-4$$

The series $(a_1 x^{1/2} + a_2 x)$ is a good approximate expression of $f(x)$ irrespective of the micellar shape. However, the expression for $g^{ex,el}$ (eq 17) does not satisfy eq 15, and hence cannot be used as for the derivation of the activity coefficients.

Another series $A(x) = a_1 x + a_2 x^2 + a_3 x^3$ was found to approximate $f(x)$ for both the plate and sphere cases (eqs 6 and 7, respectively) with acceptable deviations if s is not large, as shown in Figure 4.[27] Because $df(x)/dx > 0$ and $d^2f(x)/dx^2 < 0$,

TABLE 1: Coefficients of a Polynomial $A(x) = a_1 x + a_2 x^2 + a_3 x^3$ Fit to the Electrostatic Free Energy per Charge

	sphere ($\kappa R = 0.5$)					plate				
s	a_1	a_2	a_3	$-(a_2 + a_3)/a_3$	$a_1 + a_2 + a_3$	a_1	a_2	a_3	$-(a_2 + a_3)/a_3$	$a_1 + a_2 + a_3$
10	2.263	−0.162	−0.126		1.975	5.290	−3.321	1.016	2.27	2.985
20	4.686	0.103	3.254	13.9	3.254	9.938	−9.940	4.223	1.35	4.221
40	9.520	−7.201	2.451	3.9	4.77	16.57	−21.17	10.20	1.08	5.6
50	11.725	−10.48	4.039	1.6	5.284	19.06	−25.67	12.6	1.03	6.05
60	13.76	−13.73	5.687	1.4	5.717	21.21	−29.61	14.85	0.99	6.45
100	20.44	−25.42	11.93	1.1	6.95	27.63	−41.73	21.66	0.93	7.56
300	37.84	−59.24	31.07	0.91	9.67					

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we have $a_1 > 0$, $a_2 < 0$, and $a_3 < -a_2/3$. The obtained parameters are given in Table 1.

We have the following expression for $g^{ex,el}(x)$.

$$g^{ex,el} = g^{el}(x) - xg^{el}(x = 1) =$$
$$-\{a_1 + (a_2 + a_3)(1 + x) + a_3 x^2\}x(1 - x) \quad (18)$$

Because it is not easy to evaluate three parameters from experimental cmc data, we are obliged to adopt the following approximation in the present study to reduce the number of parameters.

$$-(a_2 + a_3)(1 + x) \gg a_3 x^2 \quad \text{or} \quad -\frac{a_2 + a_3}{a_3} \gg \frac{x^2}{1 + x} \quad (19)$$

The $x^2/(1 + x)$ term takes the maximum value of 0.5, and this provides a criterion for the validity of the approximation. As seen in Table 1, the approximation is expected to be valid if a_1 is smaller than about 10.

Under this approximation, we cannot evaluate a_2 and a_3 separately but only their sum $(a_2 + a_3)$, which is denoted as a_2* from this point on. Now eq 18 is rewritten as

$$g^{ex,el}(x) = -\{a_1 + a_2*(1 + x)\}x(1 - x) \quad (20)$$

When the nonelectric contribution (eq 11) is added, g^{ex} is given as follows with $a_1* = a_1 - \beta^{non}$:

$$g^{ex}(x) = -\{a_1* + a_2*(1 + x)\}x(1 - x) = \beta(x) x(1 - x) \quad (21)$$

We define $\beta(x)$ in eq 22:

$$\beta(x) = -\{a_1* + a_2*(1 + x)\} \quad (22)$$

In this way, a linear relation is derived between $\beta(x)$ and x, as previously observed.[12,24]

Activity coefficients are

$$\ln \gamma_I = \beta(x)(1 - x)^2 + I(x) \quad (23)$$

$$\ln \gamma_N = \beta(x) x^2 + N(x) \quad (24)$$

Generally, $I(x)$ and $N(x)$ are not identical, and different β_{RST} values are obtained depending on the surfactant species chosen. According to the present analysis, $I(x)$ and $N(x)$ are explicitly given as

$$I(x) = x(1 - x)^2 \frac{d\beta(x)}{dx} = -a_2* x(1 - x)^2 \quad (25)$$

$$N(x) = x^2(1 - x) \frac{d\beta(x)}{dx} = a_2* x^2(1 - x) \quad (26)$$

With these $I(x)$ and $N(x)$ functions, the activity coefficients fulfill eq 15. Therefore, we can accept eq 21 as a proper, though not accurate, expression for g^{ex}.

Thus, the final expressions for the activity coefficients are

$$\ln \gamma_I = -\{a_1* + a_2* + 2a_2* x)\}(1 - x)^2 \quad (27)$$

$$\ln \gamma_N = -\{a_1* + 2a_2* x)\}x^2 \quad (28)$$

From the equilibrium conditions between the free monomer and micelles, we have

$$x\gamma_I = \frac{cmc\, x_1}{cmc_I} \quad (29)$$

$$(1 - x)\gamma_N = \frac{cmc(1 - x_1)}{cmc_N} \quad (30)$$

Here, cmc_I and cmc_N represent the cmc values of pure ionic $(x = 1)$ and nonionic $(x = 0)$ micelles, respectively.

5. Application to Experimental Data

The values of cmc are determined experimentally as a function of the overall composition, which is well approximated by the monomer composition x_1 at the cmc. The data-analysis procedure in the present study is as follows:

(1) First, we ignore the contributions from $I(x)$ and $N(x)$. Then, we can eliminate $\beta(x)$ by combining eqs 29 and 30 to obtain eq 31, which is the same as the RST result.

$$\frac{\ln\{cmc\, x_1/(cmc_I x)\}}{(1 - x)^2} = \frac{\ln[cmc(1 - x_1)/cmc_N(1 - x)]}{x^2} \quad (31)$$

The micelle composition x is evaluated with eq 31.

(2) With the obtained x values, $\beta_I(x)$ and $\beta_N(x)$ are evaluated from the following relations:

$$\ln\{cmc\, x_1/(cmc_I x)\}/(1 - x)^2 = \beta_I(x) \quad (32)$$

$$\frac{\ln\{cmc(1 - x_1)/cmc_N(1 - x)\}}{x^2} = \beta_N(x) \quad (33)$$

Because we ignore $I(x)$ and $N(x)$, $\beta_I(x)$ and $\beta_N(x)$ generally differ from each other.

(3) According to eq 22, values of $\beta_I(x)$ and $\beta_N(x)$ are plotted against x. We obtain $(a_1* + a_2*)$ and a_2* from the intercept and the slope of the plot, respectively. We need to average the results for the cases of $\beta_I(x)$ and $\beta_N(x)$. Examples of the plots are shown in Figure 5. Quantities obtained at this stage such as x_{RST}, $\beta_I(x)$, $\beta_N(x)$, a_1*, and a_2* are referred to as zeroth-order values.

(4) With the obtained zeroth-order value of a_2*, the micelle compositions are reevaluated using the following equation.

$$\frac{\ln\{cmc\, x_1/(cmc_I x)\}}{(1 - x)^2} + a_2* x =$$
$$\frac{\ln[cmc(1 - x_1)/\{cmc_N(1 - x)\}]}{x^2} - a_2*(1 - x) \quad (34)$$

(5) With the new x values, $\beta_I(x)$ and $\beta_N(x)$ are reevaluated from the following relations

$$\frac{\ln\{cmc\, x_1/(cmc_I x)\}}{(1 - x)^2} + a_2* x = \beta_I(x) \quad (35)$$

$$\frac{\ln[cmc(1 - x_1)/\{cmc_N(1 - x)\}]}{x^2} - a_2*(1 - x) = \beta_N(x) \quad (36)$$

(6) Reevaluated values of $\beta_I(x)$ and $\beta_N(x)$ are plotted against x. We obtain a_1* and a_2* as before, but it was still necessary to average the results for $\beta_I(x)$ and $\beta_N(x)$ in most cases, though in some cases $\beta_I(x)$ and $\beta_N(x)$ coincided with each other. Generally, the micelle composition changed significantly from
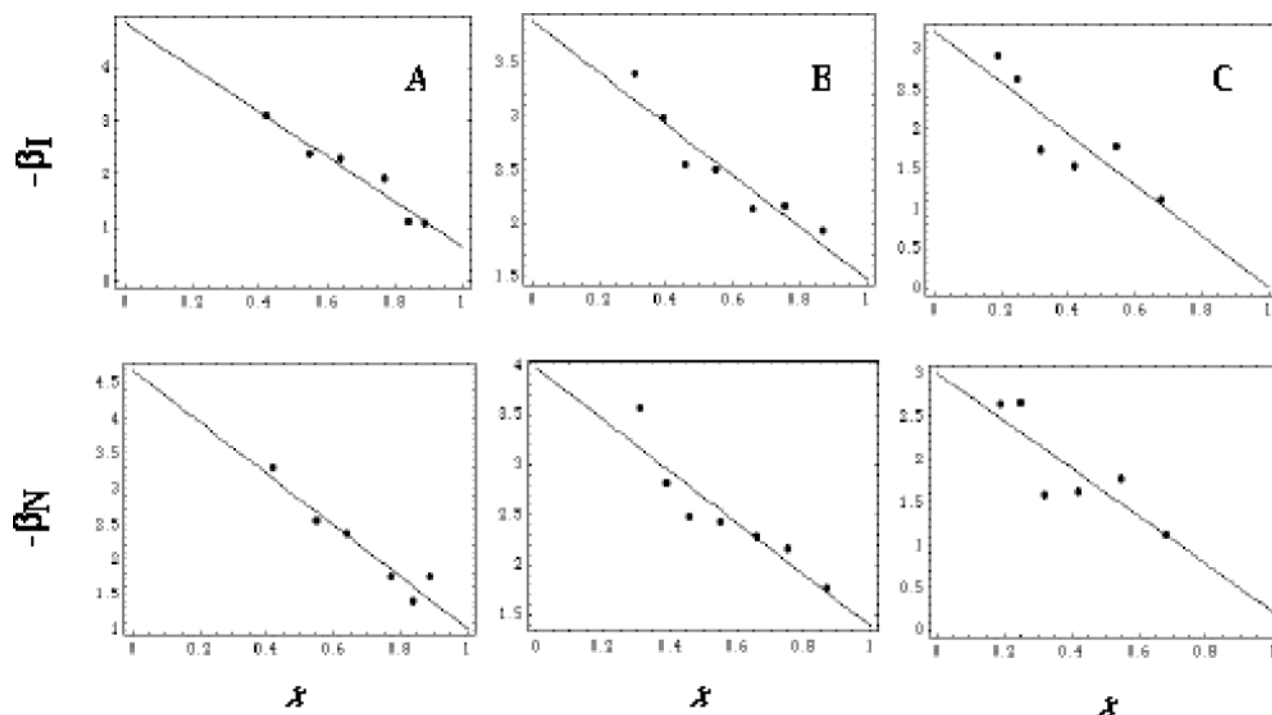
Figure 5. Examples of the plot of $\beta(x)$ against the micelle composition, x. Upper and lower panels refer to β_I and β_N, respectively. (A) NaC12BzS/C10Mal in 0.01 M NaCl, (B) SDS/C8Glc in 0.02 M NaCl, and (C) C16TAC/C9pheE10 in 0.03 M NaCl.

TABLE 2: Comparison of the Micelle Composition

0.01 M NaCl	x_{RST}	0.42	0.55	0.64	0.77	0.84	0.89		
NaC12BzS/C10Mal	x	0.35	0.45	0.53	0.65	0.74	0.84		
0.02 M NaCl	x_{RST}	0.31	0.39	0.46	0.55	0.66	0.755	0.87	
SDS/C8Glc	x	0.27	0.33	0.39	0.48	0.59	0.70	0.84	
0.03 M NaCl	x_{RST}	0.19	0.25	0.32	0.42	0.546	0.68		
C16TAC/C9pheE10	x	0.16	0.21	0.255	0.34	0.45	0.56		
0.075 M NaCl	x_{RST}	0.345	0.45	0.54	0.65	0.72	0.76	0.84	0.91
SDS/C8Glc	x	0.33	0.44	0.525	0.64	0.705	0.75	0.84	0.91
0.1 M NaCl	x_{RST}	0.27	0.345	0.45	0.58	0.63	0.81		
SDS/C12E6	x	0.24	0.31	0.41	0.53	0.585	0.78		

the RST values as a result of this iterative procedure as shown in Table 2. It is obvious that the two sets of x values are close to each other if a_2^* is small. However, the values of $\beta_I(x)$, $\beta_N(x)$, a_1^*, and a_2^* did not change significantly with the iterative procedure. Accordingly, one can obtain a_1^* and a_2^* from the zeroth-order values without performing the iterative procedure of 4–6.

Nine mixed systems were analyzed, and the obtained values of a_1^*, a_2^*, and their sum are given in Table 3 together with the β_{RST} values. The nine systems are (a) sodium dodecylbenzenesulfonate (NaC12BzS)/n-decyl-β-maltoside (C10Mal) in 0.01 M NaCl,[28] (b) NaC12BzS/octaethyleneglycol n-decyl ether (C10E8) in 0.01 M NaCl,[28] (c) sodium dodecyl sulfate (SDS)/octylglucoside (C8Glc) in 0.02, 0.075, and 0.15 M NaCl,[29] (d) hexadecyltrimethylammonium chloride (C16TAC)/decaethyleneglycol nonylphenyl ether (C9pheE10) in 0.03 M NaCl,[30] (e) hexadecylpyridinium chloride (C16PyC)/C9pheE10 in 0.03 M NaCl,[30] (f) sodium decyl sulfate (SDeS)/tetraethyleneglycol n-octyl ether (C8E4) in 0.05 M NaCl,[16] (g) decyltrimethylammonium bromide (C10TAB)/C8E4 in 0.05 M NaCl,[16] (h) SDS/hexaethyleneglycol n-dodecyl ether (C12E6) in 0.1 M NaCl,[31] and (i) dodecyldimethylhydroxylammonium chloride (C12DMAOH)/dodecyldimethylamine oxide (C12DMAO) in 0.1 M NaCl.[32] Mixtures f and g were studied at only three compositions, and hence their results are excluded in the
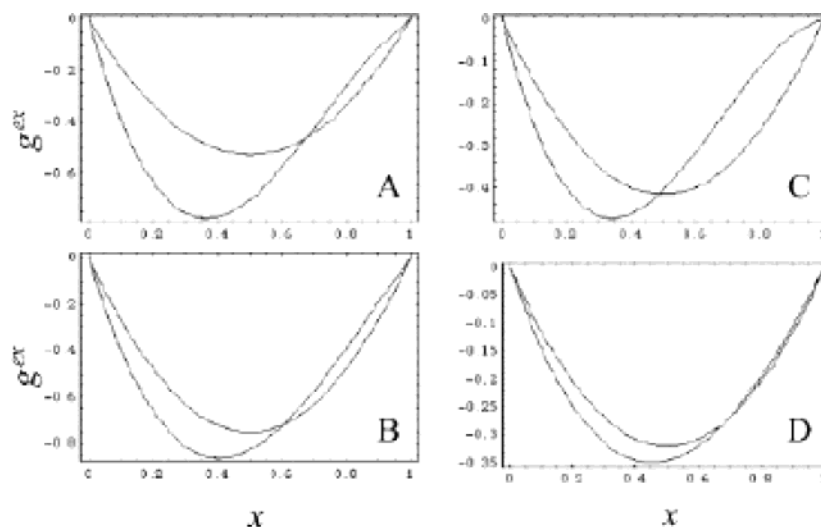
TABLE 3: Summary of the Parameters for 11 Mixed Micelles[a]

| C_s/M	mixed micelles		a_1^*	a_2^*	$a_1^* + a_2^*$	β_{RST} [b]
0.01	NaC12BzS/C10Mal	1	7.83	−3.39	4.44	−2.1
0.01	NaC12BzS/C10E8	0	7.56	−2.84	4.72	−3.0
0.02	SDS/C8Glc	1	6.24	−2.43	3.81	−2.5
0.03	C16TAC/C9pheE10	1	6.24	−3.11	3.13	−1.92
0.03	C16PyC/C9pheE10	0	2.21	−0.55	1.66	−1.42
0.05	SDeS/C8E4	0	15.74	−8.125	7.62	−4.1 (−2.7)
0.05	C10TAB/C8E4	1	3.17	−1.36	1.81	−1.8 (−3.4)
0.075	SDS/C8Glc	1	3.36	−0.70	2.66	−2.04
0.1	SDS/C12E6	1	5.40	−1.80	3.57	−2.7 (−3.4)
0.1	C12DMAOH/C12DMAO	0	4.21	−1.42	2.74	−2.15
0.15	SDS/C8Glc	0	4.67	−1.33	3.34	−2.54

[a] The third column represents the order of approximation: 0 refers to the zeroth-order values, and 1 refers to the values obtained after the iteration procedure. [b] Values in parentheses are those given by the authors.

following discussion. For all the samples except (f), a_1^* is smaller than 8. Because $a_1^* = a_1 - \beta^{non}$, we may expect a_1 to be <10 unless β^{non} is a large, positive number. We therefore conclude that the eight mixed systems conform to inequality 19.

Once a_1^* and a_2^* are obtained, we can calculate g^{ex} according to eq 21 at any concentration higher than the cmc if the micelle composition is known. In Figures 6 and 7, the evaluated g^{ex} values of eight mixtures are shown and compared with the

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Figure 6. Excess free energy per monomer g^{ex} as a function of the micelle composition, x. The result of RST is shown in each panel with a parabola. (A) NaC12BzS/C10Mal in 0.01 M NaCl, (B) NaC12BzS/C10E8 in 0.01 M NaCl, (C) C16TAC/C9pheE10 in 0.03 M NaCl, and (D) C16PyC/C9pheE10 in 0.03 M NaCl.
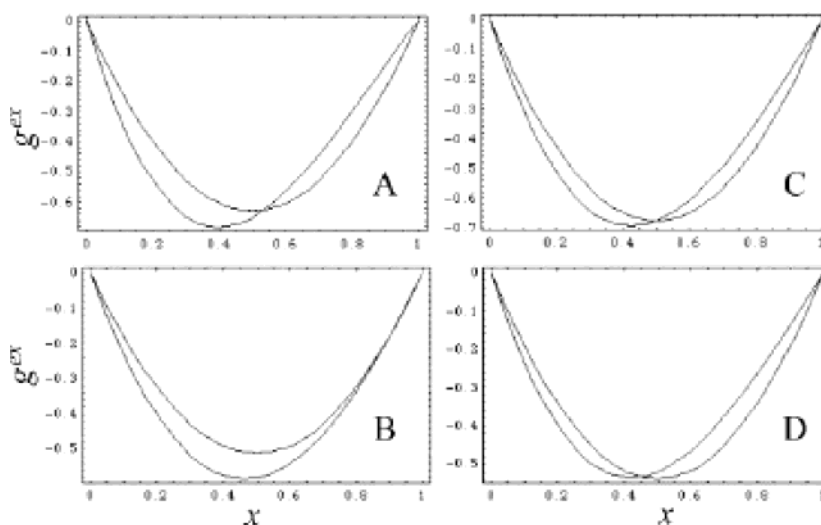
Figure 7. Excess free energy per monomer g^{ex} as a function of the micelle composition, x. The result of RST is shown in each panel with a parabola. (A) SDS/C8Glc in 0.02 M NaCl, (B) SDS/C8Glc in 0.075 M NaCl, (C) SDS/C12E6 in 0.1 M NaCl, and (D) C12DMAOH/C12DMAO in 0.1 M NaCl.

results of RST, which is represented by a parabola with the minimum at $x = 0.5$. In all examples examined here, the peak position of g^{ex} was found at $x < 0.5$, and the minimum was more negative than that of RST, $\beta_{RST}/4$, with the exception of C10TAB/C8E4 (not shown). As the salt concentration C_s increases, the minimum and its position both approach those of RST. This trend is well confirmed in the case of two mixtures in 0.1 M NaCl (Figure 7C and D). The effect of the salt concentration on a given mixture is shown in Figure 7A and B.

For the two mixtures at $C_s = 0.01$ M (Figure 6A and B), the ionic component is common. Similar values of $(a_1{}^* + a_2{}^*)$ observed suggest the contribution β^{non} to be small or similar. For the two mixtures at $C_s = 0.03$ M (Figure 6C and D), however, different $(a_1{}^* + a_2{}^*)$ values may suggest different values of $f(x = 1)$ for the two ionic components because the β values are not very different. In the present analysis, the electrostatic free energy is approximated with $f(x = 1)$ that is given by $(a_1 + a_2{}^*)$. Although $a_2{}^*$ is expected to approach zero as C_s increases, this trend is not well exhibited in Table 3.

6. Origin of Synergism Due to Electrostatic Interaction

It has been frequently stated that the synergism of ionic/nonionic mixed micelles is due to the reduction of the electrostatic repulsion by the insertion of the nonionic head-groups. However, this effect does exist even in the ideal mixing case. It is to be noted that the mechanism leading to the synergism or negative β_{RST} values resides in $d^2 g^{el}(x)/dx^2 > 0$. In contrast, $d^2 f(x)/dx^2 \leq 0$ as shown in Figures 3 and 4. Under a low charge density and/or a high ionic strength, s is small, and $f(x)$ can be well linearized: $a_2 = 0$, $a_3 = 0$, and $f(x) = a_1 x$. Then, $g(x) = a_1 x^2$ and $\beta^{el} = -a_1$, and RST holds for the case where electrostatic interaction is involved, as shown previously.[8,20]

Under the same charge density and the ionic strength, the electrostatic free energy of ionic micelles, $f(x = 1)$, is larger for the platelike shape than for the spherical shape. This is confirmed in Table 1 from the values of $f(x = 1) = a_1 + a_2 + a_3 = a_1 + a_2{}^*$.

Accordingly, $\beta^{el}(x = 0)$, which is equal to $-f(x = 1)$, is more negative for the plate than for the sphere. In Figures 1 and 2,

TABLE 4: Values of Parameter B_1 Related to Short-Range Interactions

| C_s/M	mixed micelles	cmc$_I$ (mM)	cmc$_N$ (mM)	ln(cmc$_I$/cmc$_N$)	B_1
0.01	NaC12BzS/C10Mal	0.54	2	−1.31	−5.75
0.01	NaC12BzS/C10E8	0.54	1.03	−0.646	−5.37
0.02	SDS/C8Glc	3.8	23.8	−1.83	−5.64
0.03	C16TAC/C9pheE10	0.151	0.054	1.03	−2.10
0.03	C16PyC/C9pheE10	0.0921	0.054	0.534	−1.13
0.05	SDeS/C8E4	17.8	6.3	1.04	−6.58
0.05	C10TAB/C8E4	48.3	6.4	2.02	0.211
0.075	SDS/C8Glc	1.55	19.6	−2.54	−5.20
0.1	SDS/C12E6	1	0.075	2.59	−0.979
0.1	C12DMAOH/C12DMAO	2.03	1.62	0.226	−2.51
0.15	SDS/C8Glc	0.912	17	−2.93	−6.27

however, more negative $\beta^{el}(x)$ values are sometimes observed for the sphere model than for the plate model for the same value of s in the intermediate range of x. From eqs 16 and 20,

$$\beta^{el}(x) = -\{a_1 + a_2 * (1 + x)\} = -(a_1 + a_2*) - a_2* x \quad (37)$$

As shown in Table 1, differences in $f(x = 1)$ between the sphere and the plate are not large. However, a_2* is more negative for the plate model than for the sphere model. The ratio a_2*(plate)/a_2*(sphere) becomes greater as s decreases, and reaches about 2 for s around 50. Therefore, $\beta^{el}(x)$ of the plate increases with x more steeply than that of the sphere and eventually crosses over. Thus, the synergism due to the electrostatic interaction is determined not only by the electrostatic free energy of the ionic micelle $f(x = 1)$ but also by the dependence of $\beta^{el}(x)$ on the micelle composition x.

7. Contribution from Short-Range Interactions

The present study clearly shows that $\beta^{el}(x)$ is always negative. Hence, we cannot conclude from the negative nature of β the presence of a short-range attractive interaction between the ionic and the nonionic species in the mixed micelles. In the present study, we obtain a_1* and a_2*, but we cannot assess β^{non} unless we estimate a_1 by a reasonable procedure because $a_1* = a_1 - \beta^{non}$. In this way, in the case of ionic/nonionic mixed micelles, the electrostatic interaction masks the contribution of the short-range interactions. However, we have proposed a parameter B_1 that does not contain the electrostatic free-energy contribution.[20] This parameter is related to the standard free-energy change $\Delta G*$ of the following reaction by $B_1 = \Delta G*/RT$.

nonionic micelle + ionic monomer → nonionic monomer

+ mixed micelle containing only one
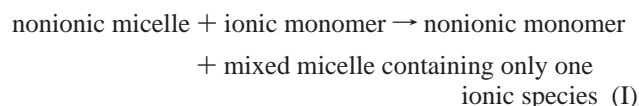
ionic species (I)

According to the previous argument,[20] $\Delta G*$ is expressed as follows:

$$\frac{\Delta G*}{RT} = \ln\left(\frac{cmc_I}{cmc_N}\right) - g^{el}(x = 1) + \frac{*\mu_I - \mu_I*^{non}}{RT} \quad (38)$$

where μ_I*^{non} represents the nonelectric part of the chemical potential of the ionic species in the pure ionic micelles and $*\mu_I$ represents that in the nonionic micelle containing only one ionic species. As in the previous study,[20] we assume that

$$\left(\frac{*\mu_I - \mu_I*^{non}}{RT}\right) = \beta^{non} \quad (39)$$

Then, we have

$$B_1 = \frac{\Delta G*}{RT} = \ln\left(\frac{cmc_I}{cmc_N}\right) - g^{el}(x = 1) + \beta^{non}$$

$$= \ln\left(\frac{cmc_I}{cmc_N}\right) + \beta^{el}(x = 0) + \beta^{non}$$

$$= \ln\left(\frac{cmc_I}{cmc_N}\right) + \beta(x = 0) \quad (40)$$

In the case in which the terms $\ln(cmc_I/cmc_N)$ and $g^{el}(x = 1)$ cancel out to a large extent, B_1 is almost identical to β^{non}. This is a special case, however, because it breaks down for $cmc_I/cmc_N < 1$.

Under the condition where RST holds,[20] $\beta(x = 0) = \beta_{RST}$. In the present study, $\beta(x = 0)$ is set equal to $-(a_1* + a_2*)$ which is in most cases less negative than $\beta(x = 0)$. The usefulness of the parameter B_1 depends on the assumption (eq 39). This issue is important, but it is related to the nonelectric interaction and hence is not discussed here.

As shown by reaction I, RTB_1 is determined by the difference between the two transfer processes: the transfer of a nonionic surfactant monomer in solution into its pure micelle and that of an ionic surfactant monomer in solution into the nonionic micelle. The free energy change associated with the former transfer is $RT \ln cmc_N$. The image charge contribution to the free energy change associated with the latter transfer is small, about $0.4RT$ at 300 K. In the case of mixed micelles where both components carry hydrocarbon chains of the same length, the headgroup contribution is important. However, in many ionic/nonionic pairs, the two components are often chosen so that their pure cmc values are of the same order of magnitude. This often requires the hydrocarbon chain of an ionic species to be longer than that of a nonionic species. For these pairs, the hydrocarbon tail contribution or the hydrocarbon tail dissimilarity (HC contribution) makes a negative bias to B_1.

Values of B_1 are given in Table 4, and we could extract information about the short-range attractive interaction from them. The SDS/C8Glc mixture at three different ionic strengths gives a practically constant value of -5.7 ± 0.6. This negligible effect of the ionic strength on B_1 clearly indicates that it is a pertinent parameter. For the two mixtures containing C9pheE10, it is difficult to conclude any short-range attractive interaction between the headgroups from the small negative B_1 values because the HC contribution is expected to be significant. When comparing these two mixtures, we can conclude that there is some attractive interaction between SDS and C8Glc because its HC contribution is expected to be similar in magnitude to that between C16TA (or C16Py) and C9pheE10. A kind of attractive interaction is suggested for the two mixtures containing NaC12BzS, SDeS/C8E4, and C12DMAOH/C12DMAO. How-

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ever, no attractive interaction is suggested for C10TAB/C8E4 and SDS/C12E6.

8. Limitations of the Present Two-Parameter Approach

As shown in Figures 1 and 2, $\beta^{el}(x)$ defined in eq 16 has negative curvatures, $d^2\beta^{el}(x)/dx^2 < 0$, and the slope $d\beta^{el}(x)/dx$ becomes small as x increases. In the region of x extending from $x = 1$ to a certain value, $\beta^{el}(x)$ varies to a small extent, and the present approach can be successfully applied. This region is tentatively referred to as region I. The x value corresponding to the lower bound of region I becomes smaller as the charge density decreases and/or the ionic strength increases. Even in region I, however, it is important that the evaluated x values from given cmc data are distributed over a wide range. Otherwise, we are obliged to approximate a narrow section of a curve with a straight line, resulting in $\beta^{el}(x)$ values that are too large (less negative) on both sides of the experimentally accessible range. The two mixtures at 0.05 M ionic strength are such an example. In the other region of x (left of region I), $\beta^{el}(x)$ drops steeply as x approaches zero. It is clear that this limiting behavior is not well represented by the linear relation (eq 37) employed in the present study. In other words, B_1 is inevitably underestimated (less negative than the correct value) when it is evaluated by setting $\beta(x = 0) = -(a_1{}^* + a_2{}^*)$. This reservation should be kept in mind.

9. Conclusions

A phenomenological procedure is presented to analyze the stability and the synergism of ionic/nonionic mixed micelles in salt solutions. Fundamental assumptions are as follows: (A) The ionic strength is independent of the mole fraction of ionic species in the micelle x. (B) The surface charge density varies linearly with x. (C) The nonelectric contribution to the excess free energy (per monomer), g^{ex}, is given by the regular solution theory (RST) with a constant β^{non}; $g^{ex,non} = \beta^{non}x(1 - x)$.

The conclusions of the present study are as follows: (1) When the electrostatic contribution to the excess free energy (per monomer), g^{ex}, is written as $g^{ex,el} = \beta^{el}(x) x(1 - x)$, $\beta^{el}(x)$ is always negative but becomes less so as x increases. This is valid irrespective of the micellar shape, whether it is spherical, rodlike, or platelike.

(2) When the electrostatic free energy per charge and per monomer are written as $f(x)$ and $g^{el}(x)$, respectively, the origin of the synergism due to the electric contribution resides in the fact that $d^2g^{el}(x)/dx^2 > 0$ whereas $d^2f(x)/dx^2 \le 0$ [$g^{el}(x) = x f(x)$].

(3) $f(x)$ can be approximated with a polynomial $A(x) = a_1x + a_2x^2 + a_3x^3$ irrespective of the micellar shape.

(4) In terms of $a_1{}^* = a_1 - \beta^{non}$ and $a_2{}^* = a_2 + a_3$, g^{ex} is given as

$$g^{ex}(x) = -\{a_1{}^* + a_2{}^*(1 + x)\}x(1 - x) = \beta(x) x(1 - x)$$

For most of the 11 mixed micelles examined, g^{ex} is not symmetric with respect to $x = 0.5$ and takes the minimum at $x < 0.5$, which is more negative than that estimated from the symmetric RST.

(5) For the 11 mixed micelles, x, $a_1{}^*$, and $a_2{}^*$ are determined from the experimentally obtained relations between the cmc and the overall composition. Values of $a_1{}^*$ and $a_2{}^*$ thus obtained are valid at other concentrations where the micelle composition differs from that at the cmc.

(6) A parameter B_1 is defined as follows in terms of the cmc of the ionic (cmc$_I$) and the nonionic (cmc$_N$) species: $B_1 = \ln(cmc_I/cmc_N) + \beta(x = 0)$. This B_1 is expected to be a proper parameter to use in assessing the nonelectric synergism. In the present study, $\beta(x = 0)$ is evaluated as $-(a_1{}^* + a_2{}^*)$.

(7) The present analysis cannot be applied when the micelle compositions x are small, smaller than about 0.2.

References and Notes

(1) Kronberg, B. *Curr. Opin. Colloid Interface Sci.* **1997**, *2*, 456.
(2) Stigter, D. *J. Phys. Chem.* **1974**, *78*, *8*, 2480.
(3) Stigter, D. *J. Colloid Interface Sci.* **1974**, *47*, 473.
(4) Gunnarsson, G.; Jönsson, B.; Wennerström, H. *J. Phys. Chem.* **1980**, *84*, 3114.
(5) Jönsson, B.; Wennerström, H. *J. Colloid Interface Sci.* **1981**, *80*, 482.
(6) Puvvada, S.; Blankschtein, D. *J. Phys. Chem.* **1992**, *96*, 5567.
(7) Sarmoria, C.; Puvvada, S.; Blankschtein, D. *Langmuir* **1992**, *8*, 2690.
(8) Shiloach, A.; Blankschtein, D. *Langmuir* **1998**, *14*, 1618.
(9) Shiloach, A.; Blankschtein, D. *Langmuir* **1998**, *14*, 7166.
(10) Nagarajan, R. *Langmuir* **1985**, *1*, 331.
(11) Nagarajan, R.; Ruckenstein, E. *Langmuir* **1991**, *7*, 2934.
(12) Reif, I.; Somasundaran, P. *Langmuir* **1999**, *15*, 3411.
(13) Bergström, M.; Eriksson, J. Ch. *Langmuir* **2000**, *16*, 7173.
(14) Bergström, M.; Jonsson, P.; Persson, M.; Eriksson, J. Ch. *Langmuir* **2003**, *19*, 10719.
(15) Rubingh, D. N. In *Solution Chemistry of Surfactants*; Mittal, K., Ed.; Plenum: New York, 1979; p 337
(16) Holland, P. M.; Rubingh, D. N. *J. Phys. Chem.* **1983**, *87*, 1984.
(17) Holland, P. M. *Adv. Colloid Interface Sci.* **1986**, *26*, 111.
(18) Motomura, K.; Yamanaka, M.; Aratono, M. *Colloid Polym. Sci.* **1984**, *262*, 948.
(19) Hoffmann, H.; Pössnecker, G. *Langmuir* **1994**, *10*, 381.
(20) Maeda, H. *J. Colloid Interface Sci.* **1995**, *172*, 98.
(21) Georgiev, G. S. *Colloid Polym. Sci.* **1996**, *274*, 49.
(22) Eads, C. D.; Robosky, L. C. *Langmuir* **1999**, *15*, 2661.
(23) Palous, J. L.; Turmine, M.; Letellier, P. *J. Phys. Chem. B* **1998**, *102*, 5886.
(24) Peyre, V. *Langmuir* **2002**, *18*, 1014.
(25) Hall, D. G. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3529.
(26) Evans, D. F.; Mitchel, D. J.; Ninham, B. W. *J. Phys. Chem.* **1984**, *88*, 6344.
(27) In the fitting curves represented by $A(x)$ in Figure 4, a positive curvature was observed at large s; $s > 100$ for spheres, and $s > 40$ for plates. The positive curvature is physically improbable, and this should be avoided by improving the fitting algorithm.
(28) Liljekvist, P.; Kronberg, B. *J. Colloid Interface Sci.* **2000**, *222*, 159.
(29) Kameyama, K.; Muroya, A.; Takagi, T. *J. Colloid Interface Sci.* **1997**, *196*, 48.
(30) Goloub, T. P.; Pugh, R. J.; Zhmud, B. V. *J. Colloid Interface Sci.* **2000**, *229*, 72.
(31) Rathman, J. F.; Scamehorn, J. F. *Langmuir* **1986**, *2*, 354.
(32) Maeda, H.; Muroi, S.; Ishii, M.; Kakehashi, R.; Kaimoto, H.; Nakahara, T.; Motomura, K. *J. Colloid Interface Sci.* **1995**, *175*, 497.