

# A Thermodynamic Analysis of Charged Mixed Micelles in Water

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A thermodynamic analysis is presented for electrically charged mixed micelles in water on the basis of the Gibbs–Duhem relation proposed by Hall in combination with the information on the degree of counterion binding. The proposed analyses are shown to work well for both ionic/nonionic mixed micelles and those consisting of ionic surfactants of like charges. Conclusions for ionic/nonionic mixed micelles are as follows. (1) The contribution from counterions is significant. (2) In media of low ionic strengths, the counterion concentration varies with the micellar mole fraction of the ionic species  $x$ . The dependency of the activity coefficients and the excess free energy on  $x$  is significantly influenced by this effect, but it can be corrected to a large extent in terms of the Corrin–Harkins relation. (3) The regular solution theory (RST) is not always valid even when the excess free energy is described well with the RST expression unless the observed range of the micelle composition is wide enough. (4) The RST overestimates  $x$  and underestimates the activity coefficient of the ionic species when applied to the mixed micelles to which it is inapplicable. For the ionic mixed micelles consisting of surfactants of like charges, the Lange–Shinoda approach is shown to be consistent with the present analysis in terms of the Gibbs–Duhem relation, but Motomura’s approach is found to be not exact but approximate.

## Introduction

Amphiphiles can form various nanostructures in aqueous media and at solid/liquid, liquid/liquid, and gas/liquid interfaces.<sup>1,2</sup> Micelles formed by amphiphiles with single lyophobic chains are undoubtedly the simplest structure among amphiphile nanostructures. Theoretical and applied aspects of micelles have been extensively studied for many decades, and our understanding single-component micelles has reached a satisfactory level.<sup>1–5</sup> On the other hand, mixtures of surfactants are of practical importance to develop better properties than those of respective component surfactants.<sup>6–9</sup> 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. Thermodynamics of charged micelles has been developed,<sup>10–13</sup> and useful and practical procedures to enumerate the electrostatic thermodynamic quantities have been proposed.<sup>12,13</sup> The stability of mixed micelles in general has been extensively studied by the molecular thermodynamic approaches<sup>14–21</sup> and by the phenomenological or thermodynamic approaches.<sup>22–34</sup> 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 always available.

In the phenomenological approach to charged mixed micelles, it would be pertinent to distinguish three regimes depending on the ionic strength of the medium. (I) High ionic strength ( $C_s > \text{about } 0.2 \text{ M}$ ). 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 ( $C_s < \text{about } 0.2 \text{ M}$ ). The ionic strength in this regime is practically kept constant independent of the micelle composition, while 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 significantly varies with the micelle composition.

The most popular procedure among the phenomenological approaches is undoubtedly the regular solution theory (RST) developed by Rubingh and Holland.<sup>23–25</sup> It works quite well in regime I and for nonionic mixtures as well. In regimes II and III, however, the application of the RST often provides us with a composition-dependent interaction parameter  $\beta_{\text{RST}}(x)$ . Curiously enough, however, composition-independent  $\beta$  values have been found sometimes in regime III. In regime II, the nonideal behavior is often not symmetric with respect to the micelle composition, and at least two parameters are required to describe the asymmetric nonideality. Our previous two-parameter phenomenological procedure<sup>34</sup> is not applicable to regime III.

In the present study, a thermodynamic approach is presented for the binary ionic (I)–nonionic (N) mixed micelles in regime III on the basis of the Gibbs–Duhem (G–D) relation proposed by Hall.<sup>35</sup> It will be shown that the RST is not valid even when the parameter  $\beta_{\text{RST}}$  is constant over the obtained range of the micelle composition  $x$ . As to the mixed micelles consisting of surfactants of like charges in regime III, we extend the procedure developed by Lange<sup>36,37</sup> and Shinoda.<sup>38</sup> It will be shown that the G–D relation is valid and consistent with the Lange–Shinoda approach, while Motomura’s approach<sup>26</sup> is significantly approximate. In the present study, we consider mostly mixed micelles in water, but the obtained results could be extended to the case where a salt with a common counterion species is present at low concentrations in conformity with regime III. Mixed micelles consisting of cationic and anionic surfactants (catanionic mixtures) are not considered in the present study.

## Results

**I. Binary Nonionic–Ionic Mixed Micelles. 1. The Excess Free Energy  $G^{\text{ex}}$  of Mixed Micelles.** The free energy of a binary

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mixed micelle of an aggregation number  $m$  and the composition  $x$  is denoted as  $G(m, x)$  where  $x$  is the micelle mole fraction of the ionic species. We define  $g(x)$  as  $G/mkT$ . Then, the excess free energy can be written as follows.

$$G^{\text{ex}}/mkT = g^{\text{ex}}(x) = g(x) - g^{\text{id}}(x) \quad (1-1)$$

For the ideal mixed micelles,

$$g^{\text{id}}(x) = x g(x=1) + (1-x) g(x=0) + \{x \ln x + (1-x) \ln(1-x)\} \quad (1-2)$$

We divide  $g^{\text{ex}}$  into the electric and the nonelectric contributions.

$$g^{\text{ex}} = g^{\text{ex,non}} + g^{\text{ex,el}} \quad (1-3)$$

The electric part is written as follows.

$$g^{\text{ex,el}} = g^{\text{el}}(x) - x g^{\text{el}}(x=1) \quad (1-4)$$

Activity coefficients of the ionic ( $f_i$ ) and the nonionic ( $f_N$ ) species in mixed micelles can be evaluated from  $G^{\text{ex}}$  using eqs 1-5, and they should satisfy eq 1-6.

$$kT \ln f_i = (\partial G^{\text{ex}} / \partial m_i)_{m_N} \quad (1-5a)$$

$$kT \ln f_N = (\partial G^{\text{ex}} / \partial m_N)_{m_i} \quad (1-5b)$$

$$g^{\text{ex}} = x \ln f_i + (1-x) \ln f_N \quad (1-6)$$

Here,  $m_i$  and  $m_N$  denote, respectively, the number of ionic and nonionic species in the micelle:  $m_i = mx$  and  $m_N = m(1-x)$ . Chemical potentials of the two species  $\mu_i$  and  $\mu_N$  are written as follows for micelles

$$\mu_i = \mu_i^* + kT \ln(x f_i); \mu_N = \mu_N^* + kT \ln((1-x) f_N) \quad (1-7)$$

where the reference states for the ionic and the nonionic species in the mixed micelles are taken, in conformity with eq 1-2, as respective pure micelles in water or in the salt solution of a given salt concentration  $C_s$ . From the equilibrium conditions at the cmc between the free monomer and micelles, the activities of the two species,  $a_i$  and  $a_N$ , are obtained if the ideal solution behavior is assumed for the monomer solution.

$$a_i = x f_i = \text{cmc } x_1 / \text{cmc}_i \quad (1-8)$$

$$a_N = (1-x) f_N = \text{cmc}(1-x_1) / \text{cmc}_N \quad (1-9)$$

Here  $\text{cmc}_i$  and  $\text{cmc}_N$  represent the cmc of pure ionic ( $x=1$ ) and nonionic ( $x=0$ ) micelles, respectively, and  $x_1$  denotes the free monomer composition and it is well approximated with  $x$ , the composition of the whole solution. Once the micelle composition  $x$  is evaluated, the activity coefficients of the ionic ( $f_i$ ) and the nonionic ( $f_N$ ) species in mixed micelles can be evaluated by eqs 1-8 and 1-9.

**2. The Gibbs–Duhem ( $G$ – $D$ ) Relation.** In water or in salt solutions of low concentrations  $C_s$ , the Gibbs–Duhem ( $G$ – $D$ ) relation is written as follows in terms of the chemical potential of counterions  $\mu_C$  and the degree of counterion binding  $\nu$ .<sup>35</sup>

$$x d\mu_i + (1-x) d\mu_N + x \nu d\mu_C = 0 \quad (2-1)$$

As far as we consider a concentration range close to the cmc and the ideal solution behavior is assumed for the free monomer solutions, the free monomer concentrations are well ap-

proximated to  $\text{cmc } x_1$  and  $\text{cmc}(1-x_1)$  for the ionic and the nonionic species, respectively. Then, eq 2-1 is written as follows in the case of a uni-univalent salt with a common counterion species.

$$x d \ln(\text{cmc } x_1) + (1-x) d \ln \{\text{cmc}(1-x_1)\} + x \nu d \ln(C_s + \text{cmc } x_1) = 0 \quad (2-2)$$

Equation 2-2 is reduced to eq 2-3 after some rearrangement.

$$\frac{(1+x\nu) \text{cmc } x_1 + C_s}{(\text{cmc } x_1 + C_s)} d \ln \text{cmc} + \left[ \frac{x}{x_1} \left\{ 1 + \frac{\nu \text{cmc } x_1}{\text{cmc } x_1 + C_s} \right\} - \frac{1-x}{1-x_1} \right] dx_1 = 0 \quad (2-3)$$

Hereafter, we consider only the case where  $C_s \ll \text{cmc } x_1$  for the sake of simplicity. Under the conditions, eq 2-3 reduces to eq 2-4.

$$(1+x\nu) d \ln \text{cmc} / dx_1 + (x-x_1) / \{x_1(1-x_1)\} + \nu x / x_1 = 0 \quad (2-4)$$

Solving eq 2-4 for  $x$ , we have

$$x = x_1 [1 - (1-x_1) d \ln \text{cmc} / dx_1] / [1 + \nu(1-x_1) \{x_1 d \ln \text{cmc} / dx_1 + 1\}] \quad (2-5)$$

When  $\nu$  is given as a function of  $x_1$ , the micelle composition  $x$  can be calculated in terms of eq 2-5. If we put  $\nu=0$  in eq 2-5, we have eq 2-6, which was proposed previously for nonionic mixtures and ionic mixed micelles in the presence of salt<sup>26,27</sup> and to the ionic/nonionic mixed micelles in water.<sup>39</sup>

$$x(\nu=0) = x_1 [1 - (1-x_1) d \ln \text{cmc} / dx_1] \quad (2-6)$$

When  $(x_1 d \ln \text{cmc} / dx_1 + 1) > 0$ , we have  $x(\nu=0) > x$ .

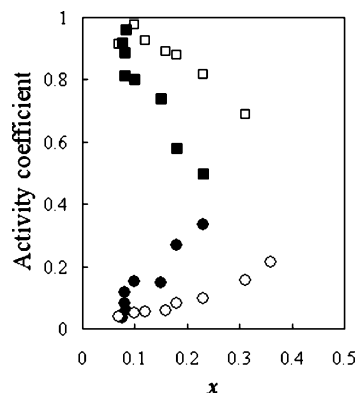
**3. Application to SDS–C12E4 Mixed Micelles.** Both  $\text{cmc}$  and  $\nu$  are measured by Treiner et al.<sup>40</sup> as functions of  $x_1$  for the mixed micelles of sodium dodecyl sulfate (SDS)–tetraethyleneglycol dodecyl ether (C12E4) in water. Micelle compositions  $x$  obtained by the present procedure, eq 2-5, and the RST are compared in Table 1. The present  $G$ – $D$  procedure gives  $x$  values that are slightly but significantly smaller than those of the RST. Activity coefficients from eqs 1-8 and 1-9 are given in Figure 1 together with the RST results. The activity coefficients obtained by the two methods differ significantly. The excess free energies  $g^{\text{ex}}$  obtained by the two methods shown in Figure 2 are rather similar. Interestingly, both the present analysis and the RST give  $g^{\text{ex}}$  that can be described in terms of the RST expression:  $g^{\text{ex}} = -4.4x(1-x)$  and  $g^{\text{ex}}(\text{RST}) = -3.9x_{\text{RST}}(1-x_{\text{RST}})$ . From the negative  $g^{\text{ex}}$  values a kind of synergetic effect is suggested for this mixed micelle.

All these results clearly indicate a mechanism underlying the paradoxical observations that constant values of the interaction parameter of the RST  $\beta_{\text{RST}}$  are sometimes obtained in regime III. The very reason resides in rather narrow ranges of  $x$  covered. Activity coefficients in Figure 1 clearly indicate that the RST does not hold in the present example despite the observed relation for  $g^{\text{ex}}(\text{RST})$ .

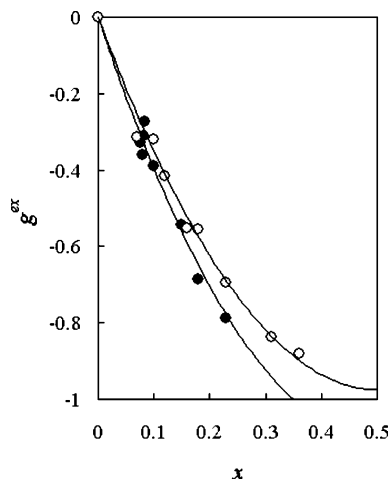
It is to be noted that the activities of ionic species are very low in this example, smaller than 0.08 for the whole range of  $x_1$  examined (Table 1). Consequently, it is not easy to assess precise values of  $d \ln \text{cmc} / dx_1$ . We have used the following

TABLE 1: SDS/C12E4 Mixed Micelles

$x_1$	0	0.363	0.505	0.592	0.694	0.784	0.865	0.948	0.973	1
cmc/mM <sup>a</sup>	0.045	0.06	0.08	0.09	0.11	0.15	0.21	0.41	0.64	8.1
$a_1$	0	0.0027	0.0050	0.0066	0.0094	0.015	0.022	0.048	0.077	1
$a_N$	1	0.849	0.880	0.816	0.748	0.720	0.630	0.474	0.384	0
$x$	0	0.075	0.084	0.081	0.080	0.10	0.15	0.18	0.23	1
$x(\text{RST})^a$	0	0.07	0.10	0.12	0.16	0.18	0.23	0.31	0.36	1

<sup>a</sup> Data taken from ref 40.

**Figure 1.** Activity coefficients of sodium dodecyl sulfate (SDS) and tetraethyleneglycol dodecyl ether (C12E4) as functions of the micelle composition  $x$ . Activity coefficients of SDS and C12E4 are represented with filled circles and squares, respectively. Open symbols refer to the results of the RST.



**Figure 2.** Excess free energy  $g^{\text{ex}}$  of sodium dodecyl sulfate (SDS)–tetraethyleneglycol dodecyl ether (C12E4) mixed micelles as a function of the micelle composition  $x$ . Filled and open circles represent  $g^{\text{ex}}$  and  $g^{\text{ex}}(\text{RST})$ , respectively. Curves are drawn according to  $g^{\text{ex}} = -4.4 x(1-x)$  and  $g^{\text{ex}}(\text{RST}) = -3.9 x_{\text{RST}}(1-x_{\text{RST}})$ .

two polynomial approximations to the  $\ln$  cmc data to limit the range of  $x$  values at a given  $x_1$  value.

$$\ln(\text{cmc}/\text{mM}) = -3.1 + 0.9x_1 + 1.2x_1^4 + 0.2x_1^8 + 0.2x_1^{12} + 1.4x_1^{42}$$

$$\ln(\text{cmc}/\text{mM}) = -3.1 + 0.9x_1 + 1.2x_1^4 + 0.2x_1^8 + 0.1x_1^{10} + 0.4x_1^{20} + 0.2x_1^{26} + 0.4x_1^{36}$$

4. Application to the Mixed Micelles Where the Degree of Counterion Binding  $\nu$  Is Not Given as a Function of the Monomer Composition  $x_1$ . For nonionic/ionic mixed micelles, the degree of counterion binding  $\nu$  is usually given as a function of the micelle composition  $x$  rather than  $x_1$ . For some mixed micelles, however, only the degree of counterion binding of

the pure ionic micelle  $\nu_0$  is known. Approximate analysis of the cmc data is possible for such mixed micelles in terms of the following relation, which has been shown to describe well the dependence of the degree of counterion binding  $\nu$  on the micelle composition  $x$ .<sup>41</sup>

$$\nu(x) = x\nu_0/(1 - \nu_0 + x\nu_0) \quad (4-1)$$

Now the term  $\nu$  in eq 2-5 is a function of  $x$ , and hence the equation should be solved in an iterative manner starting from the first guess  $\nu_0$ . In all cases examined, unique  $x$  values were obtained after two or three iterative cycles.

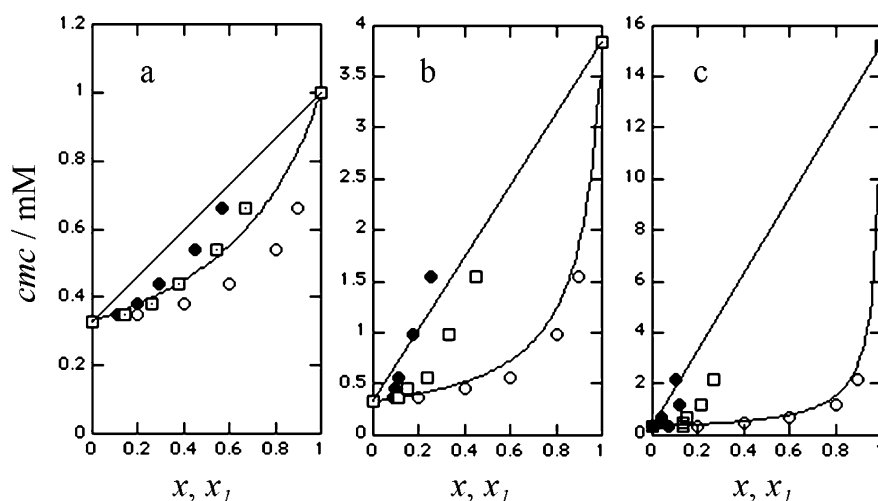
It was reported that eq 2-6 and the RST were both valid for hexadecyltrimethylammonium bromide (C16TAB)–tetraethyleneglycol dodecyl ether (C12E4) mixed micelles since the two analyses gave similar results.<sup>39</sup> When the same data are analyzed with eq 2-5 together with  $\nu_0 = 0.83$ ,<sup>42</sup> however, significantly different results are obtained, as shown in Table 2. From the results it is concluded that the contribution from counterions cannot be neglected, and we should use eq 2-5 instead of eq 2-6. As shown in Table 2, the activity coefficients cannot be described with the RST. Also  $\beta_{\text{RST}}$  was not constant but depended on  $x$ .<sup>39</sup> Consequently, the RST cannot be applied to this mixed micelle.

The data on three Triton X100–alkyltrimethylammonium bromide (CnTAB) mixed micelles<sup>43</sup> were analyzed together with the values of  $\nu_0$ , which are 0.83, 0.80 and 0.77 for hexadecyl-(C16)-, tetradecyl(C14)-, and dodecyl(C12)-TAB, respectively.<sup>42</sup> The micelle compositions  $x$  are shown in Figure 3 together with the RST results. In this figure, lines representing the ideal mixing case are shown. The relations are the same as those of the nonionic mixtures in conformity with the definition of the ideal behavior, eq 1-2. By comparing the observed cmc– $x_1$  relations (open circles) with the curves representing the ideal behavior, the interaction between the two components can be assessed qualitatively without recourse to any cmc data analysis. For C16TAB, the observed cmc values lie below the ideal mixing curve and some synergistic effect is suggested. For C14TAB and C12TAB, on the other hand, the observed cmc values are rather close to the ideal mixing curve and synergistic effects are not expected to be large for these two mixed micelles. The observed cmc– $x$  relations (filled circles) of these three mixed micelles are consistent with the expectation. For C16TAB, the observed cmc values lie below the straight line of the ideal mixing case, while they are smaller than but close to the straight line for C14TAB and C12TAB. The points (filled circles) located above the straight lines in Figure 3b,c are false, originating from the inaccurate nature of the cmc data and/or the fitting polynomials. The RST results (open squares) suggest, on the other hand, stronger synergistic behaviors in all three mixed micelles than what the present analysis predicts. It was noted before that the RST did not describe the cmc data well for the two lower homologues C14TAB and C12TAB.<sup>43</sup> The present G–D analysis gives smaller  $x$  values than the RST results. The small  $x$  values are supported by the observation using surfactant-selective electrodes that the content of C12TAB or C14TAB in the mixed micelle at the cmc was very small.<sup>44</sup>

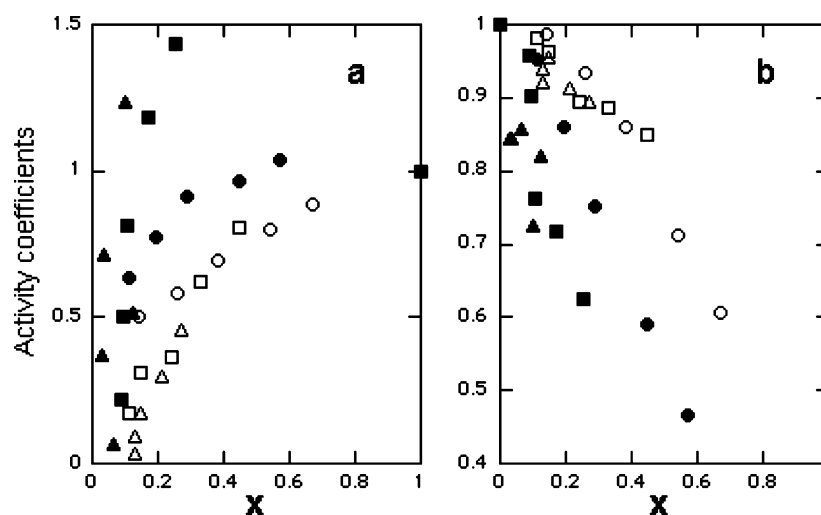
TABLE 2: C16TAB/C12E4 Mixed Micelles

$x_1$	0	0.3	0.5	0.7	0.9	0.975	1
cmc/mM <sup>a</sup>	$4.6 \times 10^{-5}$	$4.9 \times 10^{-5}$	$5.5 \times 10^{-5}$	$1.1 \times 10^{-4}$	$1.7 \times 10^{-4}$	$3.5 \times 10^{-4}$	$9 \times 10^{-4}$
$x^b$	0	0.15	0.17	0.15	0.28	0.42	1
$x(\nu=0)^c$	0	0.20	0.23	0.20	0.37	0.55	1
$x(\text{RST})^d$	0	0.17	0.25	0.22	0.42	0.58	1
$f_1$		0.109	0.180	0.570	0.607	0.903	1
$f_N$	1	0.877	0.720	0.844	0.513	0.328	
$g^{\text{ex}}$	0	-0.44	-0.56	-0.23	-0.62	-0.69	0
$f_1(\text{RST})^d$		0.096	0.122	0.389	0.405	0.654	1
$f_N(\text{RST})^d$	1	0.898	0.797	0.920	0.637	0.453	
$g^{\text{ex}}(\text{RST})^d$	0	-0.49	-0.70	-0.27	-0.64	-0.58	0

<sup>a</sup> Data taken from ref 39. <sup>b</sup> Calculated with eq 2-5. <sup>c</sup> Calculated with eq 2-6. <sup>d</sup> Calculated by the regular solution theory.



**Figure 3.** Values of the cmc as functions of the micelle composition  $x$  and the monomer composition  $x_1$  for alkyltrimethylammonium bromide (CnTAB)–Triton X100 mixed micelles. (a) C16TAB, (b) C14TAB, and (c) C12TAB. Filled and open circles represent cmc– $x$  and cmc– $x_1$  relations, respectively. Open squares represent the RST cmc– $x$  relation. Curves and straight lines represent, respectively, the cmc– $x_1$  and the cmc– $x$  relations in the case of ideal behavior.



**Figure 4.** Activity coefficients of (a) alkyltrimethylammonium cations and (b) Triton X100 as functions of the micelle composition  $x$ . Filled and open symbols refer to the G–D analysis and the RST, respectively. Circles (C16TAB), squares (C14TAB), and triangles (C12TAB).

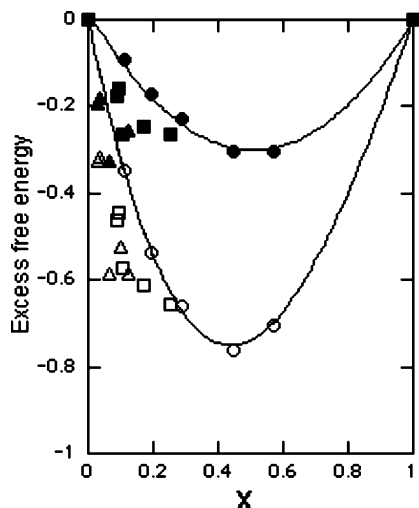
On the other hand, the micelle compositions assessed on the basis of the apparent dielectric constant using pyrene fluorescence<sup>45</sup> were in disagreement with the present results.<sup>43</sup> The present analysis concludes that the RST overestimates  $x$ , while the fluorescence polarity assessment indicates the opposite. The discrepancy is not well understood at present.

Activity coefficients are shown in Figure 4 (filled symbols) together with the results of the RST (open symbols). Activity coefficients of cationic species  $f_1$  (Figure 4a) are greater and those of Triton X100  $f_N$  (Figure 4b) are smaller than the RST

results. It is to be noted that values of  $f_1$  greater than unity are obtained, while they are smaller than unity when evaluated by the RST.

Excess free energies  $g^{\text{ex}}$  are shown in Figure 5 with filled symbols. For C16TAB,  $g^{\text{ex}}$  could be described rather well with the following relations:  $g^{\text{ex}} = -1.20x(1 - x)$ . However, the trend of more negative  $g^{\text{ex}}$  values for shorter alkyl chain length is not consistent with the results shown in Figure 3 that a synergistic interaction exists between Triton X100 and C16TAB, while much weaker synergisms are suggested for other two





**Figure 5.** Excess free energy  $g^{\text{ex}}$  ( $g^{\text{ex}*}$ ) of alkyltrimethylammonium bromide (CnTAB)–Triton X100 mixed micelles. Filled and open symbols represent  $g^{\text{ex}}$  and  $g^{\text{ex}*}$ , respectively. Circles (C16TAB), squares (C14TAB), and triangles (C12TAB). Curves are drawn for C16TAB according to  $g^{\text{ex}} = -1.20x(1-x)$  and  $g^{\text{ex}*} = (-3.71 + 1.51x)x(1-x)$ .

mixtures. This discrepancy is discussed in the next section. According to the RST analysis of the same data, the interaction parameter  $\beta$  significantly depends on  $x$ , thereby indicating that the RST is not applicable to these mixed micelles. Average values of  $\beta$  are  $-1.0$ ,  $-1.7$ , and  $-2.6$  for C16, C14, and C12 homologues, respectively.<sup>43</sup>

We have used the following polynomial approximations to evaluate  $d \ln \text{cmc}/dx_1$ .

$$\ln(\text{cmc}/\text{mM}) = -1.11 + 0.22x_1 + 0.32x_1^2 + 0.30x_1^4 + 0.24x_1^{22} \quad (\text{C16TAB})$$

$$\ln(\text{cmc}/\text{mM}) = -1.1 + 1.4x_1^2 + 0.25x_1^4 + 0.8x_1^{12} \quad (\text{C14TAB})$$

$$\ln(\text{cmc}/\text{mM}) = -1.1 + 1.9x_1^2 + 0.50x_1^{10} + 1.2x_1^{20} \quad (\text{C12TAB})$$

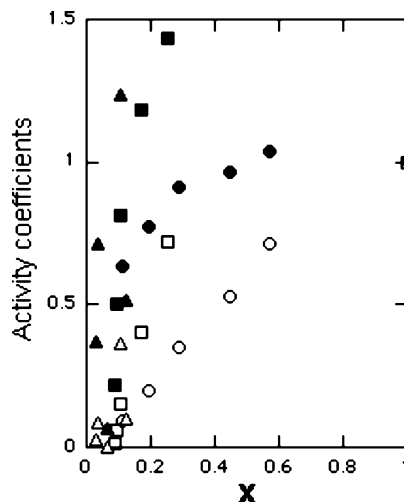
**5. Effects of Varying Counterion Concentrations with the Micelle Compositions.** In the present study, reference states of the two species in the mixed micelles are taken as their pure micelles in aqueous solutions containing no salt. This situation is expected not to affect the nonelectric interactions, and hence we confine ourselves to discuss the electric part of the excess free energy  $g^{\text{ex,el}}$ . The counterion concentration  $C_g$  increases with  $x$ , and  $g^{\text{ex,el}}$  is a difference of  $g^{\text{el}}$  values between two states of different ionic strengths, as explicitly expressed with eq 5-1.

$$g^{\text{ex,el}} = g^{\text{el}}[x, C_g(x)] - x g^{\text{el}}[x=1, C_g(x=1)] \quad (5-1)$$

When a hypothetical state of the pure ionic micelle ( $x = 1$ ) in the medium of  $C_g(x)$  is considered, the ionic micelles are less stable than they are placed in the reference state  $C_g(x=1)$ . Now we introduce a new excess free energy  $g^{\text{ex,el}*}$  measured from the above hypothetical state as follows.

$$g^{\text{ex,el}*} = g^{\text{el}}[x, C_g(x)] - x g^{\text{el}}[x=1, C_g(x)] \quad (5-2)$$

Clearly,  $g^{\text{ex}}$  is more positive or less negative than  $g^{\text{ex}*}$ . The difference ( $g^{\text{ex}} - g^{\text{ex}*}$ ) is expected to be a factor leading to the  $f_1$  value that exceeds unity (Figure 4a) as well as to the



**Figure 6.** Activity coefficients of alkyltrimethylammonium cations in alkyltrimethylammonium bromide (CnTAB)–Triton X100 mixed micelles. Filled and open symbols represent  $f_1$  and  $f_1^*$ , respectively. Circles (C16TAB), squares (C14TAB), and triangles (C12TAB).

inconsistent observation of more negative  $g^{\text{ex}}$  values for shorter alkyl chain homologues (filled symbols in Figure 5). Tentatively, we evaluate the difference ( $g^{\text{ex}} - g^{\text{ex}*}$ ) as follows in terms of the Corrin–Harkins coefficient<sup>46</sup>  $K$  for the pure ionic micelles after Lange<sup>36,37</sup> and Shinoda<sup>38</sup> as described in Part II.

$$g^{\text{ex}} - g^{\text{ex}*} = xK \ln[\text{cmc}_1/(\text{cmc } x_1)] \quad (5-3)$$

Values of  $K$  are 0.72,<sup>42</sup> 0.68,<sup>42</sup> and 0.59<sup>47</sup> for C16-, C14-, and C12TAB, respectively. Values of  $g^{\text{ex}*}$  are shown in Figure 5 with open symbols, and they are more negative than  $g^{\text{ex}}$  for all three mixtures. Furthermore, dependence of  $g^{\text{ex}*}$  on the alkyl chain length is much smaller than that of  $g^{\text{ex}}$ . It is now clear that the chain length dependent behavior of  $g^{\text{ex}}$  in Figure 5 is contributed, to a considerable extent, from the varying ionic strength. Since the Corrin–Harkins relation is not exact but approximate<sup>48</sup> and eq 5-3 is an approximation, there is a possibility that  $g^{\text{ex}*}$  is independent of the chain length if the effect under discussion is accurately corrected.

For C16TAB,  $g^{\text{ex}*}$  could be described with a RST relation  $g^{\text{ex}*} = -3.13x(1-x)$ , but systematic deviations are significant. Instead,  $g^{\text{ex}*}$  is found to be well described with the following relation, as shown in Figure 5.

$$g^{\text{ex}*} = (-3.71 + 1.51x)x(1-x) \quad (5-4)$$

Accordingly, the excess free energy for C16TAB cannot be described with the RST irrespective of whether the effect of varying ionic strengths is corrected. It is interesting to note that eq 5-4 for  $g^{\text{ex}*}$  has the identical function form with that of the two-parameter analyses developed for ionic/nonionic mixed micelles in media of moderate ionic strengths.<sup>31,33,34</sup>

Let us tentatively define the activity coefficient of the ionic species  $f_1^*$  based on  $g^{\text{ex}*}$  as follows.

$$g^{\text{ex}*} = x \ln f_1^* + (1-x) \ln f_N \quad (5-5)$$

Or, explicitly,

$$f_1^* = (\text{cmc } x_1/\text{cmc}_1)^{(1+K)/x} \quad (5-6)$$

Values of  $f_1^*$  shown in Figure 6 are smaller than unity. It can be shown easily that  $f_N$  is not influenced by the varying ionic

strength as far as eq 5-3 is valid. It is to be noted that the activity coefficient  $f_1^*$  defined by eq 5-6 was proposed by Funasaki and Hada.<sup>49</sup>

## II. Ionic Mixed Micelles with Headgroups of Like Charges.

**6. The Lange–Shinoda Approach.** In the second part we consider binary mixed micelles with headgroups of like charges, anionic/anionic or cationic/cationic. The catanionic complex is not considered here. The components having higher and lower cmc values are denoted as H and L, respectively. The micellar mole fraction of the H-component is denoted as  $x$ . The mixed system under discussion has been analyzed by many researchers.<sup>26,36–38,50</sup> In this class of mixed micelles, the dependence of  $g^{\text{ex}}$  on the composition  $x$  is mostly contributed from the varying counterion concentration  $C_g(x)$ , and the surface charge density does not change much with the micelle composition  $x$ . According to Lange<sup>36,37</sup> and Shinoda,<sup>38</sup>  $g^{\text{ex,el}}$  can be expressed as eq 6-1 in terms of the Corrin–Harkins constant<sup>46</sup>  $K$ , which is assumed to be constant irrespective of the micelle composition  $x$ . When values  $K$  differ significantly between the two components H and L, an average value could be used.

$$g^{\text{ex,el}} = K \ln[C_g(x=0)/C_g(x)] + x K \ln[C_g(x=1)/C_g(x=0)]$$

$$= K \ln(\text{cmc}_L/\text{cmc}) + x K \ln(\text{cmc}_H/\text{cmc}_L) \quad (6-1)$$

Here,  $\text{cmc}_H$  and  $\text{cmc}_L$  represent the cmc values of pure H- and L-components, respectively. From the equilibrium conditions between the micelles and the free monomers which are analogous to eqs 1-8 and 1-9, cmc is given as follows in the case of ideal behavior with respect to the nonelectric interaction, i.e.,  $f_H^{\text{non}} = f_L^{\text{non}} = 1$ .<sup>36–38</sup>

$$1/\text{cmc}^{1+K} = [x_1/\text{cmc}_H^{1+K}] + [(1-x_1)/\text{cmc}_L^{1+K}] \quad (6-2)$$

$$\text{cmc}^{1+K} = x \text{cmc}_H^{1+K} + (1-x) \text{cmc}_L^{1+K} \quad (6-3)$$

It is to be noted that eq 6-2 can predict cmc values with a single parameter  $K$ . If the cmc data can be well described with eq 6-2, we have  $f_H^{\text{non}} = f_L^{\text{non}} = 1$  and the micelle composition  $x$  is given by eq 6-3. Eliminating the term cmc from eqs 6-2 and 6-3 and denoting  $\text{cmc}_H/\text{cmc}_L$  as  $y$ , we have the following solution for  $x$ .<sup>38</sup>

$$x = x_1/[x_1 + (1-x_1)y^{1+K}] \quad (6-4)$$

Rewriting eq 6-4, we have

$$x_1/(1-x_1) = [x/(1-x)]y^{1+K} \quad (6-5)$$

Taking the logarithm of both sides of eq 6-2 followed by differentiation with respect to  $x_1$ , we have eq 6-6.

$$d \ln \text{cmc}/dx_1 = (y^{1+K} - 1)/[x_1 + (1-x_1)y^{1+K}](1+K) \quad (6-6)$$

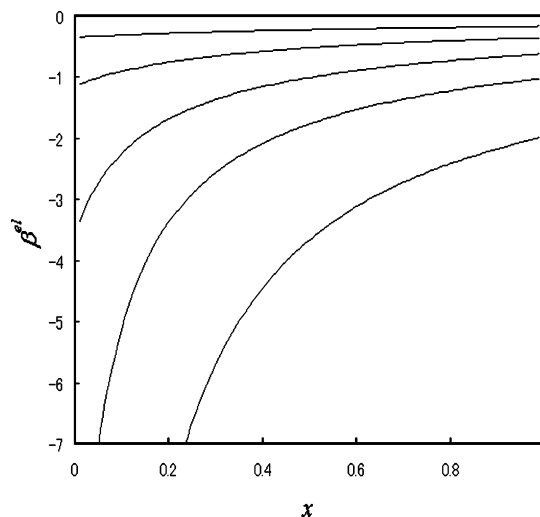
Combining eqs 6-4, 6-5, and 6-6, we have eq 6-7:

$$x = x_1 - x_1(1-x_1)(1+K) d \ln \text{cmc}/dx_1 \quad (6-7)$$

Since the term cmc in eq 6-1 is given by eq 6-3, we obtain  $g^{\text{ex,el}}$  as an explicit function of  $x$  as follows.

$$g^{\text{ex,el}} = -[K/(1+K)] \ln[x y^{1+K} + 1 - x] + x K \ln y \quad (6-8)$$

To examine the relation between the RST and the Lange–



**Figure 7.** RST parameter  $\beta^{\text{el}}$  as functions of the micelle composition  $x$  for different values of  $y$ .  $\beta^{\text{el}}$  is defined as  $g^{\text{ex,el}} = \beta^{\text{el}} x(1-x)$ , and  $g^{\text{ex,el}}$  is calculated by eq 6-8 with  $K = 0.60$ . Values of  $y$  are (from top to bottom) 2, 3, 5, 10, and 50.

Shinoda approach, we put  $g^{\text{ex,el}} = \beta^{\text{el}} x(1-x)$  and see whether a constant  $\beta^{\text{el}}$  value is obtained. In Figure 7, values of  $\beta^{\text{el}}$  are plotted against  $x$  for different  $y$  values. We can expect the RST to be consistent with the Lange–Shinoda approach if  $y$  is smaller than about 4. It is to be noted, however, that there is no use to apply the RST to the mixed micelles to which the Lange–Shinoda approach is valid. When values of  $K$  are unknown and  $y$  is smaller than 4, then the RST could be applied.

**7. The Gibbs–Duhem Relation.** For many binary mixed micelles consisting of charged identical headgroups, the Lange–Shinoda approach has been found to be valid.<sup>36–38</sup> When nonideal interactions are not negligible, we have to expect the approach to be no longer valid and we should use the Gibbs–Duhem relation for the analyses of such mixed micelles. For the binary mixtures of the surfactants of like charge with a common counterion species, the Gibbs–Duhem relation analogous to eq 2-1 is written as follows.

$$x d\mu_H + (1-x) d\mu_L + \nu d\mu_C = 0 \quad (7-1)$$

Here,  $\mu_H$  and  $\mu_L$  denote, respectively, the chemical potentials of H- and L-species. Contrary to the case of nonionic/ionic mixed micelles,  $\nu$  can be approximated to be constant irrespective of  $x$ . At cmc,  $Cg(x) = \text{cmc}$  and eq 7-1 reduces to eq 7-2.

$$x d \ln x_1 + (1-x) d \ln(1-x_1) + (1+\nu) d \ln \text{cmc} = 0 \quad (7-2)$$

It is to be noted that  $K$  and  $\nu$  are practically identical with each other in the case of single-component ionic micelles. Then, eqs 6-7 and 7-2 are identical and the Lange–Shinoda approach is shown to be consistent with the Gibbs–Duhem relation eq 7-1. When the nonideal interaction is not negligible, eq 6-7 is still valid (with  $K = \nu$ ), but eq 6-6 does not hold any more. If we put  $K = 1$  in eq 6-7, we obtain eq 7-3, which was proposed by Motomura et al.<sup>26</sup>

$$x = x_1 - 2x_1(1-x_1) d \ln \text{cmc}/dx_1 \quad (7-3)$$

It is seen that ionic mixed micelles are treated as electrically neutral entities ( $K = 1$ ) in Motomura's approach, as pointed out by Attwood–Patel.<sup>51</sup> At first sight, the difference between eqs 6-7 and 7-3 may appear not large, a factor of 2 in place of  $(1+K)$ . This is not the case, however, as shown below. Values

**TABLE 3: C16 TAB/C12 TAB Mixed Micelles**

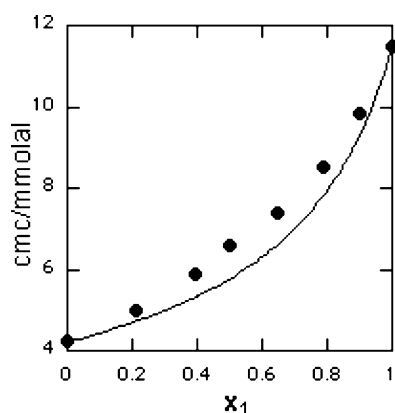
$x_1$	0	0.24	0.58	0.74	0.89	0.94	1
cmc/mM <sup>a</sup>	0.90	0.98	1.57	1.96	3.24	3.93	15.2
cmc/mM (calc) <sup>b</sup>	0.90	1.06	1.50	1.99	3.24	4.49	15.2
$x(\text{eq 6-7})^c$	0	0.00	0.01	0.02	0.07	0.12	1
$x(\text{eq 7-3})^d$	0	-0.04	-0.10	-0.12	-0.10	-0.04	1

<sup>a</sup> Data taken from ref 51. <sup>b</sup> cmc values calculated with eq 6-2. <sup>c</sup> Micelle composition  $x$  calculated with eq 6-7. <sup>d</sup> Micelle composition  $x$  calculated with eq 7-3.

**TABLE 4: C14 TAB/C12 TAB Mixed Micelles**

$x_1$	0	0.24	0.50	0.74	0.89	0.94	1
cmc/mM <sup>a</sup>	3.6	4.27	5.27	7.35	10.3	12.4	15.2
cmc/mM (calc) <sup>b</sup>	3.6	4.18	5.20	7.08	9.79	11.5	15.2
$x(\text{eq 6-7})^c$	0	0.03	0.09	0.21	0.43	0.60	1
$x(\text{eq 7-3})^d$	0	-0.02	-0.00	0.10	0.33	0.52	1

<sup>a</sup> Data taken from ref 51. <sup>b</sup> cmc values calculated with eq 6-2. <sup>c</sup> Micelle composition  $x$  calculated with eq 6-7. <sup>d</sup> Micelle composition  $x$  calculated with eq 7-3.



**Figure 8.** Values of the cmc as a function of the monomer composition  $x_1$  for dodecylpyridinium bromide–dodecylquinolinium bromide mixed micelles. The curve represents the ideal behavior, eq 6-2 with  $K = 0.64$ .

of cmc of C16TAB–C12TAB and C14TAB–C12TAB taken from the paper of Attwood and Patel<sup>51</sup> are well described with eq 6-2, as shown in Tables 3 and 4, and hence the Lange–Shinoda approach is valid for these mixtures. Consequently, the term  $d \ln \text{cmc}/dx_1$  can be given by eq 6-6. When these values are introduced into eqs 6-7 and 7-3, we have found significant differences between the micelle compositions predicted by these two equations, as shown in Tables 3 and 4. It is to be noted that eq 7-3 predicts negative  $x$  values in Table 3. It is thus important to recognize the approximate nature of eq 7-3. When the difference of the cmc values of the two pure micelles is small, i.e.,  $y$  is small, the results from eq 7-3 approach those of eq 6-7. This trend is confirmed when we compare Tables 3 and 4.

**8. Mixtures Where Nonideal Interactions Are Significant.** When the two headgroups carrying like charge have different chemical structures, nonideal interaction might be observed. We analyze the data on dodecylpyridinium bromide (C12PyBr) ( $K = 0.65$ )/dodecylquinolinium bromide (C12QBr) ( $K = 0.64$ ) binary mixed micelles.<sup>52</sup> As shown in Figure 8, the cmc data cannot be described with eq 6-2, and hence the Lange–Shinoda approach cannot be applied. Accordingly, the experimental cmc data were fitted by the following polynomial:  $\ln(\text{cmc}/\text{m molal}) = 1.447 + 0.7024x_1 + 0.2695x_1^2$ . In terms of  $d \ln \text{cmc}/dx_1$  evaluated from the polynomial, micelle compositions were calculated with eqs 6-7 and 7-3. As shown in Table 5, eq 7-3 has yielded significantly different results from those predicted by eq 6-7. We have evaluated the activity coefficients  $f$  and

**TABLE 5: C12PyBr/C12QBr Mixed Micelles**

$x_1$	0	0.214	0.394	0.501	0.647	0.787	0.898	1
cmc/m	4.22	5.01	5.89	6.61	7.41	8.51	9.82	11.48
molal <sup>a</sup>								
$x^b$	0		0.036	0.102	0.253	0.477	0.720	1
$x^c$	0		-0.043	0.015	0.167	0.409	0.681	1
$x(\text{RST})^d$	0	0.07	0.16	0.24	0.395	0.58	0.77	1
$f_H$			5.62	2.93	1.65	1.22	1.07	1
$f_L$	1		0.88	0.87	0.83	0.82	0.85	
$g^{\text{ex}}$	0		-0.06	-0.02	-0.01	-0.01	0	0
$f_H^{\text{non}}$			3.66	1.99	1.25	1.01	0.97	1
$f_{\text{ex}2k}^{\text{non}}$	1		1.09	1.16	1.19	1.29	1.46	
$g^{\text{ex,non}}$	0		0.13	0.20	0.19	0.14	0.08	0

<sup>a</sup> Data taken from ref 52. <sup>b</sup> The mole fraction of C12Py in the micelle calculated with eq 6-7. <sup>c</sup> The mole fraction of C12Py in the micelle calculated with eq 7-3. <sup>d</sup> The mole fraction of C12Py in the micelle calculated by the regular solution theory.

$f_H^{\text{non}}$  and the excess free energy  $g^{\text{ex}}$  and  $g^{\text{ex,non}}$  according to the following equations, and the results are shown in Table 5.

$$f_H = (\text{cmc}/\text{cmc}_H)(x_1/x)$$

$$f_L = (\text{cmc}/\text{cmc}_L)(1 - x_1)/(1 - x) \quad (8-1)$$

$$f_H^{\text{non}} = (\text{cmc}/\text{cmc}_H)^{1+K}(x_1/x)$$

$$f_L^{\text{non}} = (\text{cmc}/\text{cmc}_L)^{1+K}(1 - x_1)/(1 - x) \quad (8-2)$$

$$g^{\text{ex}} = x \ln f_H + (1 - x) \ln f_L$$

$$g^{\text{ex,non}} = x \ln f_H^{\text{non}} + (1 - x) \ln f_L^{\text{non}} \quad (8-3)$$

Activity coefficients are contributed significantly from  $g^{\text{ex,el}}$ , which represents the effect of varying ionic strength, and we have  $f_H > 1$  and  $f_L < 1$ . The resultant  $g^{\text{ex}}$  is close to zero, but it does not mean ideal mixing because the activity coefficients differ considerably from unity. Most of the values  $f_H^{\text{non}}$  and  $f_L^{\text{non}}$  exceed unity, and  $g^{\text{ex,non}}$  is positive, taking a maximum of about 0.2 at  $x = 0.1$ –0.2. Hence, we can conclude some repulsive interaction between C12Py and C12Q in the micelles, which is expected to be mostly nonelectric. The dependence of  $g^{\text{ex,non}}$  on  $x$  does not obey the regular solution theory. Steric repulsion between pyridinium and quinolinium rings is likely to be a possible mechanism for the suggested repulsive interaction, since the quinolinium ring is expected to lie on, rather than stretch out from, the surface of C12Py–C12Q mixed micelles.<sup>53</sup>

When the RST is applied to the cmc data, considerably different  $x$  values are obtained, as shown in Table 5, and  $g^{\text{ex}}$  (RST) is positive, taking the maximum of about 0.07 around  $x \approx 0.24$ , indicating that it cannot be applied.

## Discussion

In the present study, an analysis in terms of the Gibbs–Duhem (G–D) relation is presented in eq 2-1 for ionic/nonionic mixed micelles and in eq 7-1 for mixed micelles consisting of ionic surfactants of like charge. It is essential for the analysis to evaluate a quantity  $d \ln \text{cmc}/dx_1$  from the experimental cmc data. In the present study, we have used polynomials to approximate the cmc data. This is only a mathematical procedure without any physical basis. In practical applications, we have found that the cmc data can be fitted with different polynomials to the same extent of approximation. In other words, uniqueness about the values of  $d \ln \text{cmc}/dx_1$  is not always satisfied. It is highly important to develop an algorithm to evaluate correct values of  $d \ln \text{cmc}/dx_1$  from given cmc data. In this context, we are in a situation far from satisfactory in the respect that most reports, except a few,<sup>39</sup> using eq 2-6 or eq 7-3 do not

describe the procedure of how the values of  $d \ln \text{cmc}/dx_1$  were evaluated. To obtain reliable values of  $d \ln \text{cmc}/dx_1$  experimentally without use of any analysis, we are asked to measure accurate cmc values in an approximately equal separation with respect to cmc, not the monomer composition, over the entire cmc range.

In eq 2-1, the fundamental equation of the present analysis, the degree of counterion binding  $\nu$  is defined in the thermodynamic sense that is related to the difference between the concentration and the activity of counterions. Hence, it is not necessarily identical with the degree of binding evaluated by transport methods or spectroscopic methods. The dependence of  $\nu$  on the micelle composition  $x$  in the case of ionic/nonionic mixed micelles is assessed by eq 4-1 when the experimental data are not available. Since eq 4-1 is an approximate relation, though simple, it is to be applied with the following reservation. The validity of eq 4-1 has not been confirmed in the range of  $x$  smaller than about 0.3 because few reported data are available in this range. In particular, there are several reports indicating the presence of a critical  $x$  value for the counterion binding to occur,<sup>40,54,55</sup> which eq 4-1 fails to predict. It is this range of small  $x$  that is important in the cmc analysis, as shown in the present study. It is expected, however, that eq 4-1 can be used for the purpose of the present analysis in the range of small  $x$  without a serious error because  $\nu$  enters always as a product  $x\nu$  in eq 2-1 or eq 2-4. Needless to say, it is highly desirable to develop another analytical expression that describes correctly the degree of counterion binding at low charge densities.

## Conclusions

**I. Ionic/Nonionic Mixed Micelles in Water.** (1) The contribution of counterions to the Gibbs–Duhem relation, eq 2-1, is significant, and hence eq 2-5, instead of eq 2-6, should be employed to evaluate the micelle composition  $x$ .

(2) Effects of the varying counterion concentration on  $x$  are significant, but they can be corrected, to some extent, in terms of the Corrin–Harkins relation.

(3) The RST does not always hold even when the excess free energy is described well with the RST expression unless the observed range of  $x$  is wide enough.

(4) The RST overestimates  $x$  and underestimates the activity coefficient of the ionic species when applied to the mixed micelles to which it is inapplicable.

**II. Mixed Micelles in Water Consisting of Surfactants of Like Charges.** (1) The Gibbs–Duhem relation, eq 7-1, provides a sound basis for the cmc analysis, and the micelle composition  $x$  is given by eq 6-7.

(2) The Lange–Shinoda approach is consistent with the Gibbs–Duhem relation eq 7-1.

(3) Motomura's approach is not exact but approximate.

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