

# Molecular Modeling for Nonideal Mixing of Amphiphilic Molecules and Applications to Ionic Surfactant/Salt Solutions

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Received April 10, 2001. In Final Form: October 8, 2001

A new theory is developed to describe nonideal mixing behaviors and bulk and interfacial properties of surfactant mixtures, which cannot be described by regular solution theories. Within the framework of this model, the nature of nonideality is taken into account in the aspects of intermolecular interactions and the molecular arrangement of micelles and interfacial layers. In calculating the excess free energy of mixing, the approach separates the irregular effects, arising from changes in the size, shape, and structure of micelles and interfacial monolayers, from the exchange effect attributed to "regular" mixing. Molecular modeling is employed to calculate these effects based on the molecular structures of the constituents and equivalent information for the pure components. To check the model, the surface tension of mixed triethyleneglycol mono-*n*-dodecyl ether (C<sub>12</sub>EO<sub>3</sub>)/sodium dodecyl sulfate (SDS) aqueous solutions at the phase inversion point and the dependence of the critical micellization concentration and the surface tension of SDS aqueous solutions on the salt concentration were predicted based on our approaches. The predicted results are in excellent agreement with experiments.

## I. Introduction

For surfactant solutions, mixed surfactants can offer optimized interfacial properties, such as interfacial tensions, as compared to any single-surfactant systems.<sup>1–5</sup> Therefore, it is desirable to obtain a decent understanding of this effect and to develop an applicable model to predict the lowering of critical micellization concentration (cmc) and interfacial tension for mixed-surfactant systems. Theoretically speaking, the modeling for the structure and properties of mixed fluid interfaces is still very difficult. The reason is that the nonideal behavior of mixing, which gives rise to the synergistic mixing effect, does deviate from regular solution types of behavior in many cases. In other words, the nonideality revealed in mixing different types of surfactants has the nature of "irregularity". To model this irregular nonideality is a genuine challenge for scientists working in this area.

The adsorption of surfactants at fluid–fluid interfaces from aqueous single-surfactant solutions has been studied in great detail.<sup>6</sup> Most of the thermodynamic descriptions of single-surfactant adsorption at fluid–fluid interfaces are based on the assumption that the adsorbed surfactant molecules form a monolayer at the interface.<sup>6</sup> The theoretical approaches can be divided into two categories: (a) two-dimensional (2D) solution approaches,<sup>7,8</sup> in which the solvent is taken into account explicitly in

modeling the monolayer, and (b) 2D gas approaches,<sup>9–13</sup> in which the solvent is treated as a continuum background in modeling the monolayer. For mixed-surfactant systems, although recently some efforts have been from the point of view of the 2D gas approach,<sup>14</sup> the major focus on this issue is within the framework of 2D solution approaches.<sup>15–19</sup> To describe nonideal behavior of mixing, the most important behavior for mixed-surfactant systems, Rosen and Hua<sup>20</sup> and Holland<sup>21</sup> applied regular solution approximations to estimate the excess free energy of mixing, a major parameter characterizing the nonideality in mixing different surfactant species in both the bulk and the mixed monolayer.

Nevertheless, when molecules with different molecular structures are mixed, the nonideality of mixing reveals an eminent irregular nature (cf. section II.B). It follows that the approaches of the 2D solution models completely lose their descriptive power. The key issue is that the basic presumption<sup>22</sup> for regular solution theories is that different molecules should have a similar size and shape before and after mixing. Evidently, as one of the most important parameters to characterize the nonidealities, the exchange energy  $w_{ij}$  (or the  $\chi_{ij}$  parameter in the Flory–

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Huggins theory)<sup>23</sup> loses its “regular” physical identity and consistency in these systems. Consequently, this parameter  $w_{ij}$  reduces to an empirical parameter,<sup>23,24</sup> and the approaches reduce to empirical models. From a theoretical and practical point of view, the description of this irregular nonideality is an unsolved problem. To solve this fundamental problem, we need to develop a theory which will be capable of capturing the physical nature of the irregular nonidealities and calculating major parameters introduced.

Ruckenstein, Rao, Nagarajan, Blankschtein, and so forth<sup>25–27</sup> have also developed some molecular thermodynamics models to describe mixed micellization by predicting the excess Gibbs free energy of the mixing process. In particular, Ruckenstein and Rao<sup>27</sup> have for the first time developed an isotherm model to predict the interfacial tension of oil–brine systems in the presence of surfactant and cosurfactant, by taking into account the different sizes of the solute molecules as well as the solute–solvent and solute–solute interactions in the interfacial phase. The modeling can be regarded as one of the first comprehensive thermodynamic approaches developed so far that achieved important progress in this area.

In this paper, the statistical thermodynamic model to be presented constitutes an effort of combining statistical thermodynamic theories of mixed micellar solutions with a molecular description of the structures of mixed micelles and interfaces. Within the framework of this model, the prediction for the interfacial tensions and cmc's of mixed-surfactant systems is made on the basis of (i) the corresponding properties of pure surfactants, (ii) the molecular structures of the surfactant molecules involved in the micellization process, and (iii) solution conditions such as temperature and the presence of additives such as salts.

In comparison with previous models, our modeling will adopt a different approach, similar to that of Ruckenstein and Rao.<sup>27</sup> Our main attention will first be focused on a new general thermodynamic description of the excess free energy of mixing from the point of view of both surfactant molecules and aggregates. This will allow us to gain new physical insight into the mixing of different types of surfactants. In contrast to the above authors, the molecular theories will only be applied to estimate the key parameters in our formalism. Notice that the modeling of interfacial properties, such as mixed interfacial tension, still remains as a very difficult problem. The key issue is how to model interfacial monolayers appropriately. In this paper, a new and consistent approach for the modeling of interfacial monolayers will be presented.

## II. General Model

**A. Origin of the Interfacial Tension.** Let us first discuss the case of the interfacial monolayer. For the mixed interfacial layer, at or above the concentrations where the Gibbs equation holds, we can apply the surface pseudo-phase model.<sup>8,28</sup> Within the framework of this model, a “surface pseudo-phase” consisting of a “saturated” mono-

layer of adsorbed surfactant aggregate can be defined. This approach diverges from the standard surface solution approach<sup>5</sup> because the presence of water at the interface is excluded (or, by definition, the surface excess of water is equal to zero) and the sum of the mole fractions of surfactants at the interface is therefore assumed to be unity. According to Defay et al.,<sup>6</sup> the chemical potential of component  $i$  at the interfacial monolayer is given by

$$\mu_i^\sigma = \left( \frac{\partial G^\sigma}{\partial n_i^\sigma} \right)_{T,P,\gamma,\eta_j} - \gamma a_i \quad (1)$$

where superscript  $\sigma$  denotes the interfacial monolayer, and  $G^\sigma$  and  $n_i^\sigma$  are the Gibbs free energy and the mole of component  $i$  in the interface monolayer, respectively.  $a_i$  denotes the partial molar area of surfactant  $i$  within the mixed interfacial monolayer;  $\gamma$  denotes the interfacial tension per unit area. The monolayer will be regarded, in effect, as a two-dimensional liquid, in which  $a_i$  is independent of  $\gamma$ . It follows that the Gibbs free energy of the monolayer, which depends on the variables  $T$  and  $P$  and the concentrations of different components in different phases, is also independent of  $\gamma$ .<sup>8</sup> Under these conditions, the derivative of  $G^\sigma$  of the monolayer in eq 1 is a function independent of  $\gamma$ , and consequently (1) can be used to find  $\gamma$  if  $\mu_i^\sigma$  is known. Regarding the mixed-surfactant interfacial monolayer as a 2D solution, by analogy, the free energy can be written in the form<sup>8,22</sup>

$$G^\sigma = \sum_i n_i^\sigma [\mu_i^{\sigma 0}(T, P) + RT \ln(f_i^\sigma x_i^\sigma)] \quad (2)$$

In the above equation  $\mu_i^{\sigma 0}(T, P)$  is the standard chemical potential of component  $i$ , and  $f_i^\sigma$  is the activity coefficient of component  $i$ . From (1) and (2), we obtain

$$\mu_i^\sigma = \mu_i^{\sigma 0}(T, P) + RT \ln(f_i^\sigma x_i^\sigma) - \gamma a_i \quad (3)$$

For surfactant  $i$ , we have at equilibrium

$$\mu_{1,i} = \mu_i^\sigma \quad (4)$$

for the concentration of surfactants below the cmc of the system (subscript 1 represents monomers hereafter). Above the cmc, thermodynamic equilibrium requires that the chemical potentials of all surfactant  $i$  molecules in different aggregates are the same. Equation 4 is then rewritten as

$$\mu_{1,i} = \mu_{N,i} = \mu_i^\sigma \quad N = 2, 3, 4, \dots \quad (5)$$

Here,  $\mu_{1,i}$ ,  $\mu_{N,i}$  and  $\mu_i^\sigma$  denote the chemical potentials of surfactant  $i$  monomers in the aqueous phase, surfactant  $i$  in micelles with aggregation number  $N$ , and surfactant  $i$  within the interfacial layer, respectively.

The implication of eqs 4 and 5 is that at given  $T$  and  $P$ , the interfacial free energy per molecule ( $\gamma a_i$ ) is equivalent to the free energy change by transferring a surfactant molecule  $i$  from the aqueous phase (as a monomer or within micelles) to the interfacial layer.

Let us start with the surfactant concentration above the cmc of the mixed-surfactant system. Notice that the results of the following analysis can be extended to the case where the surfactant concentration is below the cmc. Taking into account the general situation for mixed micellar solutions, different surfactant molecules are

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mixed within micellar aggregates, and additionally micellar aggregates as independent entities are also mixed in the solutions. The chemical potential of surfactant  $i$  in micellar aggregates includes a term  $kT \ln(f_{N,i} x_{N,i})$  reflecting the mixing of different surfactants within mixed micelles and a term  $(kT/N) \ln[F_N(X_N/N)]$  reflecting the mixing of mixed micelles in the aqueous phase. Therefore, a general expression can be given as

$$\mu_{N,i} = \mu_{N,i}^0 + kT \ln(f_{N,i} x_{N,i}) + \frac{kT}{N} \ln\left(\frac{X_N}{N}\right) \quad (N = 1, 2, 3, \dots) \quad (6)$$

where  $\mu_{N,i}^0$  is the standard part of the chemical potential in aggregates of aggregation number  $N$ , which is a function of surface pressure  $\pi$  of pure surfactant  $i$  and temperature  $T$ ;  $f_{N,i}$  and  $F_N$  represent the activity coefficients for surfactant  $i$  within mixed micelles and for aggregates of size  $N$ , respectively, and  $x_{N,i}$  and  $X_N$  correspond to the mole fraction of surfactant  $i$  in mixed micelles of size  $N$  and the total concentration of different surfactant molecules incorporated in aggregates of number  $N$ , respectively ( $X_N = \sum_i X_{N,i}$ ).

In the following treatments, we assume ideal mixing of micellar aggregates, that is, it is restricted to the systems where interaggregate interactions can be ignored, meaning that  $F_N = 1$ . We notice that micellar aggregates have a certain degree of polydispersity with mean aggregation number  $\bar{N} \sim M$ .<sup>29</sup> Letting the micelles with the average size  $M$  characterize the major properties of all mixed micelles, the interfacial tension is then given according to eqs 3, 5, and 6 by

$$\gamma a_i \approx g_i^0 + kT \ln\left(\frac{f_i x_i}{f_{M,i} x_{M,i}}\right) + \frac{kT}{M} \ln\left(\frac{M}{C - X_1}\right) \quad (7)$$

with

$$g_i^0 = (\mu_i^{oo} - \mu_{M,i}^0) \quad (8)$$

and the total amphiphile concentration:

$$C = \sum_{N=1}^{\infty} X_N \quad (9)$$

In the case of pure surfactants, eq 7 reduces to

$$\gamma_i^0 a_i^0 \approx g_i^0 + \frac{kT}{M_i^0} \ln\left(\frac{M_i^0}{C - X_{1,i}^0}\right) \quad (10)$$

where superscript "o" refers to the properties associated with the single-surfactant solutions. Within eq 10, the term  $(kT/M_i^0) \ln[M_i^0/(C - X_{1,i}^0)]$  is not very sensitive to changes in the net surfactant concentration  $C$  but as a whole is very sensitive to changes in  $M$ .<sup>29</sup> Since for many pure surfactant solutions  $M_i^0$  is independent of  $C$ ,  $\gamma_i^0$  displays an approximately constant value above the cmc, as is well-known. Substituting (10) into (7) yields

$$\gamma a_i \approx \gamma_i^0 a_i^0 + kT \ln\left(\frac{f_i x_i}{f_{M,i} x_{M,i}}\right) + \left[ \frac{kT}{M} \ln\left(\frac{M}{C - X_1}\right) - \frac{kT}{M_i^0} \ln\left(\frac{M_i^0}{C - X_{1,i}^0}\right) \right] \quad (11)$$

which is a general expression of interfacial tensions for mixed-surfactant systems.

The above analysis shows that the average number of aggregates and the total surfactant concentration will determine the entropic contributions of the aggregates to interfacial and bulk properties, such as interfacial tension and cmc. In this sense, the size and concentration dispersions of aggregates also have some effects on the properties.

In the above treatment, we used the average size of aggregates. This simplified treatment is an excellent approximation when surfactant aggregates have relatively small aggregation numbers. In such systems, one can replace the entire size and composition of aggregates with a single aggregate whose size and concentration corresponds to the maximum in the distribution function. In other words, this is equivalent to approximating the size distribution or multiple equilibrium model. Actually, this represents the case where the entropic effect is most important. On the other hand, for polydispersed systems our approximation may not be so accurate. Nevertheless, this normally corresponds to aggregates with large aggregation numbers. In such systems, the entropic effect associated with aggregation becomes much less important. This implies that our approximation is still acceptable. For instance, when rodlike or large disklike micelles or the bicontinuous phase or lamellar ( $L_\alpha$ ) phase<sup>29</sup> occur in surfactant solutions, one has  $M \rightarrow \infty$ . It follows that  $(kT/M) \ln[M/(C - X_1)] \rightarrow 0$ . Then, eq 4 is rewritten as

$$\gamma a_i \approx g_i^0 + kT \ln\left(\frac{f_i x_i}{f_i^M x_i^M}\right) \quad (12)$$

Similarly, for single-surfactant solutions, eq 10 is given as in this case by

$$\gamma_i^0 a_i^0 = g_i^0 \quad (13)$$

In this case, eq 12 is reduced to

$$\gamma a_i \approx \gamma_i^0 a_i^0 + kT \ln\left(\frac{f_i x_i}{f_i^M x_i^M}\right) \quad (14)$$

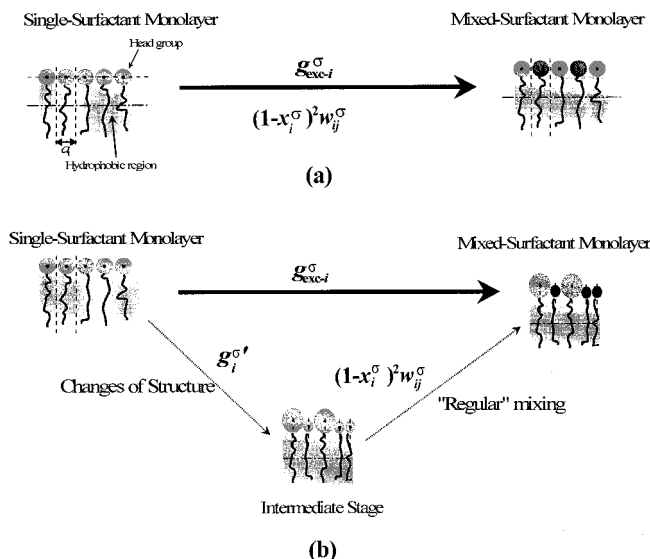
In addition, it can be seen from (11) that if the sizes of single and mixed micelles are similar ( $M_i^0 \sim M$ ),  $\{(kT/M_i^0) \ln[M_i^0/(C - X_{1,i}^0)] - (kT/M) \ln[M/(C - X_1)]\} \sim 0$ . Therefore, (14) is also obtained. This happens when the molecular structure of different surfactants and the packing for the mixed- and single-surfactant micelles have a certain similarity.

According to eqs 11 and 14, the problems associated with the prediction of interfacial tension are the calculation of  $f_{M,i}$ ,  $f_i$ ,  $x_{M,i}$ ,  $x_i$ , and so forth. These will be addressed in the following sections.

**B. The Nature of Nonideal Mixing and Excess Free Energy for Mixed-Surfactant Systems. 1. Activity Coefficient and Excess Free Energy for Mixed-Surfactant Systems.** The excess free energy  $G^E$  is defined as the free energy change in the mixing process, in addition to the entropy contribution of ideal mixing.<sup>22</sup> The activity

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**Figure 1.** Illustration of calculation of nonideality effect for a mixed-surfactant system. (a) The mixing of different types of surfactants having similar sizes and intermolecular interactions. The excess free energy and mixing behavior can be approximately described by regular solution theories. (b) The mixing of different types of surfactants having very different sizes and intermolecular interactions. The excess free energy and mixing behavior cannot be described by regular solution theories. The excess free energy can be regarded as the sum of irregular excess free energies and regular excess free energies.  $g_{exc-i}^{\sigma}$  is the partial excess free energy of species  $i$ ;  $w_{ij}^{\sigma}$  is the exchange energy between molecules  $i$  and  $j$ ;  $g_i^{\sigma'}$  is the irregular partial excess free energy of species  $i$ ;  $x_i^{\sigma}$  is the mole fraction of species  $i$ .

coefficient of component  $i$ ,  $f_i$ , can be related to the excess free energy of mixing  $G^E$  as<sup>22</sup>

$$\left( \frac{\partial G^E}{\partial n_i} \right)_{T,P,n_j} = g_{exc-i} = kT \ln f_i \quad (i, j = A, B; i \neq j) \quad (15)$$

For binary mixtures,  $g_{exc-i}$  is given according to regular solution theories (RST)<sup>22</sup> by

$$g_{exc-i} = (1 - x_j)^2 w_{ij}^{RST} \quad (16)$$

and in the context of cell models<sup>21</sup> the exchange energy is given by

$$w_{ij}^{RST} = \sum_{q=1}^m \left[ \phi_q^{ij} - \frac{1}{2}(\phi_q^{ii} + \phi_q^{jj}) \right] \quad (17)$$

( $m$  is the coordinate number of a structural unit;  $\phi_q^{ii}$ ,  $\phi_q^{jj}$  and  $\phi_q^{ij}$  denote interaction energies between  $i-i$ ,  $j-j$ , and  $i-j$  units, respectively).

We notice that within the framework of regular solution theories,<sup>22</sup> the sizes of different types of structural units must be similar;<sup>22</sup> interaction energies between structural units,  $\phi_q^{ii}$ ,  $\phi_q^{jj}$ , and  $\phi_q^{ij}$ , must remain unchanged during the mixing process. Therefore,  $w_{ij}^R$  is supposed to be constant at various compositions and concentrations. This mixing process is illustrated in Figure 1a.

In mixing different types of surfactants within micelles and interfacial layers, it is quite often found that if the size and molecular structure between different surfactant molecules are very different, the molecular packing, the average cross-sectional area of surfactant molecules in

micelles, and the molecular density of interfacial monolayers and mixed micelles will change in the mixing process. This gives rise to changes in interaction energies between surfactant molecules and consequently in  $w_{ij}^{RST}$  (cf. Figure 1b). In such a case, the properties associated with the mixing process reveal some irregular characteristics. Therefore, applying *regular solution theories* to solve these *irregular* problems will inevitably encounter some problems. Strictly speaking, *RST cannot be directly applied to the mixed-surfactant system of this kind*.

In the following, we will tackle this issue from a statistic thermodynamic point of view. As stated above,  $g_{exc-i}$  represents the partial free energy change of surfactant  $i$  (excluding the contribution of ideal mixing) when single-surfactant micelles or interfacial monolayers are transferred to mixed-surfactant micelles or mixed interfacial monolayers.  $g_{exc-i}$  can be evaluated using a thought process consisting of some reversible steps, each associated with a particular physicochemical contribution. Since the free energy change (excess free energy) is a thermodynamic property associated with the initial and the end states of the system and independent of the path connecting the initial and final states, we can then choose a series of imaginary intermediate states contributing to  $g_{exc-i}$ , whose free energy changes can be easily evaluated either by molecular theories or by available experimental data.

For the mixing in the surfactant monolayer, the similar two major steps involve the following:

(a) *The Density Change in Single-Surfactant Monolayers.* In this step, a single-surfactant monolayer with the area per molecule  $a_i^0$  is changed to the imaginary single-surfactant monolayer having the average area per molecule of the mixed-surfactant monolayer  $\bar{a}_{mix}$  (in the later discussions, we will drop the subscript "mix" for simplicity). Similarly, we denote  $g_i^{\sigma'}$  as the partial free energy associated with this step. This step can also be subdivided into some parallel substeps. (See the next section for details.)

(b) *The Mixing of Different Imaginary Single Surfactants into Genuine Mixed Monolayers without Changing the Average Molecular Packing.* The composition of the monolayers is changed from single-surfactant to mixed-surfactant  $x_i^{\sigma}$ , while the basic molecular packing remains unchanged. Therefore, the partial excess free energy  $g_{exc-i}$  associated with this step can also be approximately described, by the mean field approach, as  $(1 - x_j^{\sigma})^2 w_{ij}^{\sigma}$ .

Similar steps can be obtained for mixed micelles where the change of curvature of micelles is taken into account. The essential point of our approach is to split the partial excess free energy  $g_{exc-i}$  into two parts: the irregular part, denoted by  $g_i^{\sigma'}$ , and the regular part, denoted by  $(1 - x_j^{\sigma})^2 w_{ij}^{\sigma}$ .  $g_i^{\sigma'}$  is associated with the free energy change per molecule due to the change of molecule packing of micelle or interfacial monolayers, without taking into account the pure exchange (or mixing) effect.  $(1 - x_j^{\sigma})^2 w_{ij}^{\sigma}$  describes the pure exchange (or mixing) effect (excluding the ideal mixing entropy) at the given composition. In general,  $g_{exc-i}$  is then expressed within our framework as

$$g_{exc-i} = kT \ln f_i = g_i^{\sigma'} + (1 - x_j^{\sigma})^2 w_{ij}^{\sigma} \quad (18)$$

Notice that although the expression of the regular term  $(1 - x_j^{\sigma})^2 w_{ij}^{\sigma}$  in eq 18 is very similar to the partial excess free energy of mixing in RST (cf. eq 16), the physical implication is very different. Here, the exchange energy  $w_{ij}$  is given by eq 17. However,  $\phi_q^{ii}$ ,  $\phi_q^{jj}$ , and  $\phi_q^{ij}$  depend on the packing structure of micelles or interfacial monolayers. Since the structure changes with composition,  $w_{ij}$  is in

principle a function of  $x_i$ . This is completely different from  $w_{ij}^{\text{RST}}$ .

Equation 18 is a general expression for the partial excess free energy of mixing. If the regular term  $(1 - x_j)^2 w_{ij}$  describes the regular exchange effect due to the mixing, the irregular term  $g'_i$  characterizes then the deviation from this effect due to the change of micelle and interfacial monolayer structure. If the structure change in mixing is negligible, we then have  $g'_i \rightarrow 0$  and  $w_{ij} \approx w_{ij}^{\text{RST}}$ . Equation 18 reduces then to eq 16.

**2. Calculation of Excess Free Energies of Mixed Micelles Based on Molecular Models. (1) Irregular Effects.** The irregular effects correspond to the partial free energy change associated with structural changes in micelles or surfactant monolayers on mixing. This change includes the curvatures ( $R_i^0$  to  $R_{\text{mix}}$ ) or the area per molecule at the interface ( $\bar{a}_i^0$  to  $\bar{a}$ ), which may arise from the different physical natures associated with head-head and tail-tail interaction groups and changes in experimental conditions. For the mixing of micelles, these contributions are examined as follows:

(i) *Aggregate Core-Water Interfacial Free Energy Contribution  $g_{M,i}(\text{int})$ .* Between a micelle and the aqueous solution, there is an interface between the hydrophobic core region consisting of the surfactant tails and the surrounding water medium. Taking into account the interfacial tension  $\gamma$  and the curvature, the free energy per molecule for single-surfactant micelles is obtained using the well-known Gibbs-Tolman-Koenig-Buff equation<sup>26</sup> as

$$\Delta\mu_i^0(\text{int}) = \gamma_0(\bar{a}_{M,i}^0 - \bar{a}_{M,i}^{0-T}) \left[ 1 - \frac{(s_i - 1)d_i^{\text{Tol}}}{R_i^0} \right] \quad (19)$$

where  $\bar{a}_{M,i}^0$  denotes the area per molecule at the hydrophobic core surface.  $\bar{a}_{M,i}^{0-T}$  is the area screened out by headgroups.  $s_i$  is a shape factor (3 for spheres; 2 for infinite-size cylinders and for bilayers). In eq 19,  $d_i^{\text{Tol}}$  is the Tolman distance (a measure of interfacial thickness) and can be approximated for hydrocarbon tails with a total carbon number  $n$  by<sup>30</sup>

$$d_i^{\text{Tol}} \cong 2.25 \frac{l_{\text{max}}(n)}{l_{\text{max}}(n=12)} \quad (20)$$

where  $l_{\text{max}}$ , the fully extended length of the tail, is given by  $l_{\text{max}}(n) = 1.54 + 1.265(n - 1)$  (in Å) for hydrocarbons.<sup>26</sup>

Changing the basic structure of micelles by mixing, the partial free energy change per molecule associated with the core interfacial free energy can be expressed as

$$g_{M,i}(\text{int}) = \gamma_0 \left\{ (\bar{a}_{M,i}^{\text{int}} - \bar{a}_{M,i}^{0-T}) \left[ 1 - \frac{(s_{\text{mix}} - 1)}{R_{\text{mix}}} d_{\text{mix}}^{\text{Tol}} \right] - (\bar{a}_{M,i}^{0,\text{int}} - \bar{a}_{M,i}^{0-T}) \left[ 1 - \frac{(s_i - 1)}{R_i^0} d_i^{\text{Tol}} \right] \right\} \quad (21)$$

where  $\bar{a}_{M,i}^{\text{int}}$  and  $\bar{a}_{M,i}^{0,\text{int}}$  denote the areas occupied by a surfactant  $i$  molecule at the water/hydrophobic interface of single- and mixed-surfactant aggregates, respectively.

(ii) *Deformation Free Energy of the Surfactant Tail  $g_{M,i}(\text{def})$ .* The surfactant tails inside the hydrophobic core of the aggregate are not in a state identical to that in liquid hydrocarbons (or fluorocarbons). Since mixing

different surfactants within micelles changes the shape and aggregation number, the free energy change will then contribute to the irregular excess free energy.

Using a lattice picture for the micellar core, simple analytical expressions can be developed for the chain deformation free energy as an explicit function of the micelle aggregation number and micellar shape.<sup>25,31</sup> Based on the lattice models suggested by Dill and Flory,<sup>31</sup> we arrived at the partial excess free energy attributed to this irregular effect for the mixing of surfactant tails as

$$g_{M,i}(\text{def}) \approx kT \left\{ \left( \frac{10p_{\text{mix}}\tau^2}{80} \right) \frac{(R_{\text{mix}})^2}{l_{\text{max}}^{\text{mix}} L_{\text{mix}}} - \left( \frac{10p_i\tau^2}{80} \right) \frac{(R_i^0)^2}{l_{\text{max}} L_i} \right\} \quad (22)$$

In the equation, the subscript "mix" refers to composition averaged quantities,  $l_{\text{max},i}$  ( $i = \text{A, B}$ ) is the extended length of a surfactant  $i$  tail,  $L$  denotes the linear dimension of the lattice size and for hydrocarbon tails is equal to 4.6 Å,<sup>31</sup> and  $p$  is the packing factor, defined as<sup>25</sup>

$$p = \frac{v}{a_M R} \quad (23)$$

( $p_i \leq 1/3$  for spherical aggregates,  $p_i \sim 1/2$  for cylindrical aggregates,  $p_i \sim 1$  for planar aggregates). Here,  $v$  is the molecular volume of the hydrophobic tails,  $a_M$  refers to the surface area of the hydrophobic core of the micelle per surfactant molecule, and  $R$  is the radius of hydrophobic cores of surfactant  $i$  aggregates. In the case of planar bilayers,  $R$  refers to half of the bilayer thickness. For more details concerning this effect, we refer to refs 25 and 31.

(iii) *Headgroup Steric Contribution  $g_{M,i}$ .* The formation of micelles brings the polar headgroups of the surfactant molecules to the surface of the aggregate where they are crowded compared to their isolated states as singly dispersed surfactant molecules. This generates steric repulsion among the headgroups. Based on an excluded area concept from statistic thermodynamics,<sup>22</sup> the contribution of this repulsive free energy to the irregular excess free energy can be generally given as<sup>25</sup>

$$g_{M,i}(\text{steric}) \cong -kT \left\{ \ln \left[ 1 - \frac{\bar{a}_M^{0-h}}{\bar{a}_M^0} \right] - \ln \left[ 1 - \frac{\bar{a}_{M,i}^{0-h}}{\bar{a}_{M,i}^0} \right] \right\} \quad (24)$$

Here,  $\bar{a}_{M,i}^0$  and  $\bar{a}_{M,i}^{0-h}$  denote the areas occupied by the virtual headgroup (including the hydration layers etc.) of a surfactant  $i$  and by the physical headgroup of the surfactant at the interface, respectively.  $\bar{a}_M^0 (= \sum_i x_{M,i} \bar{a}_{M,i}^0)$  and  $\bar{a}_M^{0-h} (= \sum_i x_{M,i} \bar{a}_{M,i}^{0-h})$  are the average areas, respectively.

(iv) *Headgroup Dipole Contribution  $g_{M,i}(\text{dipole})$ .* For zwitterionic surfactants having a constant separation between the two opposite signed charges, we have to consider the interaction between the permanent dipoles of polar headgroups. This repulsive interaction is a function of the curvature and area of dipole headgroups and therefore will contribute to the irregular excess free energy during the mixing. If the arrangement of the poles of the dipoles is regarded as constituting an electrical capacitor with the distance between the curved plates of the capacitor being equal to the distance of charge separation on the zwitterionic headgroup,<sup>26</sup> the contributions for dipoles having a charge separation  $d$  and an

(30) Tanford, C. *The Hydrophobic Effect*; Wiley: New York, 1980.

(31) Dill, K. A.; Flory, P. J. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 3115.

aggregate radius of  $R_i^o$  has a form<sup>32</sup>

$$g_{M,i}(\text{dipole}) \cong \frac{2\pi e^2 d}{\epsilon} \left[ \frac{R_{\text{mix}}}{\bar{a}_M(d + R_{\text{mix}})} - \frac{R_i^o}{a_i^{\text{dipole}}(d + R_i^o)} \right] q^2 \quad (25)$$

In the above relation,  $e$  denotes the electronic charge,  $\epsilon$  is the dielectric constant of solutions in the headgroup region,  $a_i^{\text{dipole}}$  is the area per dipole molecule at the hydrophobic core surface, and  $\pm q$  are the charges of the dipole (in  $e$ ). This expression can also be directly applied to disk-like micelles or aggregates by taking  $R_i^o \rightarrow \infty$ . For rodlike micelles, eq 25 can also be modified correspondingly. We notice that  $\epsilon$  is normally different from the dielectric constant of the solvent. Nevertheless, one can take the dielectric constant of the solvent as an approximation.<sup>26</sup>

(v) *Headgroup Ionic Contribution  $g_{M,i}(\text{ionic})$ .* For ionic surfactant solutions, two types of interactions associated with ionic interactions arise: (a) interactions between charged surfactant aggregates and (b) interactions between aggregates and counterions. If the concentration of charged aggregates is relatively low, the average distance between aggregates is very large, and the interaction between aggregates can be negligible. Then the first can be neglected. Here, we will focus our attention on this situation. Variations in the surface charge density and in the shape of charged amphiphilic aggregates due to the change in composition will alter the free energies of electrostatic double layers and the system and therefore contribute to  $g_{M,i}(\text{ionic})$ . This free energy contribution is given on the basis of Stern's treatment for the electric double layer and Evans and Ninham's expression<sup>28,33</sup> for the diffuse electrostatic double layers by

$$g_{M,i}(\text{ionic}) \approx 2kT \left\{ \ln \left[ \left( \frac{S_{\text{mix}}}{2} \right) + \sqrt{1 + \left( \frac{S_{\text{mix}}}{2} \right)^2} \right] - \frac{2}{S_{\text{mix}}} \left[ \sqrt{1 + \left( \frac{S_{\text{mix}}}{2} \right)^2} - 1 \right] - \ln \left[ \left( \frac{S_i}{2} \right) + \sqrt{1 + \left( \frac{S_i}{2} \right)^2} \right] + \frac{2}{S_i} \left[ \sqrt{1 + \left( \frac{S_i}{2} \right)^2} - 1 \right] \right\} + 4kT \frac{1}{\kappa} \left\{ \frac{(S_i - 1)C_g^{\text{mix}}}{S_i} \ln \left[ \frac{1}{2} + \frac{1}{2} \sqrt{1 + \left( \frac{S_i}{2} \right)^2} \right] - \frac{(S_{\text{mix}} - 1)C_g^{\text{mix}}}{S_{\text{mix}}} \ln \left[ \frac{1}{2} + \frac{1}{2} \sqrt{1 + \left( \frac{S_{\text{mix}}}{2} \right)^2} \right] \right\} - \delta_c kT \left[ S_{\text{mix}} \frac{R_{\text{mix}} + \delta}{R_{\text{mix}} + \delta + \delta_c} - S_i \frac{R_i + \delta}{R_i + \delta + \delta_c} \right] \quad (26)$$

with

$$S_i = \frac{4\pi(z_i e)^2 \vartheta_i}{\epsilon \kappa a_i^{\delta} kT} \quad S_{\text{mix}} = \frac{4\pi(z_i e)^2 \vartheta_{\text{mix}}}{\epsilon \kappa \bar{a}^{\delta} kT}$$

$$\kappa = \sqrt{\frac{8\pi n_0 (z_i e)^2}{\epsilon kT}} \quad n_0 = \frac{C_{\text{ion}} + C_{\text{add}}}{10^3} N_{\text{Av}}$$

$$\vartheta_i = \frac{x_c \exp(\delta_c S_i / \vartheta_i)}{1 + x_c \exp(\delta_c S_i / \vartheta_i)}$$

$$\vartheta_{\text{mix}} = \frac{x_c \exp(\delta_c S_{\text{mix}} / \vartheta_{\text{mix}})}{1 + x_c \exp(\delta_c S_{\text{mix}} / \vartheta_{\text{mix}})} \quad (27)$$

where  $S_{\text{mix}}$  is the shape factor for mixed micelles and is equal to 3, 2, and 1 for spherical, rodlike, and planar aggregates, respectively,  $\delta_c$  is the diameter of counterions, and  $x_c$  denotes the molar fraction of counterions in the bulk phase. In eq 27, the area per molecule  $a_i^{\delta}$  is evaluated at a distance  $\delta$  from the hydrophobic core surface.  $z_i$  denotes the electric valence of surfactant  $i$  molecules,  $\kappa^{-1}$  is the reciprocal Debye length,  $n_0$  is the number of counterions in solution per  $\text{cm}^3$ ,  $C_{\text{ion}}$  is the molar concentration of singly dispersed ionic surfactant molecules,  $C_{\text{add}}$  is the molar concentration of the salt added to the surfactant solution, and  $N_{\text{Av}}$  is Avogadro's number. The last term on the right-hand side of eq 26 is the curvature correction term where  $C_g$  is given for single and mixed surfactants by

$$C_g = \frac{1}{R_i^o + \delta} \quad C_g^{\text{mix}} = \frac{1}{R_{\text{mix}} + \delta} \quad (28)$$

Taking the above-mentioned effects into account, the general expression for the irregular excess free energy for micelles in mixing is given by the sum of all the above contributions as

$$g_{M,i}' = g_{M,i}(\text{ionic}) + g_{M,i}(\text{dipole}) + g_{M,i}(\text{int}) + g_{M,i}(\text{def}) + g_{M,i}(\text{steric}) \quad (29)$$

**(2) Regular Effects.** (i) *Contribution of Mixing of Surfactant Tails  $w_{ij}(\text{tail})$ .* This contribution accounts for the free energy of mixing the surfactant tails of molecules A and B in the hydrophobic core, with respect to the reference states of pure A and pure B micellar cores. In this case, eq 17 can be applied. For more general cases, we can calculate this free energy using Hildebrand's solubility parameter theory.<sup>35,36</sup> It follows that the free energy of mixing inside the micelle core and within the surfactant monolayers can be approximated as

$$x_i x_j w_{ij}(\text{tail}) \cong \sum_i [x_i v_i (\delta_i'' - \delta_{\text{mix}}'')^2] \quad (30)$$

$\delta_i''$  refers to the solubility parameter of  $i$  (not of the surfactant as a whole, but only of the tail) while  $\delta_{\text{mix}}''$  is the volume fraction ( $\varphi_i$ ) averaged solubility parameter of all the components within the micelle core or the surfactant monolayer,  $\delta_{\text{mix}}'' = \sum_i \varphi_i \delta_i''$ . The solubility for the hydrocarbon and fluorocarbon of the tail of the surfactants can be estimated using a group contribution approach on the basis of tabulated data available.<sup>35,36</sup> Normally,  $\delta_i''$  can also be found in chemical-physics handbooks, such as the CRC handbooks of chemistry and physics.

(ii) *Headgroup Ionic Contribution  $w_{ij}(\text{ionic})$ .* The contributions of headgroups to  $w_{ij}^o$  can consist of (a) van der Waals interaction, (b) electrostatic interaction, and/or (c) dipole-dipole interaction contributions. If the headgroups are not too bulky, we can focus our attention on electrostatic and/or dipole-dipole effects.

(32) Israelachvili, J. N.; Mitchell, D. J.; Ninham, B. W. *J. Chem. Soc., Faraday Trans. 2* **1976**, 72, 1525.

(33) Evans, D. F.; Ninham, B. W. *J. Chem. Phys.* **1983**, 87, 5025.

(34) Puvvada, S.; Blankschtein, D. *J. Chem. Phys.* **1992**, 96, 5567. Zoeller, N.; Shiloach, A.; Blankschtein, D. *IEEC* **1995**, 34, 4150. Ruckenstein, E.; Nagarajan, R. *J. Phys. Chem.* **1975**, 79, 2622. Warr, G. G.; White, L. R. *J. Chem. Soc., Faraday Trans. 1* **1985**, 81, 549. Tanford, C. *J. Phys. Chem.* **1974**, 78, 2469.

(35) Prausnitz, J. M. *Molecular Thermodynamics of Fluid-Phase Equilibria*; Prentice-Hall: Englewood Cliffs, NJ, 1969.

(36) Hildebrand, J. H.; Prausnitz, J. M.; Scott, R. L. *Regular and Related Solutions*; van Nostrand Reinhold: New York, 1970.



Despite the irregular excess free energy, an exchange between charged headgroups and between charged and uncharged headgroups will certainly give rise to an exchange free energy of mixing and therefore the ionic interactions contribute also to the regular excess free energy.

In practice, it is difficult to calculate this exchange free energy  $w_{ij}(\text{ionic})$ . Nevertheless, a reasonable approximate calculation is possible based on mean field approximations. For the estimation of  $w_{ij}(\text{ionic})$ , eq 17 can be utilized. Applying Evans and Ninham's expression for the ionic interaction energy at an electrostatic double layer<sup>33</sup> and taking the approximation of  $\phi_{ij}$  as suggested by Samoria et al.,<sup>37</sup>

$$\phi_{ij}(\text{ionic}) \approx 2K_{\text{elect}}Z_iZ_j \quad (31)$$

with

$$K_{\text{elect}} \cong kT \left\{ \ln \left[ \left( \frac{S_{\text{mix}}}{2} \right) + \sqrt{1 + \left( \frac{S_{\text{mix}}}{2} \right)^2} \right] - \frac{2}{S} \left[ \sqrt{1 + \left( \frac{S_{\text{mix}}}{2} \right)^2} - 1 \right] - \frac{2C_g^{\text{mix}}(S_{\text{mix}} - 1)}{\kappa S_{\text{mix}}} \ln \left[ \frac{1}{2} + \frac{1}{2} \sqrt{1 + \left( \frac{S_{\text{mix}}}{2} \right)^2} \right] \right\} / Z_i^2 \quad (32)$$

According to eq 17, we have then

$$w_{ij}(\text{ionic}) \cong -K_{\text{elect}}(Z_i - Z_j)^2 \quad (33)$$

Obviously, here the key step in the evaluation of  $w_{ij}(\text{elect})$  is to estimate  $K_{\text{elect}}$ .

(iii) *Headgroup Dipole Contribution  $w_{ij}(\text{dipole})$ .* Mixing of zwitterionic surfactants will certainly contribute to the regular excess free energy. Since the interactions between dipoles and the ionic headgroup can be quite complicated, we will in the following only concentrate on the situation where mixing occurs between different zwitterionic surfactants with the same dipole groups and between zwitterionic and nonionic surfactants. In such a case, the analyses for the estimation of ionic exchange interactions also hold. Therefore, a general expression can be given as

$$w_{ij}(\text{dipole}) \cong -K_{\text{dipole}}(q_i - q_j)^2 \quad (34)$$

Referring to eq 19, we have

$$K_{\text{dipole}} \cong \frac{2\pi e^2}{\epsilon \bar{a}_\delta} \frac{R_{\text{mix}} d}{R_{\text{mix}} + d} \quad (35)$$

In general, the regular excess free energy in terms of the exchange energy can be given as

$$w_{ij} \cong w_{ij}(\text{tail}) + w_{ij}(\text{ionic}) + w_{ij}(\text{dipole}) \quad (36)$$

which holds both for mixed micelles and the mixed interfacial monolayer.

**3. Calculation of Excess Free Energies of Mixed Interfacial Monolayers.** Following similar principles,

the excess free energies of mixed interfacial monolayers can be calculated from the formalisms derived for mixed micelles. In this case, we also have the irregular and regular effects for the excess free energy of mixing for interfacial monolayers. The irregular excess free energy for the mixing of surfactant monolayers is given by<sup>25</sup>

$$g_i^{\sigma'} \cong g_i^{\sigma}(\text{int}) + g_i^{\sigma}(\text{steric}) + g_i^{\sigma}(\text{dipole}) + g_i^{\sigma}(\text{def}) + g_i^{\sigma}(\text{ionic}) \quad (37)$$

and the exchange energy in the regular term is given by

$$w_{ij}^{\sigma} \cong w_{ij}^{\sigma}(\text{int}) + w_{ij}^{\sigma}(\text{dipole}) + w_{ij}^{\sigma}(\text{ionic}) \quad (38)$$

Note that due to the differences in molecular packing, the formalisms used in calculating the individual terms should be modified before they can be directly applied to interfacial monolayers.

### C. Molecular Area, Composition, and Aggregation Number of Mixed Micelles and Interfacial Layers.

The estimation of activity coefficients, which has been formulated in section II.B.2, turns out to be one of the most important steps in modeling mixed surfactants. In calculating the coefficients, we also need to know the composition, surfactant molecular area at the surface of aggregates, and the average aggregation number of mixed micelles and surfactant monolayers and the concentration of surfactant monomers in the solutions.

For single surfactants, core minor radius  $R_i$  or the area occupied by surfactants at the aggregate surface  $a_{M,i}$  can in principle be obtained either from experiments or by minimizing the free energy of micellization with respect to  $R_i$  or  $a_{M,i}$ .<sup>25,26,38</sup> These two parameters can be related by the following equation:

$$R_i = \frac{S_i v_i}{a_i} \quad (39)$$

where the volume of the tail  $v_i = 27.4 + 26.9(n - 1)$  (in  $\text{\AA}^3$ ) for hydrocarbons and  $v_i = 45.8 + 38.7(n - 1)$  (in  $\text{\AA}^3$ ) for fluorocarbons.<sup>25,29</sup> As pointed out section II.A, the entropy effect associated with aggregation turns out to be important in our modeling when the aggregation number is small. This happens when the packing factor is smaller than  $1/3$  (the aggregates are spherical). In this case, the average aggregation number  $M_i$  can also be associated with  $R_i$  (or  $a_{M,i}$ ) by

$$M_i \approx \frac{4\pi R_i^3}{3v_i} \quad (40)$$

For mixed micelles,  $R_{\text{mix}}$ ,  $\bar{a}$ , and  $l_{\text{mix}}$  are given according to the previous sections by

$$R_{\text{mix}} \text{ (or } \bar{a}, l_{\text{mix}}) \approx \sum x_i R_i \text{ (or } a_i, l_i). \quad (41)$$

For the composition of surfactants in mixed micelles, the following two situations are to be discussed: (i) the composition at the cmc and (ii) the composition above the cmc. In the first case, the micelle mole fraction  $x_{M,i}$  can be calculated together with  $g_{M,i}'$  and  $w_{M,i,j}$  by iteratively solving

(37) Samoria, C.; Puvvada, S.; Blankschtein, D. *Langmuir* **1992**, *8*, 2690.

(38) Puvvada, S.; Blankschtein, D. *J. Phys. Chem.* **1992**, *96*, 5579.

eqs 18, 29, 36, and 41 together with the following constraints:

$$\ln(\sum_i f_{M,i} C_i^0) \approx \ln(C_i^0) + \ln(f_{M,i} x_{M,i}) + \frac{1}{M} \ln \left[ \frac{0.05 C_i^*}{M} \right] - \frac{1}{M_i^0} \ln \left[ \frac{0.05 C_i^0}{M_i^0} \right] \quad (42)$$

$$\sum_i x_{M,i} = 1 \quad (43)$$

(For the details concerning eq 42, see eq A-4 in the Appendix.)

At concentrations above the cmc, we obtained the micellar composition expression for a binary system, based on the pseudo-phase separation assumption,

$$x_{M,i} = \frac{\alpha_i C}{f_{M,i} C_i^0 - f_{M,j} C_j^0 + \alpha_j C / x_{M,j}} \quad (44)$$

(see eq A-12 in the Appendix for details). Substituting eq 18 and the constraint in eq 43 into eq 44 yields

$$x_{M,i} = \alpha_i C / [\exp\{[g_{M,i}' + (1 - x_{M,i})^2 w_{M,ij}] / kT\} C_i^0 - \exp\{[g_{M,j}' + (x_{M,i})^2 w_{M,ij}] / kT\} C_j^0 + (1 - \alpha_j) C / (1 - x_{M,i})] \quad (45)$$

By interactively solving (45) with (29) or (36), we can obtain  $x_{M,i}$ ,  $g_{M,i}'$ , and  $w_{M,ij}$  at the concentration above cmc.

Concerning the concentration of monomers  $X_{i,i}$  of a binary surfactant system above the cmc, we can substitute  $X_i^1 \approx C_i^0 f_{M,i} x_{M,i}$  and (45) into (42) and solve the equation. This gives rise to the following expression for  $X_{i,i}$ :

$$X_{i,i} = \exp\{[g_{M,i}' + (1 - x_{M,i})^2 w_{M,ij}]\} C_i^0 \{-(C - \Delta) \pm \sqrt{(C - \Delta)^2 + 4\alpha_i C_j^0 / (-2\Delta)}\} \quad (46)$$

with

$$\Delta = \exp\{[g_{M,i}' + (1 - x_{M,i})^2 w_{M,ij}] / kT\} C_i^0 - \exp\{[g_{M,j}' + (x_{M,i})^2 w_{M,ij}] / kT\} C_j^0 \quad (47)$$

From  $X_{i,i}$  we can obtain  $X_{i,j}$  by combining (42) and (44):

$$X_{i,j} = \left(1 - \frac{X_{i,i}}{f_{M,i} C_i^0}\right) f_{M,j} C_j^0 \quad (48)$$

For interfacial monolayers, the calculation of the composition of surfactants  $x_i^0$  and other relevant parameters, such as  $w_{ij}^0$ ,  $g_i^0$  and  $\gamma$ ,  $x_{M,i}$ ,  $x_{M,j}$ ,  $a_i$ ,  $g_{M,i}$ ,  $w_{M,ij}$  and so forth are required as input parameters. Therefore, the modeling of interfacial monolayers can only be carried out when the modeling of mixed micelles is completed. For interfacial monolayers, the pseudo-phase separation condition holds, and thus eq 14 can be applied. For a binary surfactant system consisting of surfactant  $i$  and  $j$ , simul-

taneously applying (14) for surfactants  $i$  and  $j$  leads to the following expression:

$$(\gamma_i^0 - \gamma_j^0) + kT \ln \frac{(1 - x_{M,i})^{1/\alpha_j}}{(x_{M,i})^{1/\alpha_j}} + \{g_i^0 + (1 - x_i^0)^2 w_{ij}^0\} - \{[g_{M,i}' + (1 - x_{M,i})^2 w_{M,ij}]\} / a_i^0 - \{[g_j^0 + (x_i^0)^2 w_{ij}^0]\} - [g_{M,j}' + (x_{M,i})^2 w_{M,ij}] / a_j^0 = kT \ln \frac{(1 - x_i^0)^{1/\alpha_j}}{(x_i^0)^{1/\alpha_j}} \quad (49)$$

### III. Applications

In this section, the formalisms developed in the foregoing sections will be directly applied to ionic single-surfactant/mixed-surfactant systems to predict the dependence of the surface tension and cmc (or crc) on salt concentration/surfactant composition, respectively. To check the validation of the formalisms, the results will be confronted with the results from experiments directly. Before carrying out any prediction, some experimental details and procedures will be given as follows.

**A. Experimental. 1. Materials.**  $C_{12}EO_3$  with a purity of 99% was obtained from Nikko Chemical Co.; sodium dodecyl sulfate (SDS) from Sigma was 99% (G.C.) pure and was further purified by recrystallization. Water used was distilled. Sodium chloride was analytical grade, obtained from Sigma.

**2. Procedures.** Surface tension at the air/water interface was measured both by the ring method and the plate method of Wilhelmy.<sup>39</sup> For these different methods, a platinum ring and a ground glass Wilhelmy plate were used, respectively, cleaned by chromic acid and rinsing with distilled water. The platinum ring was further cleaned by flaming. A Kruss K12 automatic tensiometer was used for the ring method of measurement. Measurements by the plate method of Wilhelmy were carried out in a Cahn microbalance. The apparatus was calibrated with known weights and zeroed prior to use. A ground glass Wilhelmy plate was cleaned (chromic acid), and its length and thickness were measured to determine the perimeter of the area of the plate in contact with the solution and the plate constant,  $P_c$  ( $P_c$  = perimeter  $\times$  0.5g, where  $g$  is the acceleration due to gravity). The required solution was placed in a clean glass dish, thermostated at the given temperature, and carefully raised until it just contacted the glass plate. The counterweight was then increased until the apparatus rezeroed. Using this weight and the plate constant, it was possible to calculate the force applied to the plate.

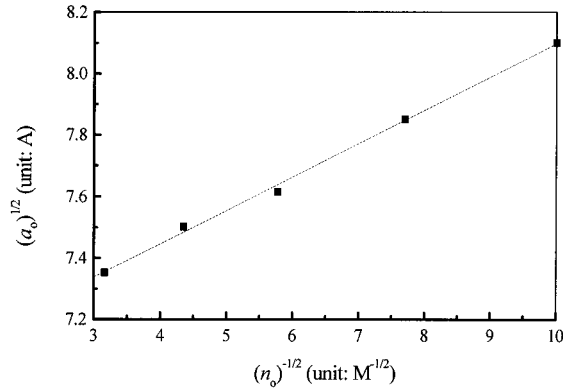
The results from both methods were compared with each other for a consistency check. It was found that the measurements by the Kruss K12 automatic tensiometer are quite inaccurate when the solution becomes viscous. In this case, the plate method of Wilhelmy by the Cahn microbalance is much more reliable to obtain accurate data.

#### B. Application to Single Ionic Surfactant Systems.

In this case, the change of the interfacial tension and cmc with the electrolyte concentration will contribute solely to the irregular effects (the regular effects do not occur for single-surfactant systems because of  $x_i = 1$ , cf. eq 11.) It is known from classical colloidal theories<sup>28</sup> that the change in the electrolyte concentration will directly alter the Debye length  $\kappa^{-1}$  (cf. eq 27) and the dissociation constant

(39) Evans, D. F.; Wennerström, H. *The colloidal domain where physics, chemistry, biology, and technology meet*; VCH: New York, 1994.





**Figure 2.** Relation between the headgroup area  $a_i$  of ionic surfactant molecules and the total electrolyte concentration  $n_0$ .  $(a_i)^{1/2}$  turns out to be proportional to  $(n_0)^{-1/2}$ , as indicated by eq 52. (For SDS aqueous solution systems,  $a_i$  and  $n_0$  were quoted from ref 39.)

of ionic surfactants. Therefore, this change affects the effective size of surfactant headgroups and the electrostatic double-layer structure. Consequently, the free energies associated with the shape, size, and charge density of micelles will respond to these changes correspondingly, giving rise to the partial free energy change described by  $g'_i$ . Rewriting (11) for this case, we have

$$\gamma a_i \approx \gamma_i^0 a_i^0 + (g_i^{0'} - g_{M,i}') + \left[ \frac{kT}{M} \ln \left( \frac{M}{C - X_i^0} \right) - \frac{kT}{M_i} \ln \left( \frac{M_i}{C - X_i^0} \right) \right] \quad (50)$$

For the cmc, one has<sup>34</sup>

$$\frac{1}{C_i^*} = \frac{1}{C_i^0} \exp \left( - \frac{g_{M,i}'}{kT} \right) \frac{\left[ \frac{C_i^0(1-\eta)}{M_i} \right]^{1/M_i}}{\left[ \frac{C_i^*(1-\eta)}{M_i} \right]^{1/M_i}} \quad (51)$$

Here,  $g_{M,i}'$  and  $g_i^{0'}$  can be calculated using eqs 29 or 37. The same as mixed-surfactant systems,  $g'_i$  includes  $g_r$  (int),  $g_i$  (def),  $g_i$  (steric), and  $g_i$  (ionic). To calculate these terms, eqs 21, 22, 24, and 26 can be applied directly.

We notice that as an input parameter in eqs 50 and 51, the size of surfactant headgroups  $a_i$  also changes with the electrolyte concentration. In practice, we can predict unknown  $a_i$  from experimental data available for the prediction of cmc and interfacial tension. Taking colloidal interactions into account, the size of ionic surfactant headgroups is to a large extent determined by the repulsion between two overlapping electrostatic double layers, and the characteristic thickness of double layers is determined by the Debye length  $\kappa^{-1}$ .<sup>28</sup> It follows that  $(a_i)^{1/2}$  can be approximately taken proportional to the Debye length  $\kappa^{-1}$  within a certain range of the salt concentration.

According to eq 27 ( $\kappa = ze(8\pi n_0/\epsilon kT)^{1/2}$ ), we have

$$(a_i)^{1/2} \cong B_0(n_0)^{-1/2} + B_1 \quad (52)$$

where  $B_0$  and  $B_1$  are constants for a given surfactant system. To demonstrate this relation, we plotted in Figure 2 the measured  $(a_i)^{1/2}$  against  $(n_0)^{-1/2}$  for SDS aqueous

**Table 1. Experimental Conditions and Input Parameters: Predicted and Measured cmc for SDS Aqueous Solutions at 25 °C<sup>a</sup>**

$C_{\text{NaCl}}$ (M)	$R_i$ (Å)	$M$	$p$	$g_{M,i}$ (int) (kJ)	$g_{M,i}$ (def) (kJ)	$g_{M,i}$ (steric) (kJ)	$g_{M,i}$ (ionic) (kJ)
0	12.0	22	0.259	0.803	-1.29	-0.0807	2.51
0.01	13.1	29	0.281	0.477	-0.858	-0.0508	1.84
0.03	13.9	35	0.300	0.239	-0.462	-0.0263	1.02
0.05	14.3	38	0.308	0.133	-0.267	-0.0149	0.570
0.1	14.8	42	0.319	0	0	0	0
0.3	15.5	48	0.333	-0.177	0.395	0.0209	-0.729

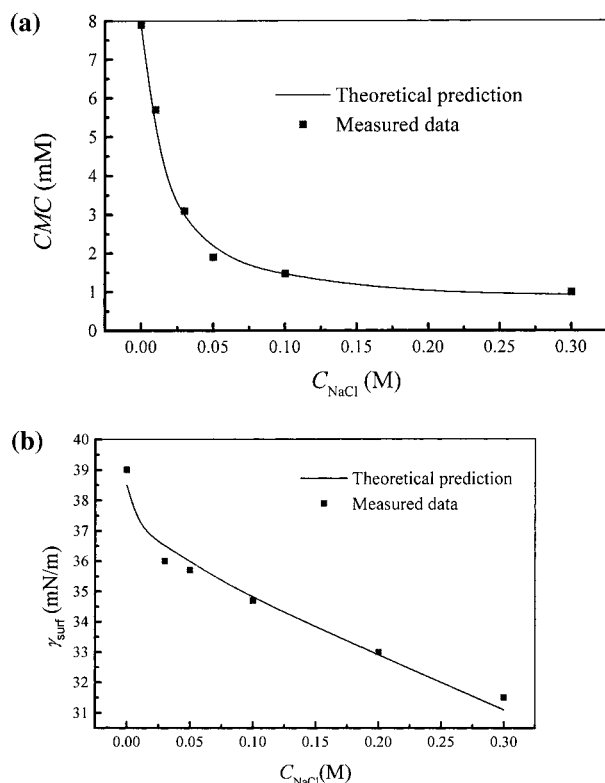
<sup>a</sup> Other parameters used in the calculations:  $\delta = 3.7$  Å,  $\gamma_0 \approx 51$  mN/m,  $l_{\text{max}} = 15.45$  Å,  $d^{\text{fol}} = 2.25$  Å,  $a^{p-h} = 25$  Å<sup>2</sup>,  $a^{p-T} = 21$  Å<sup>2</sup>,  $s = 3$ ;  $v_i = 323.3$  Å<sup>3</sup>.

solutions. As can be seen in the figure, the regression shows unambiguously the linear relation between  $(a_i)^{1/2}$  and  $(n_0)^{-1/2}$  as given by (52).

In the following, we will take SDS aqueous solutions as an example to predict the dependence of cmc and surface tension on the concentration of NaCl at 25 °C. In this case, the SDS solution with 0.1 M salt is taken as the reference. The cmc and surface tension at different salt concentrations will be predicted with respect to this reference. The minimization approach will be applied to evaluate  $R_i$  (see ref 28 for the details).

In addition to  $R_i$ ,  $\delta$  in eq 26 is determined by the molecular structure of surfactant headgroups and is taken to be 3.7 Å for SDS molecules. According to the geometry of the aggregates,  $a_0$  can be related to  $a_{M,i}$  by  $a_0 = [(R_i + \delta)/\delta]^{s-1} a_{M,i}$ . The interfacial tension between the SDS aggregate core–water interface  $\gamma_0$  is about 51 mN/m. The major experimental conditions and some input parameters and the free energy contributions are summarized in Table 1. Based on these, cmc's are predicted for the solutions with different salt concentrations, which are plotted in Figure 3a, together with experimental data. For the surface tension of the systems, the similar parameters and the predicted and experimental results are given in Table 2 and Figure 3b, respectively. It can be seen from both parts a and b of Figure 3 that the predicted and measured data are in very good agreement with each other. Although the simple predictions for the dependence of cmc on composition (we have here the concentration of salt  $C_{\text{NaCl}}$ ) can be found in the literature,<sup>34</sup> the precise prediction for  $\gamma_{\text{surf}}$  as a function of composition or  $C_{\text{NaCl}}$  has never been reported yet. It is surprising to see from both parts a and b of Figure 3 that the change of  $\gamma_{\text{surf}}$  with  $C_{\text{NaCl}}$  is somewhat different from cmc. The cmc decreases drastically with  $C_{\text{NaCl}}$  at very low salt concentrations and soon levels off at relatively high  $C_{\text{NaCl}}$ . In contrast, apart from the sharp drop at very low  $C_{\text{NaCl}}$ ,  $\gamma_{\text{surf}}$  keeps decreasing as  $C_{\text{NaCl}}$  increases with a certain range. Such a difference between cmc and  $\gamma_{\text{surf}}$  can be understood as follows: cmc is determined by the concentration at which the free surface of surfactant solutions is fully covered by surfactant monolayers,<sup>39</sup> whereas  $\gamma_{\text{surf}}$  is to a large extent determined by the packing of the surfactant molecules at the surface monolayers. With increasing salt concentrations, the saturation concentration of surfactant may not change much at relatively high concentrations. However, within a certain range, the molecular packing of SDS monolayers will be optimized continuously as  $C_{\text{NaCl}}$  increases. This, therefore, leads to a monotonic decrease of  $\gamma_{\text{surf}}$ .

**C. Phase Inversion Point of Mixed Surfactants.** In many cases, the interfacial tension minima  $(\gamma)_{\text{min}}$  can be achieved by mixing different types of surfactants (see

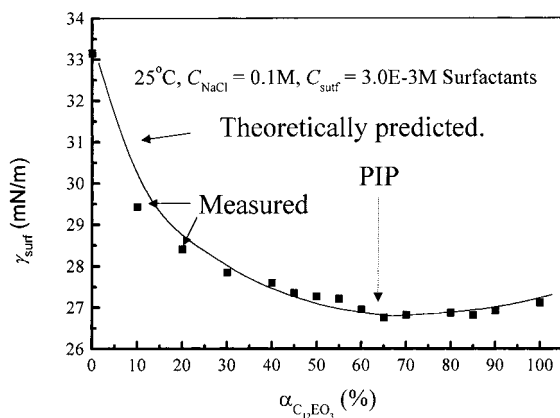


**Figure 3.** (a) Dependence of cmc of SDS solutions on the salt concentration  $C_{\text{NaCl}}$  at  $T = 25\text{ }^{\circ}\text{C}$ ; (b) surface tension of SDS solutions at cmc as a function of  $C_{\text{NaCl}}$  at  $T = 25\text{ }^{\circ}\text{C}$ . Solid lines: prediction; square points: measured points.

**Table 2. Experimental Conditions and Input Parameters: Predicted and Measured Surface Tensions  $\gamma$  at and above cmc for SDS Aqueous Solutions at  $25\text{ }^{\circ}\text{C}$ <sup>a</sup>**

$C_{\text{NaCl}}$ (M)	$g^{\text{p}}(\text{int})$ (kJ)	$g^{\text{p}}(\text{steric})$ (kJ)	$g^{\text{p}}(\text{ionic})$ (kJ)
0	1.11	-0.121	2.03
0.01	0.864	-0.0984	1.49
0.03	0.615	-0.0734	0.853
0.05	0.317	-0.0402	0.517
0.1	0	0	0
0.3	-0.340	0.0498	-0.835

<sup>a</sup> The experimental results obtained in this work.



**Figure 4.** Surface tension of mixed SDS/ $\text{C}_{12}\text{EO}_3$  solutions as a function of composition ( $\alpha_{\text{C}_{12}\text{EO}_3}$  is the mole fraction of  $\text{C}_{12}\text{EO}_3$  in the mixture of surfactants). The total surfactant concentration  $C_{\text{surf}} = 3\text{ mM}$ ,  $C_{\text{NaCl}} = 0.1\text{ M}$ ,  $T = 25\text{ }^{\circ}\text{C}$ . Solid line: predicted; square points: measured.

Figure 4). The composition where the interfacial tension minimum ( $\gamma_{\text{min}}$ ) occurs is known as the *phase inversion point* (PIP, cf. Figure 4).<sup>40,41</sup> The interfacial tension minima

**Table 3. Comparison between the Predicted and the Measured PIP and the Related Properties for Mixed SDS/ $\text{C}_{12}\text{EO}_3$**

	$\alpha_{\text{C}_{12}\text{EO}_3} _{\text{PIP}}^a$	$(\Delta\gamma_{\text{SDS}})_{\text{PIP}}$ (mN/m)	$(\gamma_{\text{mix}})_{\text{PIP}}$ (mN/m)
prediction	0.66	-6.3	26.9
measurement <sup>b</sup>	0.68	-6.4	26.8

<sup>a</sup> The total composition of  $\text{C}_{12}\text{EO}_3$  in the system at the PIP. <sup>b</sup> This work.

( $\gamma$ )<sub>min</sub> are to a large extent attributed to the change of structures at both the surfactant interface and surfactant aggregates in the mixing process. By changing the composition from a single-surfactant micellar solution to a mixed-surfactant solution where the phase inversion point occurs, surfactant aggregates will change from a spherical or rodlike to a planar shape or lamellar phase.<sup>40,41</sup> The molecular packing at the interfaces also changes correspondingly. Because of this change, no theories are capable of describing this nonideal mixing effect quantitatively. Here, the formalisms given above will be applied to estimate the composition of surfactants in the aggregates (or in the interfacial monolayer)  $x_i|_{\text{PIP}}$ , the total composition of surfactants in the system  $\alpha_i|_{\text{PIP}}$ , the interfacial tension lowering  $(\Delta\gamma)_{\text{min}}$ , and the mixed cac at the PIP for an SDS/ $\text{C}_{12}\text{EO}_3$  mixed-surfactant system.

The calculation of  $(\Delta\gamma_{\text{SDS}})_{\text{min}}$  is based on eq 11. The equation can be further simplified in this case, by taking into account the characteristics of surfactant aggregates when the phase inversion occurs. At PIPs, the compositions of surfactants at the interfaces and in surfactant aggregates are identical,  $x_i^{\text{g}} = x_{M,i}^{\text{a}}$ .<sup>41-44</sup> In addition, the planar aggregates have a very large aggregation number,  $M \rightarrow \infty$ . It follows then that eq 11 is rewritten in this case as

$$\gamma_{\text{min}} a_i \approx \gamma_i^0 a_i^0 + kT \ln \left( \frac{f_i}{f_{M,i}^0} \right) - \frac{kT}{M_i^0} \ln \left( \frac{M_i^0}{C - X_{i,i}^0} \right) \quad (53)$$

Mixed SDS/ $\text{C}_{12}\text{EO}_3$  solutions of 3 mM total surfactant concentration and 0.1 M NaCl were examined at  $25\text{ }^{\circ}\text{C}$ . Under the same condition, SDS forms spherical micellar solutions while  $\text{C}_{12}\text{EO}_3$  forms a dispersed lamellar phase. As the first step of the prediction, the parameters of surfactant molecules should be obtained. For SDS molecules, one can easily obtain from the molecular structure  $a_i^{0-h} = 25\text{ }^{\circ}\text{\AA}$  and  $\delta = 3.7\text{ }^{\circ}\text{\AA}$ . For single SDS solutions at 0.1 M NaCl, one has  $\text{cmc} = 1.47\text{ mM}$ .<sup>36,45</sup> In such solutions,  $R_i^0 = 14.78\text{ }^{\circ}\text{\AA}$ ,  $a_i^{\text{int}} = 65.6\text{ }^{\circ}\text{\AA}$ ,  $a_i^{\text{g}} \approx 35.4\text{ }^{\circ}\text{\AA}$ ,  $a_i^{\text{d}} = 100\text{ }^{\circ}\text{\AA}$ , and  $M^0 = 42$ .<sup>37</sup> Similarly to SDS, the parameters for  $\text{C}_{12}\text{EO}_3$  should also be given as follows:  $a_i^{0-h} = 24.3\text{ }^{\circ}\text{\AA}$ ,  $a_i^{\text{int}} = 36\text{ }^{\circ}\text{\AA}$ ,  $a_i^{\text{g}} = 36\text{ }^{\circ}\text{\AA}$ ,  $a_i^{\text{d}} = 36\text{ }^{\circ}\text{\AA}$ ,  $M^0 = \infty$ , and  $\text{cmc} = 0.015$  for  $T = 25\text{ }^{\circ}\text{C}$ .<sup>26</sup>

Following the procedures outlined in section II.B, the condition of the phase inversion and relevant properties at the PIP was estimated. Both the predicted and the measured data are given in Table 3.

(40) Aveyard, R.; Binks, B. P.; Clark, S.; Mead, J. *J. Chem. Soc., Faraday Trans. 1* **1986**, 82, 125.

(41) Aveyard, R.; Lawless, T. A. *J. Chem. Soc., Faraday Trans. 1* **1986**, 82, 2951.

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(43) Rosen, M. J.; Murphy, D. S. *J. Colloid Interface Sci.* **1986**, 110, 224.

(44) Gu, B.; Rosen, M. J. *J. Colloid Interface Sci.* **1989**, 129, 573.

(45) Hines, J. D. *J. Colloid Interface Sci.* **1996**, 180, 488.

Apart from the PIP, the surface tension of the mixed  $C_{12}EO_3$ /SDS solutions at other compositions  $\alpha_{C_{12}EO_3}$  ( $\alpha_{C_{12}EO_3}$  is the mole fraction of  $C_{12}EO_3$  in the mixture of surfactants) is also predicted based on the similar principle, as plotted in Figure 4, together with experimental results. All the predicted results are in very good agreement with the experimental ones.

#### IV. Discussion and Conclusions

In this section, we discuss the physical origin of the effect of mixing on the change of the interfacial energy. As mentioned in section II.A, the occurrence of the interfacial free energy is due to the specific free energy change by transferring a surfactant molecule from the surfactant solution or a micelle to the interfacial monolayer. From this point of view, the less the difference between micelles and interfacial monolayers, the lower the interfacial free energy. If no phase separation occurs, the mixing of different surfactants will result in decreases of the free energy in both micelles and the interfacial monolayer. Taking a corresponding single-surfactant system as a reference, the changes of free energy in micelles and in the interfacial monolayer have a counterimpact on the interfacial free energy (cf. Figure 1). As shown Figure 1, the decrease in the free energy of mixed micelles will enhance the interfacial free energy, whereas the free energy decrease of the mixed interfacial monolayer will lower the interfacial free energy. If the effect resulting from the mixed interfacial monolayer overrides the effect in mixed micelles [ $(\Delta g_{\text{mix}}^0 - \Delta g_{M,\text{mix}}^0) < 0$ ], a lowering in the interfacial free energy will be obtained. Otherwise, we will expect an increase in the interfacial free energy after mixing.

Concerning different contributions of irregular effects to the partial excess free energy in mixing micelles and the interfacial monolayer, the aggregate core–water interfacial free energy contribution turns out to be a countereffect for both the headgroup steric and the deformation contributions of the surfactant tail. An increase in the surface area per surfactant molecule results in a positive  $g_i(\text{int})$  (cf. eq 21) but negative  $g_i(\text{steric})$  and  $g_i(\text{def})$ . As a result, these effects cancel in part with each other.

In the case where an ionic surfactant occurs in the system, *ionic interactions will contribute significantly to the excess free energy of mixing*. It follows from our calculation that  $g_i(\text{ionic})$  turns out to be one of the major contributions to the partial irregular excess free energy. For the regular effects, as we have already mentioned in section II.B, the contributions from different surfactant tails can be neglected if the different tails belong to the same homologue. Therefore, the dipole and the ionic exchange energies contribute mainly to  $w_{ij}$ . The effect of ionic surfactants can be understood in different aspects. First, ionic interactions turn out to be one of the strongest interactions between surfactant molecules. This implies that mixing ionic surfactants with other types of surfactants will give rise to a large excess free energy. Second, the virtual size of ionic surfactant headgroups is much larger than the physical size of the groups due to electrostatic double layers. It follows from the formalisms given in section II.B that this will significantly enhance other contributions to the excess free energy for the mixing of ionic surfactants with other types of surfactants.

#### Appendix

For any surfactant system, at and above the cmc, the chemical potentials of surfactant molecules in mixed micelles and as monomers are equal. Following from eq 6, we then write a basic equation for mixed-micelle systems as

$$kT \ln X_{i,i} \approx (\mu_{M,i}^0 - \mu_{1,i}^0) + kT \ln(f_{M,i} x_{M,i}) + \frac{kT}{M} \ln\left(\frac{C - X_i}{M}\right) \quad (\text{A-1})$$

In the literature published so far,<sup>1,2,8,21,25,39</sup> the cmc has been defined in terms of a variety of properties of solutions, including surface tension, conductivity, and so forth. Theoretically, one of the most extensively used criteria identified the cmc as the surfactant concentration where monomers constitute 95% of the total surfactant.<sup>37,38</sup> In this report, we utilize this criterion to calculate the cmc of the mixed micellar solution. Based on this criterion, eq A-1 can be rewritten as

$$kT \ln(\gamma \alpha_i C^*) \approx (\mu_{M,i}^0 - \mu_{1,i}^0) + kT \ln(f_{M,i} x_{M,i}) + \frac{kT}{M} \ln\left[\frac{C^*(1 - \eta)}{M}\right] \quad (\text{A-2})$$

with  $\eta \sim 0.95$ . Taking  $x_{M,i}$  as unity, eq A-2 is then reduced to the single-surfactant case, for which we obtain

$$kT \ln(\eta C_i^0) \approx (\mu_{M,i}^0 - \mu_{1,i}^0) + \frac{kT}{M_i^0} \ln\left[\frac{C_i^0(1 - \eta)}{M_i^0}\right] \quad (\text{A-3})$$

where  $C_i^0$  denotes the cmc for single-surfactant  $i$ . Substituting (A-3) into (A-2) yields

$$\ln(\alpha_i C^*) \approx \ln(C_i^0) + \ln(f_{M,i} x_{M,i}) + \frac{1}{M} \ln\left[\frac{C^*(1 - \eta)}{M}\right] - \frac{1}{M_i^0} \ln\left[\frac{C_i^0(1 - \eta)}{M_i^0}\right] \quad (\text{A-4})$$

The above equation provides a basic link between the mixed cmc and the cmc of single-surfactant systems.

Substituting eq A-3 into eq A-1 and applying the pseudo-phase separation condition yields

$$\ln(X_i^1) \approx \ln(C_i^0) + \ln(f_{M,i} x_{M,i}) \quad (\text{A-5})$$

or

$$X_i^1 \approx C_i^0 f_{M,i} x_{M,i} \quad (\text{A-6})$$

Based on the concentration constraint, the following relation should be satisfied:

$$\alpha_i C \approx X_{M,i} + X_{1,i} \quad (\text{A-7})$$

Combining (A-6) and (A-7), we then have

$$\alpha_i C \approx X_{M,i} + C_i^0 f_{M,i} x_{M,i} \quad (\text{A-8})$$



which can be rewritten as

$$\frac{\alpha_i C}{x_{M,i}} \approx \frac{X_{M,i}}{x_{M,i}} + C_i^0 f_{M,i} \quad (\text{A-9})$$

According to the definition of  $X_{M,i}$  ( $= N_{\text{micelle}} M x_{M,i} / V$ ;  $N_{\text{micelle}}$  is the number of micelles in the system, and  $V$  is the volume of the system), surfactants  $i$  and  $j$  are related by

$$\frac{X_{M,i}}{x_{M,i}} = \frac{X_{M,j}}{x_{M,j}} \quad (\text{A-10})$$

It then follows from (A-8) that

$$C \left( \frac{\alpha_i}{x_{M,i}} - \frac{\alpha_j}{x_{M,j}} \right) \approx C_i^0 f_{M,i} - C_j^0 f_{M,j} \quad (\text{A-11})$$

Rearranging (A-11), we obtain

$$x_{M,i} = \frac{\alpha_i C}{f_{M,i} C_i^0 - f_{M,j} C_j^0 + \alpha_j C / x_{M,i}} \quad (\text{A-12})$$

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