Molecular Thermodynamic Model for Gibbs Energy of Mixing of Nonionic Surfactant Solutions

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A segment-based molecular thermodynamic model for the Gibbs energy of polymer solutions or oligomer solutions is used to represent the Gibbs energy of mixing for aqueous nonionic surfactant solutions. In contrast to the mass-action models and pseudophase models, which are often discussed in the literature, the Gibbs-energy model provides an explicit account of the solution nonideality, including activity coefficients of monomeric amphiphiles in the aqueous phase. The equilibrium between monomeric amphiphiles and micellar amphiphiles is described by the equal-activity relationship. The Gibbs-energy model makes it possible to use a well-accepted molecular thermodynamic framework to correlate and represent phase behaviors of aqueous nonionic surfactant solutions.

Introduction

As shown in Figure 1, amphiphilic molecules (amphiphiles or surfactants) are often characterized by the existence of two molecular moieties: one hydrophilic moiety (the "head") with a strong affinity to water molecules and one hydrophobic moiety (the "tail") with a strong repulsion to water molecules. This ambivalence of amphiphile molecules toward aqueous environments leads to the micellization (Figure 2) that is not exhibited by solutions of simpler molecules and water (Tanford, 1980; Rosen, 1989).

Numerous publications have summarized well two major thermodynamic treatments that are often employed to describe the phase behavior of surfactant solutions (Nakagaki and Handa, 1984; Scamehorn, 1986; Cox and Benson, 1986; Schick, 1987; Zana, 1987; Clint, 1992; Holland and Rubingh, 1992; Ogino and Abe, 1993). The pseudo-phase treatment suggests that micellization be represented as a phase-separation phenomenon similar to the vapor–liquid phase equilibrium of the air–water system or to the liquid–liquid phase equilibrium of aqueous–organic mixtures (see Figure 3). The micelles would represent the vapor phase or the second liquid phase. Employing an appropriately defined standard state, the critical micellar concentration (cmc) values provide a measure of the chemical potential change during the micellization process (Hoffmann and Ulbricht, 1986):

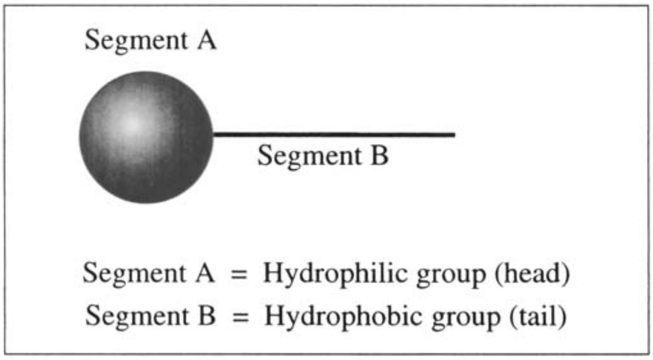

Figure 1. Common representation of a surfactant.

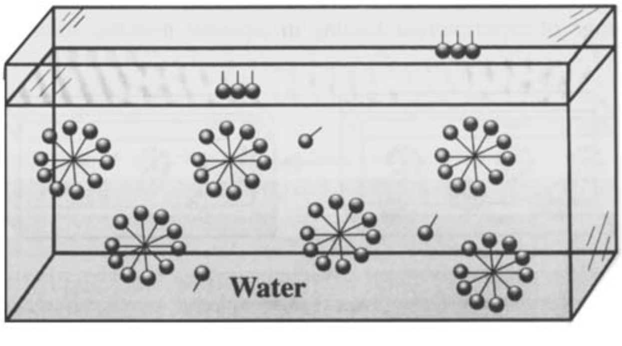

Figure 2. Surfactants form colloidal clusters called micelles.

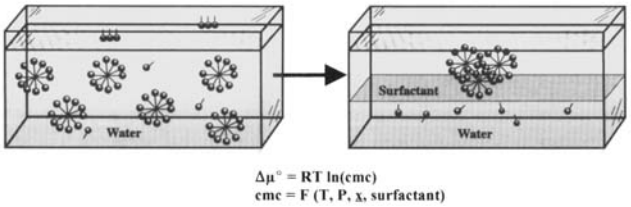

Figure 3. Pseudo-phase treatment.

$$\Delta \mu^o = RT \ln(\text{cmc}). \quad (1)$$

The mass-action treatment suggests that micelles be considered as chemical aggregates of amphiphiles bound together as a result of multiple chemical equilibria (Hoffmann and Ulbricht, 1986). By applying the mass-action model to the micellar aggregation process (see Figure 4), one can calculate the chemical equilibrium constant K for the aggregation step according to

$$A_{n-1} + A_1 \overset{K}{\rightleftharpoons} A_n \quad (2)$$

$$K = \frac{C_{A_n}}{C_{A_1} * C_{A_{n-1}}} \quad (3)$$

$$K = \frac{1}{\text{cmc}} \quad (4)$$

$$K = e^{-\Delta \mu^0 / RT}. \quad (5)$$

Taking advantages of low concentrations of monomeric amphiphiles in aqueous solutions, these two conventional treatments often assume unity activity coefficients for the monomeric amphiphiles. The investigation on the driving force for micelle formation was then relegated to "thermodynamics of micellization." Various empirical and semiempirical models were proposed to represent cmc or Gibbs energy of micellization (Cox and Benson, 1986; Blankschtein, 1986; van Lent and Scheutjens, 1989; Rosen, 1989; Puvvada and Blankschtein, 1990 and 1992).

Blankschtein (1986) proposed a "molecular thermodynamic" approach that blends a molecular model for Gibbs energy of micellization with a thermodynamic theory of phase behavior and phase separation of isotropic micellar solutions. The molecular model attempts to incorporate the effects of surfactant molecular architecture and solvent properties on the physical factors that contribute to micelle formation and growth. Although the model was able to "describe a wide range of experimental finding in aqueous micellar solutions of nonionic surfactants," the model suffers from its "thought" process to "visualize" the reversible formation of micelles from individual surfactants. Specifically, the "thought" process decomposes the Gibbs energy of micellization into six contributions: (1) electrostatic plus bond breaking; (2) hydrophobic; (3) interfacial; (4) configurational; (5) interfacial plus bond forming plus steric; and (6) electrostatic. Some of these steps could be viewed as ill-understood as the micellization process in question and they could only be estimated from experimental data or with empirical or semiempirical correlations. Furthermore, the model does not take advantage of the vast amount of molecular thermodynamic modeling work carried out in the past decades for solutions of nonelectrolytes, electrolytes, polymers, and so forth (Prausnitz, 1979).

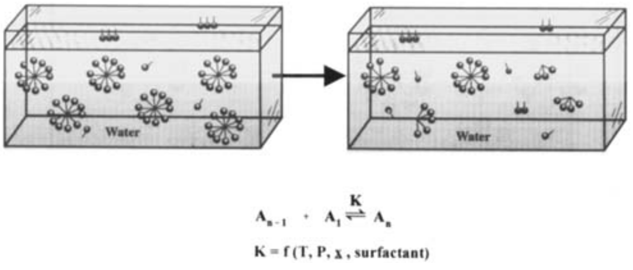

Figure 4. Mass-action treatment.

The self-consistent field theory of Scheutjens and Fleer (1985) for the adsorption of homopolymers has been modified to study the adsorption of block copolymers from a select solvent (van Lent and Scheutjens, 1989). With this extension it is possible to calculate the critical micelle concentration and to show the influence of the self-aggregation of surfactant block copolymers on their adsorption behavior. The cmc is determined from a "small system thermodynamics" of Hall and Pethica (1976). The model employs an extended Flory–Huggins expression for the chemical potential of surfactant block copolymers. The excess Gibbs energy of a "small" micellar solution is computed from an entropy term and a Gibbs energy of micellization term with Flory–Huggins interaction parameters.

While the micellization models are designed to describe the propensity of surfactants to form micelles, a more profitable alternative would be to focus directly on the main contributing factors to the nonideality (or activity coefficients) of monomeric amphiphiles in solution. After all, it is the nonideality of monomeric amphiphiles in aqueous solutions that is the key driving force for micelle formation.

In industrial applications, there can be monomers, solvents, electrolytes, polymers, and other molecules present in surfactant solutions (Shinoda and Arai, 1965; Crook et al., 1965; Wasan et al., 1988; Piirma, 1992). Molecular thermodynamic models have been extensively employed to model solution-phase behaviors of nonelectrolytes, electrolytes, zwitterions, polymers, and so forth (Prausnitz, 1979; Chen and Evans, 1986; Chen et al., 1989; Chen, 1993). These models provide semiempirical thermodynamic functions to correlate experimental data, and large databases for the model parameters have been established from fitting vast amounts of phase equilibrium data (Fredenslund et al., 1975; Gmehling et al., 1981a). Furthermore, the theoretical basis of these molecular thermodynamic models provides helpful insights and better understanding for the complex phase behaviors in this study without introducing excessive modeling complexities. In short, it should be highly advantageous if the surfactant solution nonideality could be described with established molecular thermodynamic models.

It is the objective of this study to develop a Gibbs energy of mixing expression for surfactant solutions based on established molecular thermodynamic models. The aim is not to demonstrate the strength or weakness of various micellization models proposed for aqueous surfactant solutions. Rather, the aim is to show the feasibility of modeling the phase behavior of surfactant solutions with existing molecular thermodynamic modeling methodology. Specifically we apply the segment-based local-composition Gibbs-energy expression of Chen (1993) to account for the solution nonideality of aqueous nonionic surfactant solutions. From the Gibbs-energy expression, we then derive activity-coefficient expressions for monomeric amphiphiles and determine critical micellar concentrations from the activity coefficients. Such a Gibbs-energy model should provide a practical thermodynamic framework for chemical engineers to correlate and represent phase behaviors of aqueous nonionic surfactant solutions.

In lieu of treating micellar amphiphiles as pseudophases or chemical aggregates, we propose that micellar amphiphiles be treated as a special conformation of the surfactants dissolved in aqueous solution. These micellar amphiphiles exist neither as a separate liquid phase (as proposed by the pseudophase treatment) nor as a distinct chemical species resulting from multiple chemical equilibria (as proposed by the mass-action treatment). Rather, micellar amphiphiles are dissolved physical aggregates that resulted from thermodynamically preferred physical rearrangements of monomeric amphiphiles in aqueous solutions. In other words, surfactants may exist in two molecular conformations with which amphiphiles are solubilized in aqueous solutions: monomeric amphiphiles and micellar amphiphiles. Unlike the pseudophase treatment, we make no assumptions on the micellar size nor the aggregation number. The equilibrium of monomeric amphiphiles and micellar amphiphiles should follow the equal-activity relationship, and their equilibrium distributions should correspond to the minimal Gibbs energy of the solution.

Although we focused this study on the phase behavior of aqueous nonionic-surfactant solutions, the model can be further extended to represent the Gibbs energy of ionic-surfactant solutions by properly taking into account both the short-range physical interactions and the long-range electrostatic interactions derived from the existence of ionic charges on ionic-surfactant molecules.

Nature of Amphiphilic Molecules

To successfully model the phase behaviors of amphiphilic solutions, the challenge is to properly account for the solution nonideality derived from the molecular architecture of amphiphiles and their defining physical interactions in the aqueous environment. As dissolved aqueous species, the chemical potentials of either monomeric amphiphiles or micellar amphiphiles are determined by the number, types, and sequence of segments that make up the molecules and how the segments interact with their surrounding species.

As shown in Figure 1, one may conveniently consider a simplest amphiphile molecule as one with two distinct segments, a hydrophilic segment A and a hydrophobic segment B. More than two segments may be present in more complex and larger amphiphile molecules. In the amphiphile molecule AB, each segment exerts unique physical interactions with its immediate neighboring species or segments, while each hydrophilic segment is chemically bound to a hydrophobic segment and vice versa.

When the two-segment amphiphiles are dissolved in excess water as monomeric amphiphiles, both segments A and segments B are exposed to and surrounded by water molecules (see Figure 5). The physical interactions of the amphiphile system are characterized by the segment-A-water interaction and the segment-B-water interaction. The segment-A-water interaction represents a stabilizing factor since segments A are hydrophilic. On the other hand, the segment-B-water interaction represents a destabilizing factor since segments B are hydrophobic. The segment-A-water interaction is attractive in nature; the segment-B-water interaction is repulsive in nature.

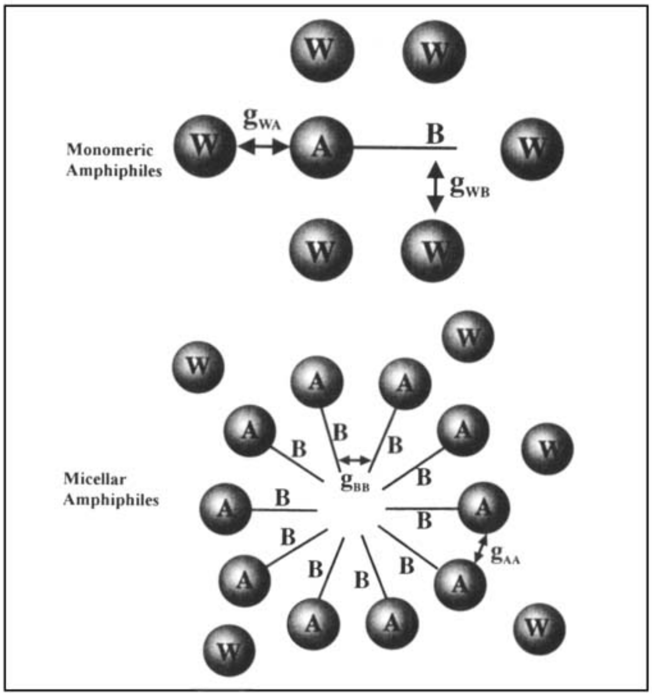

Figure 5. Nature of amphiphilic molecules.

When the amphiphiles form micellar aggregates, aggregated segments A and segments B can be approximated as effectively removed from the aqueous environment (see Figure 5). Both segments A and B are now placed in "idealized states," because segments A are surrounded by segments A and segments B are surrounded by segments B. In such "idealized states," the physical interactions of the micellar amphiphiles are characterized by the segment-A-segment-A interaction and the segment-B-segment-B interaction. In our treatment, this "idealized state" corresponds to the reference state chosen for the segments.

As to be discussed later, it is a reasonable approximation to assume segment B is totally removed from water when in micelles due to the repulsive nature of segment-B-water interaction. On the other hand, it is a severe approximation to assume that segment A is totally removed from water when in micelles. However, due to the hydrophilic nature of the segment-A-water interaction, the contribution of this segment-A-water interaction to the nonideality of the solution is less significant. In other words, this severe approximation is not critical to the success of the model.

Segment-based Local Composition Model

The proposed molecular thermodynamic model for the Gibbs energy of mixing of nonionic-surfactant solutions is the segment-based local composition model presented by Chen (1993) for the Gibbs energy of polymer solutions. The model was originally developed to represent the configurational entropy contribution and the weak physical interaction contribution of solutions with nonionic polymers or oligomers. This molecular thermodynamic model represents a synergistic combination of the Flory–Huggins description for the configurational entropy of mixing for molecules of different sizes and the nonrandom two-liquid (NRTL) theory for the local composition contribution from mixing solvents and polymer segments. It reduces to the well-known NRTL equation (Renon and Prausnitz, 1968) if polymers are removed from the system.

The development of the polymer NRTL equation followed the idea that the local composition concept should be applied to the individual segments and solvent molecules, not the macromolecule as a whole. This segment-based local composition approach reflects the hypothesis that each segment should independently exert unique physical interactions with its immediate neighboring solvent species or segments. Such physical interactions of segments determine the most favorable local compositions around each segment.

The NRTL model has been successfully used for the excess Gibbs energy of chemical systems, including nonelectrolytes (Renon and Prausnitz, 1968), electrolytes (Chen and Evans, 1986; Mock et al., 1986), zwitterions (Chen et al., 1989; Zhu et al., 1990), and polymers (Chen, 1993). Of particular significance to this current study are the recent successes of the NRTL model in representing the "hydrophobicity scale" of amino acid residues (Chen et al., 1992), the Gibbs energy for the formation of α-helical structure in homopolypeptides and heteropolypeptides (Chen et al., 1992; Zhu et al., 1992), and both intramolecular docking and intermolecular docking of helical structures in polypeptide chains (Chen et al., 1995). The NRTL model provides a practical thermodynamic framework to account for the intramolecular and intermolecular physical interactions that govern phase behaviors of complex, but structured, macromolecular systems.

The polymer NRTL model treats the Gibbs energy of mixing for a surfactant solution as the sum of the local composition contribution and the configurational entropy of mixing:

$$\frac{\Delta G}{RT} = \frac{\Delta G^{lc}}{RT} - \frac{\Delta S^{\text{config}}}{R}. \tag{6}$$

The Flory–Huggins entropy of mixing expression accounts for the configurational entropy of mixing water and monomeric amphiphiles as oligomers.

$$\frac{-\Delta S^{\text{config}}}{R} = \frac{-\Delta S^{FH}}{R} = \Sigma_I n_I \ln \phi_I (\Sigma_J n_J m_J), \tag{7}$$

where

$$\phi_I = \frac{n_I m_I}{\Sigma_J n_J m_J}. \tag{8}$$

Note that m_I is the ratio of the volume of amphiphile I to that of a reference solvent. As a dimer, m_I could be approximated as 2. For larger amphiphile molecules, m_I should be the number of segments that constitute the surfactant oligomers.

The NRTL equation is the basic expression to account for the local composition contribution. The reference states for the segment-based NRTL equation are pure liquids for solvents and hypothetical liquid-segment aggregate states for segments. In such hypothetical liquid aggregate states, all segments are surrounded by segments of the same type. The reference states for solvents are characterized by the solvent–solvent physical interactions. The reference states for segments are characterized by the segment–segment physical interactions. For amphiphile molecules, this reference state for segments closely resembles that of the micellar aggregate state.

Micellar amphiphiles exist as aggregates with the aggregation number in the range of tens to thousands. Similar to monomeric amphiphiles, micellar amphiphiles are fully dissolved in the aqueous phase with various forms of micelles such as spheroidal, cylindrical, or disclike in shape. Due to the relatively structured form of micelles, the entropy of mixing of water and micellar amphiphiles can be neglected as the quantity is insignificant in comparison to the entropy of mixing of water and monomers, monomeric amphiphiles, or chainlike polymeric species. Likewise, the enthalpy of mixing of water and micelles can be treated as negligible since only the hydrophilic segment of micellar amphiphiles are in physical contact with water. In other words, micellar amphiphiles make little contribution to the Gibbs energy of mixing of water and surfactants.

For a system with multiple solvents and multiple monomeric amphiphiles with multiple segments, the expression for the local composition contribution is as follows:

$$\frac{\Delta G^{lc}}{RT} = \frac{\Delta G^{\text{NRTL}}}{RT} = \Sigma_s n_s \frac{\Sigma_j X_j G_{js} \tau_{js}}{\Sigma_j X_j G_{js}} + n_p \Sigma_i r_{i,p} \frac{\Sigma_j X_j G_{ji} \tau_{ji}}{\Sigma_j X_j G_{ji}}. \tag{9}$$

Here i represents the segments in polymer or oligomer species p, and j stands for all segments and all solvents.

Note that the local composition concept is applied to solvents and segments, but not to polymer species. Following the NRTL convention, the effective local mole fractions X_{ji} and X_{ii} of species j and i, respectively, in the immediate neighborhood of a central species i are related by

$$\frac{X_{ji}}{X_{ii}} = \left(\frac{X_j}{X_i}\right) G_{ji}, \tag{10}$$

where

$$X_i = \frac{x_I r_{i,I}}{\Sigma_J \Sigma_j x_J r_{j,J}} \tag{11}$$

$$G_{ji} = \exp(-\alpha_{ji} \tau_{ji}) \tag{12}$$

$$\tau_{ji} = \frac{g_{ji} - g_{ii}}{RT}. \tag{13}$$

Here the species i and j can be solvent molecules or segments; α is the nonrandomness factor; and the quantities g_{ji}

and g_{ii} are, respectively, the energies of interaction between j-i and i-i pairs of species.

The model for the Gibbs energy of mixing can be obtained from combining Eq. 7 and Eq. 9:

$$\frac{\Delta G}{RT} = \Sigma_s n_s \frac{\Sigma_j X_j G_{js} \tau_{js}}{\Sigma_j X_j G_{js}} + n_p \Sigma_i r_{i,p} \frac{\Sigma_j X_j G_{ji} \tau_{ji}}{\Sigma_j X_j G_{ji}} + \Sigma_I n_I \ln \phi_I (\Sigma_I n_I m_I). \quad (14)$$

The excess Gibbs energy expression can be obtained by subtracting the ideal entropy of mixing from Eq. 14:

$$\frac{\Delta G^{ex}}{RT} = \Sigma_s n_s \frac{\Sigma_j X_j G_{js} \tau_{js}}{\Sigma_j X_j G_{js}} + n_p \Sigma_i r_{i,p} \frac{\Sigma_j X_j G_{ji} \tau_{ji}}{\Sigma_j X_j G_{ji}} + \Sigma_I n_I \ln \left(\frac{\phi_I}{x_I} \right) (\Sigma_I n_I m_I). \quad (15)$$

The activity coefficient of each species I in the solution can also be considered as the sum of two contributions:

$$\ln \gamma_I = \ln \gamma_I^{\mathrm{NRTL}} + \ln \gamma_I^{FH} \quad (16)$$

where

$$\ln \gamma_{I=s}^{\mathrm{NRTL}} = \frac{\Sigma_j X_j G_{js} \tau_{js}}{\Sigma_k X_k G_{ks}} + \Sigma_j \frac{X_j G_{sj}}{\Sigma_k X_k G_{kj}} \left(\tau_{sj} - \frac{\Sigma_k X_k G_{kj} \tau_{kj}}{\Sigma_k X_k G_{kj}} \right) \quad (17)$$

$$\ln \gamma_{I=p}^{\mathrm{NRTL}} = \Sigma_i r_{i,p} \left[\frac{\Sigma_j X_j G_{ji} \tau_{ji}}{\Sigma_k X_k G_{ki}} + \Sigma_j \frac{X_j G_{ij}}{\Sigma_k X_k G_{kj}} \left(\tau_{ij} - \frac{\Sigma_k X_k G_{kj} \tau_{kj}}{\Sigma_k X_k G_{kj}} \right) \right] \quad (18)$$

$$\ln \gamma_i^{FH} = \ln \left(\frac{\phi_I}{x_I} \right) + 1 - m_I \Sigma_J \left(\frac{\phi_J}{m_J} \right). \quad (19)$$

The NRTL term in Eq. 18 is additive in terms of individual segment contributions to the logarithm of the monomeric amphiphile activity coefficient in aqueous solutions.

It should be noted that, although the NRTL model has been successfully applied to represent the nonideality of electrolyte systems (Chen and Evans, 1986; Mock et al., 1986), the polymer NRTL model used in this work is not applicable to molecules with ionic charges.

Application to Surfactant Solutions

The model requires two binary interaction parameters, τ_{ij} and τ_{ji}, for each of the solvent–solvent interaction pairs, the solvent–segment interaction pairs, and the segment–segment interaction pairs. These binary interaction parameters become correlation variables in treating the phase behaviors of surfactant solutions. The nonrandomness factor (α), in the range of 0.2 to 0.3, has no significant impact on the behavior of the model. In this work, it is fixed at 0.3.

For the simplest amphiphile molecules AB, the model provides two binary interaction parameters for the segment-A–water interaction pair, τ_{Aw} and τ_{wA}, and two binary interaction parameters for the segment-B– water interaction pair, τ_{Bw} and τ_{wB}. As shown in Eq. 13, these τ's are directly related to the pairwise physical interaction energy, g's. The more negative the g's are, the stronger the physical adhesive (or attractive) interactions. The more positive the g's are, the stronger the repulsive interactions. Typically, hydrophilic groups exhibit strong adhesion with hydrophilic groups and hydrophobic groups exhibit strong adhesion with hydrophobic groups. Also, hydrophilic groups exhibit strong repulsion with hydrophobic groups and vice versa. Therefore, positive values for the τ's signify repulsive interactions, while negative values for the τ's signify attractive interactions. It is expected that τ_{wA} and τ_{Aw} could be either small negative numbers or small positive numbers since both water and segment A are hydrophilic in nature. Since water is hydrophilic and segment B is hydrophobic, τ_{wB} and τ_{Bw} should be large positive numbers. Strong repulsive interactions exist between these two interacting entities.

The water–methanol binary system is an example of an interaction pair for water–hydrophilic segment interactions. Gmehling et al. (1981a) recommended τ_{wA} and τ_{Aw} to be $845.2/RT$ and $-253.88/RT$, respectively ($\alpha = 0.2994$), around room temperatures. Another example is the water–1,2-ethanediol binary system. Again, Gmehling et al. (1981b) reported τ_{wA} and τ_{Aw} to be $16.67/RT$ and $41.79/RT$ at 80°C, respectively ($\alpha = 0.3043$). Note that R is the gas constant ($R = 1.987$ cal/mol K) and the temperature T is in K.

The water–hexane binary system is an example of an interaction pair for water–hydrophobic segment interactions. Along with extensive compilation of liquid–liquid equilibrium data for many binary systems, Sorensen and Arlt (1979a) reported τ_{wB} and τ_{Bw} to be $3{,}279.6/T$ and $1{,}853.3/T$ at 25°C, respectively, (with $\alpha = 0.2$), for the water–hexane binary system. Sorensen and Arlt (1979b) also reported τ_{wB} and τ_{Bw} to be $3{,}792.6/T$ and $1{,}876.0/T$ at 25°C, respectively, (with $\alpha = 0.2$) for the water–heptane system.

Figure 6 shows activity coefficients of dimer amphiphile AB in an aqueous solution from infinite dilution to 1 molal. The amphiphile system has a set of assumed values for the τ's ($\tau_{wA} = 0$, $\tau_{Aw} = -2$, $\tau_{wB} = 12$, $\tau_{Bw} = 6$). The computed infinite

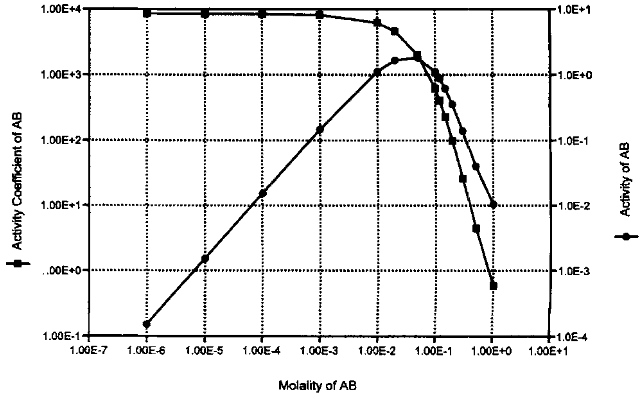

Figure 6. Activity coefficients of dimer amphiphile *AB* in aqueous solutions from infinite dilution to 1 molal.

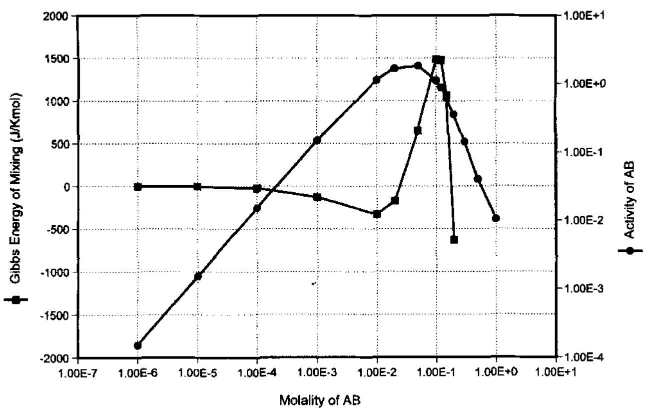

Figure 7. Gibbs energy of mixing of dimer amphiphile *AB* in aqueous solutions from infinite dilution to 1 molal.

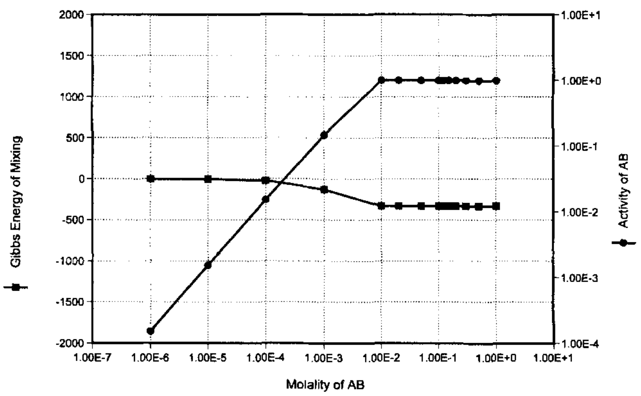

Figure 8. Gibbs energy of mixing of dimer amphiphile *AB* in aqueous solutions with micelles formed at critical micelle concentration.

dilution-activity coefficient for AB is about 8,400, while the contribution to the activity coefficient of AB from the Flory–Huggins term is a nearly constant 0.043. It clearly shows that the activity coefficients of AB are dominated by the local composition term, which more than compensates for the entropic effect derived from the Flory–Huggins term. The activity coefficient of the amphiphile would remain very high at the dilute amphiphile-concentration range. It would then drop precipitously with the increase of amphiphile concentration. On the other hand, the activity of amphiphile AB first increases with concentration, and then reaches a maximum. As shown in the next section, monomeric amphiphile would form micelles, as the amphiphile activity exceeds unity at the critical micellar concentration (about 8.6×10^{-3} m or mole fraction of 0.000156).

Figure 7 shows the Gibbs energy of mixing for dimer amphiphile AB in an aqueous solution from infinite dilution to 1 molal. Interestingly, at the critical micellar concentration of 8.6×10^{-3} m, the Gibbs energy of mixing reaches a local minimum. It points out a phase instability region. Figure 8 shows the corresponding Gibbs energy of mixing with micelles formed when the amphiphile activity reaches unity.

Critical Micellar Concentration

At critical micellar concentration (cmc), the monomeric amphiphile concentration at the onset of micelle formation, the chemical potential of monomeric amphiphiles equals that of micellar amphiphiles. As mentioned before, we have chosen the reference state as the hypothetical segment aggregate state for each segment. In this hypothetical aggregate state, all segments are surrounded by segments of the same type. In other words, this hypothetical segment aggregate state corresponds to the micellar amphiphile state for single surfactant systems. Therefore, for single surfactant systems, the activities of the two conformations of amphiphiles should be the same at cmc and their activities should be in unison.

$$a_{AB}^{\mathrm{cmc}} = a_m = 1, \tag{20}$$

where

$$a_{AB}^{\mathrm{cmc}} = x_{AB}^{\mathrm{cmc}} \gamma_{AB}^{\mathrm{cmc}} \tag{21}$$

Activity coefficients of monomeric amphiphiles are functions of surfactant segment compositions (surfactant architecture) and solvent compositions. Therefore, cmc is also a function of surfactant segment compositions and solvent compositions. The polymer NRTL model should provide us with a thermodynamic framework to account for the impact of segment compositions and solvent compositions on cmc's for surfactant solutions.

The most extensively investigated nonionic surfactants are those having a polyoxyethylene chain as the hydrophilic group (Sjoblom et al., 1987). These polyoxyethylene alcohol surfactants are often referenced as C_iE_j. Here i is the number of alkyl carbon and j is the number of oxyethylene segment. Extensive cmc values have been reported in the literature (Mukerjee and Mysels, 1971). Here we use the cmc values compiled by Hinz (1986) for selected C_iE_6 homologs. Increasing the chain length of the hydrophobic alkyl segment C would enhance the repulsive hydrocarbon–water interaction. This increases the tendency to push the hydrocarbons out of the aqueous medium, and it therefore leads to a cmc depression. This tendency should be reflected by the increase in the number of the hydrophobic alkyl segment C and the values of τ_{wC} and τ_{Cw}. Hinz (1986) also compiled cmc values for selected $C_{10}E_j$ and $C_{12}E_j$ homologs. For these surfactants the number of segment E (oxyethylene) and the attractive segment-E–water interactions would determine the cmc values. These attractive segment-E–water interactions should be reflected by the values of τ_{wE} and τ_{Ew}.

From fitting vapor–liquid phase equilibrium data of binary water–polyethylene glycol (PEG) system, Chen (1993) reported values of τ_{wE} and τ_{Ew} for oxyethylene segment at various temperatures. In this work, we refitted all the available data for water–PEG ($MW = 300$) binary systems at 30°C, 50°C, and 65°C. The PEG polymer with $MW = 300$ is treated as a 7-mer. The resulting values for the binary parameters are as follows:

$$\tau_{wE} = 1.957 - \frac{936.2}{T} \tag{22}$$

$$\tau_{Ew} = -4.304 + \frac{2{,}169.1}{T}. \tag{23}$$

We also fitted the liquid–liquid equilibrium data reported

Table 1. Predicted cmc Values at 25°C for Selected Surfactants with Different Constitution of the Hydrophobic Alkyl Chain

			cmc (mol/L)			
Surfactant Name	Formula	Abbr.	Exp*	NRTL**	NRTL†	UNIFAC
n-Butyl-hexaoxyethylene-alcohol	$C_4H_9(OC_2H_4)_6OH$	C_4E_6	7.8×10^{-1}	n.a.	8.71×10^{-1}	n.a.
n-Hexyl-hexaoxyethylene-alcohol	$C_6H_{13}(OC_2H_4)_6OH$	C_6E_6	7.0×10^{-2}	n.a.	4.39×10^{-2}	3.44×10^{-4}
n-Octyl-hexaoxyethylene-alcohol	$C_8H_{17}(OC_2H_4)_6OH$	C_8E_6	9.9×10^{-3}	2.56×10^{-3}	5.15×10^{-3}	5.09×10^{-5}
n-Decyl-hexaoxyethylene-alcohol	$C_{10}H_{21}(OC_2H_4)_6OH$	$C_{10}E_6$	9.0×10^{-4}	1.01×10^{-4}	6.67×10^{-4}	7.37×10^{-6}
n-Dodecyl-hexaoxyethylene-alcohol	$C_{12}H_{25}(OC_2H_4)_6OH$	$C_{12}E_6$	8.7×10^{-5}	4.05×10^{-6}	8.82×10^{-5}	1.04×10^{-6}
n-Tetradecyl-hexaoxyethylene-alcohol	$C_{14}H_{29}(OC_2H_4)_6OH$	$C_{14}E_6$	1.0×10^{-5}	1.64×10^{-7}	1.17×10^{-5}	1.46×10^{-7}
n-Hexadecyl-hexaoxyethylene-alcohol	$C_{16}H_{33}(OC_2H_4)_6OH$	$C_{16}E_6$	1.3×10^{-6}	6.63×10^{-9}	1.56×10^{-6}	2.01×10^{-8}

*Experimental data taken from Hinz (1986).
**NRTL parameters regressed from VLE/LLE data of homooligomers.
†NRTL parameters regressed from cmc data.

by Sorensen and Arlt (1979a,b) for the water–*n*-hexane system, the water–*n*-octane system, the water–*n*-decane system, and the water–*n*-dodecane system. Here we treat *n*-hexane, *n*-octane, *n*-decane, and *n*-dodecane as 3-mer, 4-mer, 5-mer, and 6-mer with ethylene as the repeat unit, or segment. The data cover a temperature range of 0°C to 40°C. The binary parameters are as follows:

$$\tau_{wC} = -0.884 + \frac{1{,}249.8}{T} \tag{24}$$

$$\tau_{Cw} = -7.642 + \frac{4{,}306.4}{T}. \tag{25}$$

Given these regressed τ's we used POLYMERS PLUS™ software system (Aspen Technology, 1995) to compute the cmc's for the polyoxyethylene alcohol surfactants compiled by Hinz (1986). The results are given in Tables 1 and 2 and in Figures 9 and 10. In general, the NRTL model with the regressed segment–water interaction parameters slightly overpredicts the activity coefficients of surfactants and underpredicts the cmc's. Specifically, the NRTL model slightly overpredicts the observed effects of hydrophobic alkyl chain and notably overpredicts the effect of hydrophilic oxyethylene headgroup. This might be due to the less than adequate assumption that hydrophilic groups in micelles could be considered as "ideal." These hydrophilic groups are, in fact, surrounded by neighboring water molecules that may penetrate the hydrophilic layer of the micelles. On the other hand, the assumption that hydrophobic groups in micelles are "ideal" may be a more realistic one.

The match between the reported experimental data and the predictions is much improved if the NRTL binary parameters are adjusted to fit the cmc data. The results are also given in Tables 1 and 2 and Figures 9 and 10. It is interesting to note that these results are similar to the prediction results based on the Blankschtein model (Puvvada and Blankschtein, 1990). The corresponding NRTL binary parameters are given below. As will be shown later, Eqs. 22–25 give reasonable predictions for the temperature effect on cmc. We only fitted the temperature-independent parameters:

$$\tau_{wE} = 2.693 - \frac{936.2}{T} \tag{26}$$

$$\tau_{Ew} = -2.718 + \frac{2{,}169.1}{T} \tag{27}$$

$$\tau_{wC} = -1.620 + \frac{1{,}249.8}{T} \tag{28}$$

$$\tau_{Cw} = -3.699 + \frac{4{,}306.4}{T}. \tag{29}$$

Also shown in the tables are the computed cmc's with the surfactant activity coefficients predicted directly with the UNIFAC method (Fredenslund et al., 1975). The UNIFAC method considers the Gibbs energy of a solution as the sum of a combinatorial term similar to the Flory–Huggins equation and a residual term that accounts for weak physical interactions among molecules. The group contribution concept was applied so that the weak physical interactions for each molecule is accounted for based on the contributions of each individual functional group that constitute the molecule. The UNIFAC parameters for the contribution of each functional group have been compiled by regressing phase equilibrium data of a wide variety of nonelectrolyte systems. Given the functional groups and the corresponding UNIFAC parameters for the functional groups, one could then predict the activity coefficient of concerned molecules in a solution.

Table 2. Predicted cmc Values at 25°C for Selected *n*-Decyl-surfactants with Different Hydrophobic Oxyethylene Headgroups

			cmc (mol/L)			
Surfactant Name	Formula	Abbr.	Exp*	NRTL**	NRTL†	UNIFAC
n-Decyl-trioxyethylene-alcohol	$C_{10}H_{21}(OC_2H_4)_3OH$	$C_{10}E_3$	6.0×10^{-4}	5.16×10^{-6}	2.62×10^{-4}	2.40×10^{-5}
n-Decyl-pentaoxyethylene-alcohol	$C_{10}H_{21}(OC_2H_4)_5OH$	$C_{10}E_5$	8.0×10^{-4}	3.76×10^{-5}	4.91×10^{-4}	1.12×10^{-5}
n-Decyl-hexaoxyethylene-alcohol	$C_{10}H_{21}(OC_2H_4)_6OH$	$C_{10}E_6$	9.0×10^{-4}	1.01×10^{-4}	6.67×10^{-4}	7.36×10^{-6}
n-Decyl-nonaoxyethylene-alcohol	$C_{10}H_{21}(OC_2H_4)_9OH$	$C_{10}E_9$	1.3×10^{-3}	1.93×10^{-3}	1.65×10^{-3}	1.90×10^{-6}

*Experimental data taken from Hinz (1986).
**NRTL parameters regressed from VLE/LLE data of homooligomers.
†NRTL parameters regressed from cmc data.

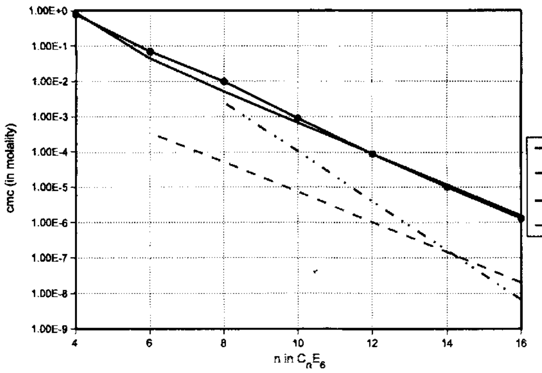

Figure 9. Predicted cmc values at 25°C for selected surfactants with different constitution of the hydrophobic alkyl chain.

Expt.: experimental data from Hinz (1986); NRTL[1]: NRTL predictions with parameters regressed from VLE/LLE data of homooligomers; NRTL[2]: NRTL predictions with parameters regressed from the experimental data in Tables 1 and 2; UNIFAC: UNIFAC predictions.

POLYMERS PLUS was used to identify the set of UNIFAC functional groups for the segments and to calculate the surfactant activity coefficients.

It turns out the UNIFAC model does not have the oxyethylene group. We used the combination of an oxymethylene group and a methylene group to represent the oxyethylene group. The ethylene repeat unit is represented as two methylene groups. The UNIFAC results are also given in Tables 1 and 2 and in Figures 9 and 10. The predicted results are quite consistent with the observed trend of the hydrophobic alkyl chain. However, the UNIFAC representation clearly underestimates the hydrophilicity of oxyethylene group in the surfactant. In fact, the UNIFAC predictions seem to suggest that the oxyethylene headgroups become more hydrophobic as the number of oxyethylene groups increases.

Table 3 and Figure 11 show the temperature effect on cmc of $C_{12}E_8$ with data taken from Meguro et al. (1987). The temperature effect on cmc's is quite well represented by the polymer NRTL model.

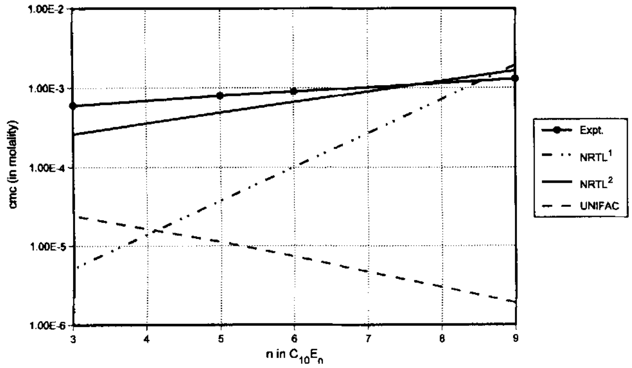

Figure 10. Predicted cmc values at 25°C for selected *n*-decyl-surfactants with different constitution of the hydrophilic oxyethylene headgroups.

Expt.: experimental data from Hinz (1986); NRTL[1]: NRTL predictions with parameters regressed from VLE/LLE data of homooligomers; NRTL[2]: NRTL predictions with parameters regressed from the experimental data in Tables 1 and 2; UNIFAC: UNIFAC predictions.

Table 3. Predicted cmc Values for an *n*-Dodecyl-surfactant, $C_{12}E_8$, at Different Temperatures

Surfactant Temp.	cmc (mol/L) Exp.*	NRTL**	NRTL†	UNIFAC
15°C	9.7×10^{-5}	4.07×10^{-5}	2.54×10^{-4}	4.38×10^{-7}
20°C	8.3×10^{-5}	3.39×10^{-5}	2.02×10^{-4}	4.39×10^{-7}
25°C	7.1×10^{-5}	2.88×10^{-5}	1.61×10^{-4}	4.42×10^{-7}
30°C	6.9×10^{-5}	2.50×10^{-5}	1.30×10^{-4}	4.48×10^{-7}
40°C	5.8×10^{-5}	2.00×10^{-5}	8.65×10^{-4}	4.68×10^{-7}

*Experimental data taken from Meguro et al. (1987).
**NRTL parameters regressed from VLE/LLE data of homooligomers.
†NRTL parameters regressed from cmc data.

Figures 12 and 13 show the significant sensitivities of the cmc predictions to the values of τ_{wE} and τ_{wC}, respectively. The more negative the τ_{wE} is, the more hydrophilic the surfactant behaves and the larger the cmc becomes. On the other hand, the larger the τ_{wC} is, the more hydrophobic the surfactant behaves and the smaller the cmc becomes.

It should be emphasized that, although we focus our discussion on polyoxyethylene alcohol surfactants in this article, the methodology presented should be applicable to other nonionic surfactants. The key to the ultimate predictive capability of the NRTL model rests with the determination and compilation of the interaction parameters associated with the segment–water pairs. These parameters can be best determined from phase equilibrium data of the corresponding oligomer–water systems or from proven functional group contribution methods.

Mixed Surfactant Systems

Multiple amphiphile components may exist in micelles of mixed surfactant systems. The micelle-formation equation, Eq. 20, can be generalized for mixed-surfactant systems as follows:

$$\sum_{AB} a_{AB} = a_T^{\text{cmc}} = 1 \qquad (30)$$

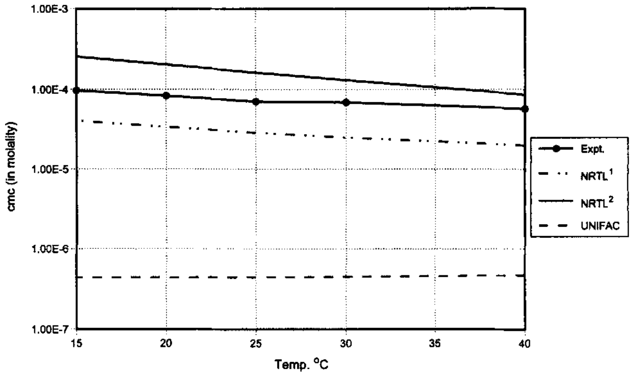

Figure 11. Predicted cmc values for a *n*-dodecyl-surfactant, $C_{12}E_8$, at different temperatures.

Expt.: experimental data from Hinz (1986); NRTL[1]: NRTL predictions with parameters regressed from VLE/LLE data of homooligomers; NRTL[2]: NRTL predictions with parameters regressed from the experimental data in Tables 1 and 2; UNIFAC: UNIFAC predictions.

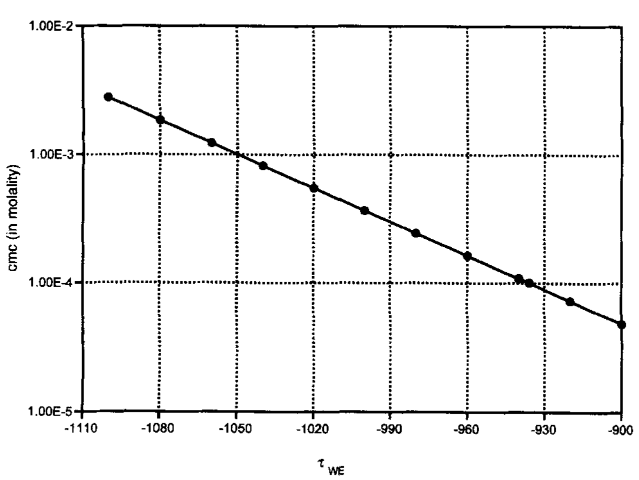

Figure 12. Sensitivities of cmc predictions to the values of τ_{WE}.

$$a_T^{\mathrm{cmc}} = x_T^{\mathrm{cmc}} * \gamma_T^{\mathrm{cmc}}, \tag{31}$$

where T stands for the total surfactant mixture.

For each individual surfactant AB, the activity of monomeric amphiphile is the product of monomeric amphiphile composition and its activity coefficient. At low amphiphile concentrations, such as cmc, γ_{AB} can be approximated as γ_{AB}^{∞} (see Figure 6):

$$a_{AB} = x_{AB}\gamma_{AB} \approx x_{AB}\gamma_{AB}^{\infty}. \tag{32}$$

Therefore Eq. 30 can be rewritten as follows:

$$\sum_{AB} x_{AB}\gamma_{AB}^{\infty} \approx \sum_{AB} x_{AB}\frac{1}{x_{AB}^{\mathrm{cmc}}} = a_T^{\mathrm{cmc}} = 1 \tag{33}$$

$$x_T^{\mathrm{cmc}} = \left(\sum_{AB}\frac{x_{AB}}{x_T^{\mathrm{cmc}}}\frac{1}{x_{AB}^{\mathrm{cmc}}}\right)^{-1} \tag{34}$$

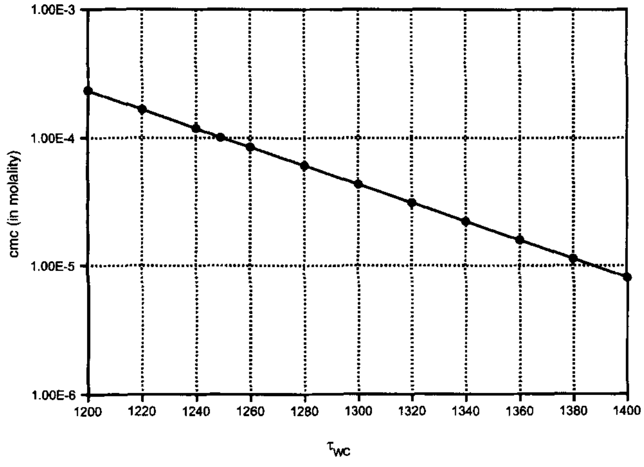

Figure 13. Sensitivities of cmc predictions to the values of τ_{WC}.

$$x_T^{\mathrm{cmc}} = \left(\sum_{AB}\frac{\alpha_{AB}}{x_{AB}^{\mathrm{cmc}}}\right)^{-1}. \tag{35}$$

Here α is the fraction of surfactant AB in the total surfactant mixture. Equation 35 relates the cmc of a mixed surfactant system with the cmc's of single surfactant systems. It is equivalent to the "generalized relationship for the micellization of mixed surfactants" (Nagarajan, 1985; Holland, 1986) if one assumes that activity coefficients of surfactants in the mixed micelles are in unison.

In reality, activity coefficients of surfactants in mixed micelles should be a function of the surfactant compositions in the mixed micelles. In extreme cases, there can be formation of homogeneous azeotropes and heterogeneous azeotropes. The formation of heterogeneous azeotropes suggest the simultaneous presence of micelles having distinctly different surfactant compositions (Cox and Benson, 1986). Holland (1986) reported the use of the two-suffix Margules activity coefficient equation to describe the nonideality in the mixed micelles for more than thirty mixed surfactant systems. In recent process modeling with nonelectrolytes, the use of Margules equation for the solution nonideality has been largely replaced by local composition models such as the NRTL model. Although it is not the aim of this article to illustrate the use of the NRTL model for mixed surfactant solutions, the NRTL model does provide a versatile thermodynamic framework to describe the solution nonideality of mixed micelles for mixed surfactant systems.

Conclusions

The segment-based polymer NRTL model has been shown to successfully represent the Gibbs energy of mixing of nonionic surfactant solutions. The model provides a semiempirical activity coefficient expression to represent the surfactant solution nonideality with binary adjustable parameters associated with the physical interactions between various species and segments of amphiphile molecules. Many of the solvent–solvent binary parameters are readily available in the literature (Chen, 1993). The Gibbs energy expression satisfactorily represents important phase behaviors of surfactant solutions, including infinite dilution-activity coefficients of monomeric amphiphiles and critical micellar concentrations. From a process-modeling viewpoint, the model provides a convenient and versatile thermodynamic framework to correlate phase behaviors of surfactant solutions, which often include water, organic monomers, surfactants, polymers, electrolytes, and so forth.

Acknowledgment

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Notation

C = concentration
n = number of moles
r = number of segments per polymeric species, degree of polymerization
x = liquid-phase mole fraction (based on number of moles of monomeric amphiphiles and solvent water)
τ = NRTL binary interaction parameter
ϕ = volume fraction of polymer or segment mole fraction

Superscripts and subscripts

∞ = infinite dilution
o = reference state
J = any species, solvent, or polymer
k = any species, solvent, or segment
m = micellar amphiphiles
n = number of amphiphiles in a micelle
s = solvent species

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