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Prediction of Critical Micelle Concentrations of Nonionic Surfactants in Aqueous and Nonaqueous Solvents with UNIFAC

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The UNIFAC group-contribution model is used to predict the critical micelle concentration (cmc) of nonionic surfactants in aqueous and nonaqueous solvents. For predicting the cmc, the phase-separation thermodynamic framework approach is used, where the micellar phase is approximated as a second liquid phase resulting from the liquid−liquid equilibrium between the solvent and the surfactant. The necessary activity coefficients are predicted by UNIFAC. The most promising UNIFAC model for this purpose was found to be the UNIFAC-Lyngby (*Ind. Eng. Chem. Res.* **1987**, *26*, 2274). To improve the results for surfactants containing oxyethylene chains, a new set of parameters was evaluated for this group, leading to still better cmc predictions for both water and organic solvents, as well as binary solvent systems.

Introduction

Surfactants are amphiphilic molecules that contain a nonpolar segment, commonly called "the tail", and a polar segment, called "the head". This characteristic of being an amphiphilic molecule leads to aggregation. When a surfactant is dissolved at low concentrations, the molecules exist as individual entities. However, as the concentration of the surfactant increases the molecules tend to associate to form aggregates. The "aggregation number" indicates how many molecules are present in an aggregate and often involves a rather narrow size range.

In aqueous solutions, the hydrophobic tails of the surfactant associate, leaving the (hydrophilic) head-groups exposed to the solvent. This structure is the "normal" micelle. The transition from a monomeric solution to an aggregated form can be seen as a change in the slope of plots against surfactant concentration of many physical properties, e.g., viscosity, conductance, surface tension.[1−3] The concentration at which this change takes place is called the critical micelle concentration (cmc). Once the micelles are formed, further increase of the total surfactant concentration does not change the concentration of the free monomer. The surfactant added is completely incorporated into the micelles. In other words, the concentration of the free surfactant molecules remains constant after the micelles are formed.

In nonpolar solvents, the hydrophilic segment can be poorly solvated, so the heads will form the interior of the aggregates. The hydrophobic segments surround the polar core and are responsible for the solubility of the aggregates.[3] The structures formed are called reverse micelles. The aggregates can be formed at low surfactant concentrations, but the aggregation numbers for reverse micelles are usually relatively small. Therefore, because of the nature of the monomer−micelle equilibrium, the cmc is not as well-defined as in aqueous solutions. In fact, the cmc is a transition region over a small composition range, so exact determination is difficult.[4] However, experimental data show an apparent change in the slope of plots against surfactant concentration of surfactant physical properties.

Several models have been proposed to predict cmc's in aqueous solutions, but not in organic solvents. The early models are based on semiempirical equations that relate, using experimentally determined parameters, the cmc and the properties of the surfactants.[5,6] More recently, thermodynamic frameworks have been employed to describe the phase behavior of surfactant solutions in an attempt to predict cmc's.[7−9] The thermodynamic frameworks most commonly used are the phase-separation and mass-action approaches.[3,10] The phase-separation framework represents micellization as an equilibrium between two pseudo-phases: the micelles and the monomers in solution. The cmc can be calculated through the standard free energy of micellization. This simple approach allows for a qualitative understanding of the micellar solution, but it cannot provide information on the size of the micelle.

The mass-action framework, on the other hand, assumes an equilibrium between the monomer itself and the micellar species formed by M molecules of monomer, where M is the aggregation number. For this model, each aggregate with different aggregation number is considered as a different species. Each one has a characteristic chemical potential for the surfactant monomer in the aggregate that varies with micellar size and shape.

It is the aim of this work to demonstrate the feasibility of using UNIFAC[11] with the phase-separation framework to predict cmc's for nonionic surfactants in aqueous and nonaqueous systems. The process of surfactant

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aggregation can be seen as an extreme case of local composition changes. The groups in the core of the micelle interact so favorably with each other that they are surrounded almost completely by their own kind. Thus, there are grounds for hoping that UNIFAC might correctly predict aggregation to micelles. It must be noted, however, that this is a very extreme case of the types of local composition changes that UNIFAC was designed to handle. The group parameters used in UNIFAC are derived principally from data for mixtures of small molecules that do not show strong aggregation.

Modeling

As mentioned above two thermodynamic frameworks have mainly been proposed for cmc calculations: phase-separation and mass-action. In this study, the former has been used. The phase-separation framework assumes that micelles represent a distinct phase or pseudophase, where the chemical potential of the monomer in the aggregate has a well-defined value, independent of the size of the aggregate or the total amount of the "micellar phase" present. Within the phase-separation framework, two different approaches for the calculation of cmc's can be used. In the first, micelles are considered as large aggregates of surfactants, excluding solvent from their interiors, which suggests that these structures can be approximated as pure liquid surfactant. Thus, the standard-state chemical potential of the monomer in the micelle equals zero, or equivalently, the monomer activity equals unity. The cmc thus corresponds to the mole fraction of the dispersed surfactant in the solvent, x_1, for which the surfactant activity $\alpha_1 = x_1\gamma_1$ equals unity (γ_1 is the symmetric convention, mole fraction basis, activity coefficient of the surfactant in the solution). This approach was recently used by Chen[8] to model the cmc's of polyoxyethylene alcohol surfactants in water with the NRTL activity coefficient model and by Li et al.[9] to model the same systems with the SAFT equation of state and the UNIQUAC activity coefficient model.

Another approach, which is used in this work, to micelle formation suggests that these structures might exclude solvent from their core but that solvent molecules exist on the surface of the aggregate as an integral part of the micelle. Thus, the micellar phase can be approximated as a second liquid-phase resulting from the liquid−liquid equilibrium between the solvent and the surfactant. In this case two phases coexist: one solvent-rich phase whose surfactant concentration is the cmc, and one surfactant-rich phase approximating the micellar phase. The solution for the cmc demands that the activities of both solvent and surfactant be the same in the two phases (isoactivity criterion).

The first test was to investigate whether this approach, with the necessary activity coefficients predicted by UNIFAC, can be applied for cmc prediction in surfactant/solvent systems. Figure 1A presents a plot of the molar Gibbs energy of mixing for *n*-dodecylpentaoxyethylene glycol (1) [$C_{12}(EO)_5$] in hexadecane (2) at 20 °C and 1 atm versus the $C_{12}(EO)_5$ composition expressed in terms of mole fraction. This is a classical plot of a partially miscible system, which indicates that, if started from a total $C_{12}(EO)_5$ mole fraction equal to x^o, the mixture will split into two stable liquid phases having mole fractions equal to x' and x''. In the two points with compositions equal to x' and x'', the following
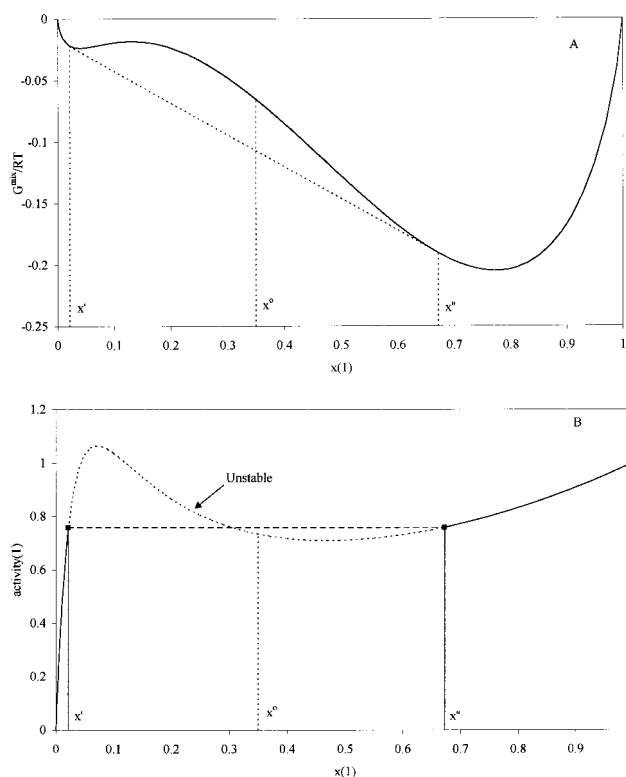
Figure 1. Plots of (a) Gibbs free energy of mixing and (b) activity versus the $C_{12}(EO)_5$ mole fraction for the [$C_{12}(EO)_5$] (1)/hexadecane (2) system at 20 °C and 1 atm.

condition for instability of a binary liquid mixture is fulfilled

$$\left(\frac{\partial^2 \Delta G^{\text{mixture}}}{RT}\right)_{T,P} < 0 \qquad (1)$$

Figure 1B presents a plot of the activity (*a*) of $C_{12}(EO)_5$ versus its total mole fraction for the same system. As shown, the curve has a maximum and a minimum; there are two stable liquid phases whose compositions are also given by x' and x''. The two points with compositions x' and x'' fulfill the liquid−liquid phase split criterion, i.e., $a_1' = a_1''$. Notice that the obtained x' value, which is the predicted cmc, is equal to 0.021, which is in good agreement with the experimental cmc (0.019). It must be noted that the calculations presented in Figure 1A and B have been performed using the UNIFAC model of Hansen et al.[17]

It must be noted that, using this approach, the formation of a separate surfactant-rich phase that includes a relatively high amount of solvent is predicted. This picture might be different in structure from the micelles actually formed. Nevertheless, the prediction for the surfactant-poor phase is quite accurate for the solution of free monomer in the solvent. The concentration of the free monomer in this phase can, thus, be taken as the predicted cmc.

In the following calculations, this approach has been used with the necessary activity coefficients predicted by the UNIFAC group-contribution activity coefficient model.

Selection of the Best-Suited UNIFAC Model

Several UNIFAC-based models have been proposed in the literature. Preliminary calculations suggest that
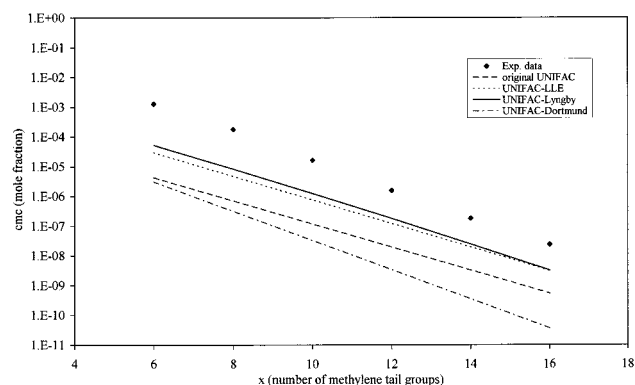
Figure 2. Prediction of the cmc's of different *n*-alkyl hexaoxyethylene alcohol $C_x(EO)_6$ surfactants in water as a function of the number (*x*) of alkyl groups in the chain at 25 °C. Experimental data from Chen.[8]

the best-suited UNIFAC model for cmc predictions is the UNIFAC-Lyngby.[13] This is shown in Figures 2 and 3A−C for the cmc's of polyoxyethylene alcohols in water and alkanes, respectively. The experimental data for polyoxyethylene alcohols in alkanes are shown in Table 1. In the case of polyoxyethylene alcohols in water the UNIFAC-Lyngby and UNIFAC-LLE[16] models give comparable results although they underestimate the experimental data, whereas the original UNIFAC[17] and the UNIFAC-Dortmund[18] approaches give poor results. In the case of polyoxyethylene alcohols in alkanes, only the UNIFAC-Lyngby model gives reasonable predictions, whereas the original UNIFAC and the UNIFAC-LLE models give poor results. This performance of the UNIFAC-Lyngby model can be attributed to the fact that this model uses a better combinatorial expression[19] than the other models, which plays an important role in mixtures with a large asymmetry in molecular size,

Table 1. Experimental Systems and cmc Values Used for the Predictions

surfactant	solvent	temp (°C)	exp cmc (mole fraction)	ref
$C_{12}H_{25}(EO)_6$	hexadecane	20	0.0158	12
$C_{12}H_{25}(EO)_5$		20	0.01914	12
$C_{12}H_{25}(EO)_4$		20	0.0244	12
$C_{12}H_{25}(EO)_6$	decane	10	0.00315	12
$C_{12}H_{25}(EO)_6$		20	0.01064	12
$C_{12}H_{25}(EO)_6$		45	0.01125	12
$C_{12}H_{25}(EO)_4$	decane	20	0.0174	12
$C_{12}H_{25}(EO)_6$	cyclohexane	10	0.00613	12
Triton X-100	cyclohexane	30	0.00435	14
Triton X-35	heptane	25	0.015	15

such as those considered here. Consequently, in the rest of this work the UNIFAC-Lyngby model is considered.

Because most of the experimental cmc values refer to surfactants that contain ethylene oxide (EO) groups (−CH_2−CH_2−O−), special attention was paid to this group. As shown in Figure 4, UNIFAC predicts the wrong trend with increasing number of EO groups for $C_{10}(EO)_y$ surfactant molecules in water. This is attributed to the fact that the UNIFAC interaction parameter tables do not include a separate EO group; instead the EO group is treated as a sum of CH_2 and methylene oxide (MO) groups (−CH_2−O). Using this assignment, the increase in the number of EO groups in the molecule results in a decrease in their predicted solubility, and consequently cmc, in water because of the increase in the number of hydrophobic methylene (−CH_2−) groups in the molecule whose contribution, according to UNIFAC, has a more significant effect than that of the hydrophilic MO group. This, however, is also contrary to the fact that poyethylene oxide (PEO) is soluble in water, whereas polymethylenoxide (PMO) is
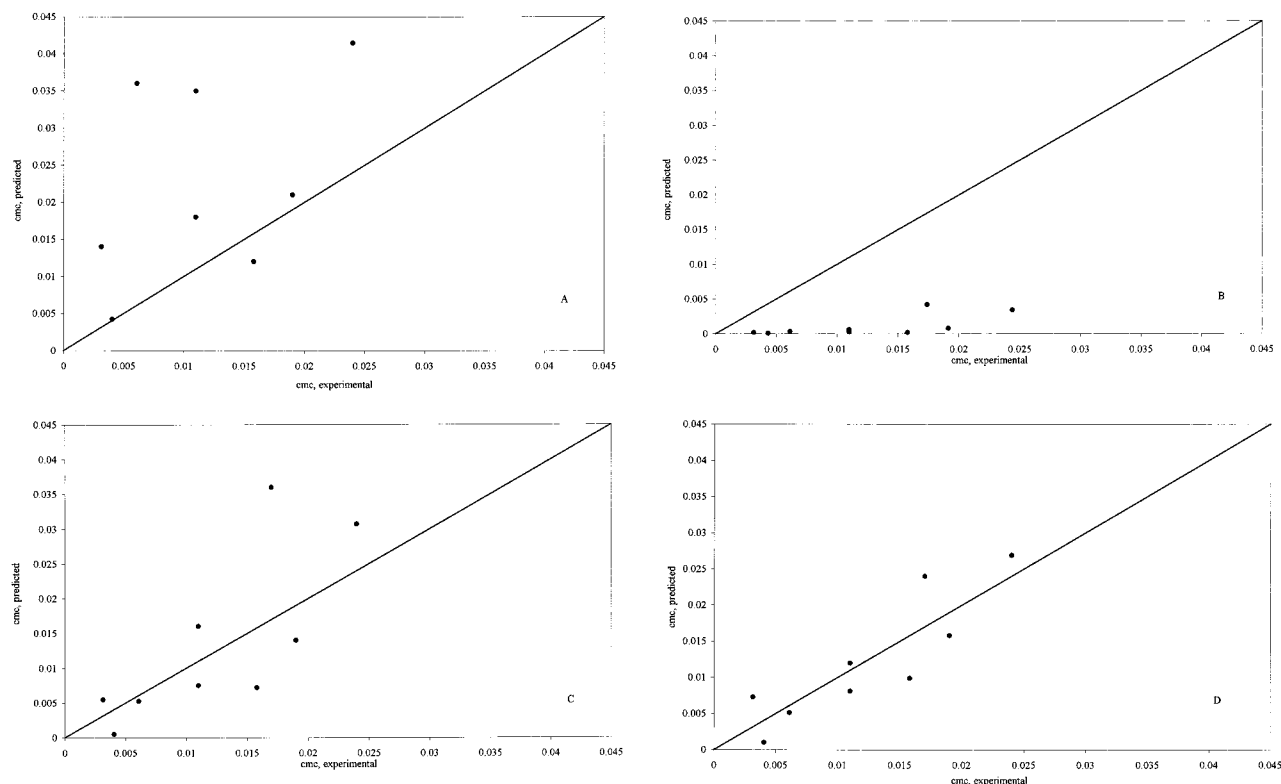
Figure 3. Comparison between predicted and experimental cmc values for the poly(ethylene glycol)/alkane systems shown in Table 1: (A) original UNIFAC, (B) UNIFAC-LLE, (C) UNIFAC-Lyngby, and (D) UNIFAC-Lyngby with the new set of parameters for the ethylene oxide (EO) group. cmc values are expressed in terms of mole fraction.
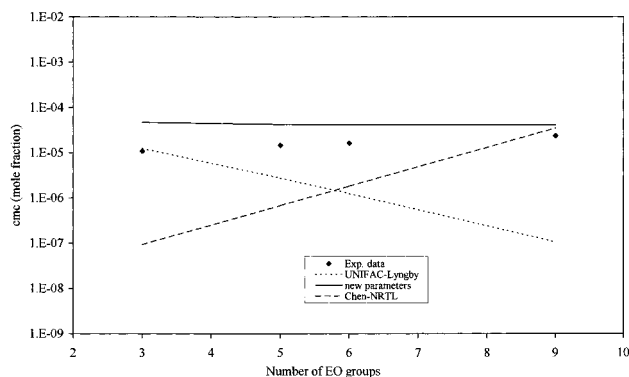
Figure 4. Prediction of the cmc's of different n-decyl polyoxyethylene alcohol $C_{10}(EO)_x$ surfactants in water as a function of the number (x) of EO groups in the chain. Experimental data from Chen.[8]

Table 2. New UNIFAC-Lyngby Interaction Parameters

group n	group m	$A_{nm}{}^a$ (K)	A_{mn} (K)
EO[b]	CH$_2$	-254.31	449.30
EO	OH	310.57	174.41
EO	H$_2$O	809.80	-279.74
EO	ACH	-249.91	310.08

[a] Temperature-independent parameter of the group interaction parameter (Ψ_{mn}) in the residual term of UNIFAC defined by $\Psi_{mn} = \exp(-A_{mn}/T)$. [b] The van der Waals volume parameter of EO (R) has a value of 1.5927, and the van der Waals area parameter (Q) has a value of 1.32.

not.[20] Therefore, it is apparent that the introduction of a new UNIFAC group for EO is necessary.

Evaluation of New Interaction Parameters for the EO Group

The interaction parameters for the new group, EO ($-CH_2-CH_2-O-$), with the other groups were evaluated using the following procedure. First, the CH$_2$/EO pair was evaluated by fitting activity coefficient data for alkane/ether mixtures.[21] Next, the OH/EO pair was evaluated by fitting activity coefficient data for alcohol/ether mixtures.[22,23] Then, the H$_2$O/EO pair was evaluated by fitting activity coefficient data for triethylene, tetraethylene, and polyethylene (with molecular weights in the range of 200–1450) glycols with water mixtures.[24–27] Finally, the ACH/EO pair was evaluated by fitting activity coefficient data for aromatic hydrocarbon/ether mixtures.[21] The values of the new parameters are presented in Table 2.

Results and Discussion

(i) Prediction of cmc's in Water. Figure 5A and B presents experimental and predicted cmc values for different n-alkyl hexaoxyethylene alcohol [$C_x(EO)_6$] and octaoxyethylene [$C_x(EO)_8$] surfactants in water as a function of the number (x) of alkyl groups in the chain. As shown, the UNIFAC-Lyngby approach with the new parameters gives better results than the old models, with typical deviations from the experimental data of about half an order of magnitude. Also it gives better results than those obtained using the Chen-NRTL model with binary segment parameters obtained by fitting activity coefficient data for binary mixtures of oligomers.[8]

Figures 4 and 6 present experimental and predicted cmc values for different n-decyl and n-dodecyl polyoxyethylene alcohol [$C_{10}(EO)_x$ and $C_{12}(EO)_x$] surfactants in
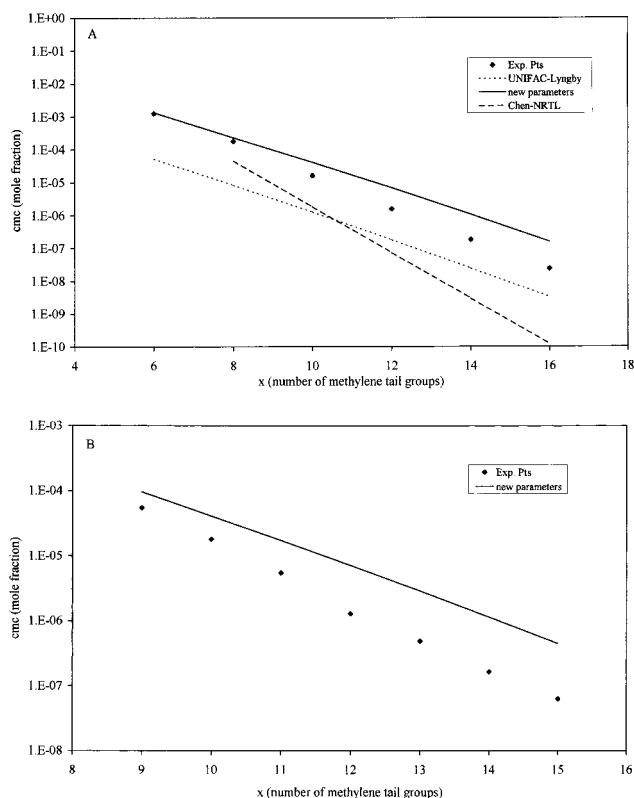

Figure 5. (a) Prediction of the cmc's of different n-alkyl polyoxyethylene alcohol $C_x(EO)_6$ surfactants in water as a function of the number (x) of alkyl groups in the chain. Experimental data from Chen.[8] (b) Prediction of the cmc's of different n-alkyl polyoxyethylene alcohol $C_x(EO)_8$ surfactants in water as a function of the number (x) of alkyl groups in the chain. Experimental data from Li et al.[9]
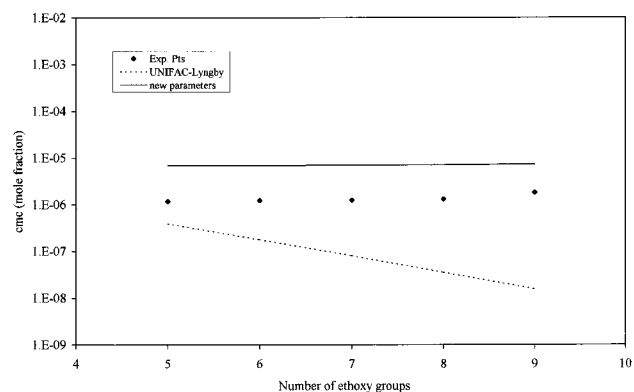
Figure 6. Prediction of the cmc's of different n-dodecyl polyoxyethylene alcohol $C_{12}(EO)_x$ surfactants in water as a function of the number (x) of EO groups in the chain. Experimental data from Li et al.[9]

water as a function of the number (x) of EO groups in the chain. As shown, the new parameters allow for better overall cmc predictions than the old parameters, correctly indicating a small increase in the cmc values with the number of EO groups in the surfactant. Also, the UNIFAC-Lyngby model with the new parameters provides better results than the Chen-NRTL model (Figure 4). Finally, the model predicts quite well the effect of temperature on the cmc's. Thus, for the C_{12}-$(EO)_8$ surfactant in water, the experimental data[8] show a 30% decrease in the cmc of $C_{12}(EO)_8$ for a temperature increase from 20 to 40 °C, whereas the model predicts a 42% decrease.
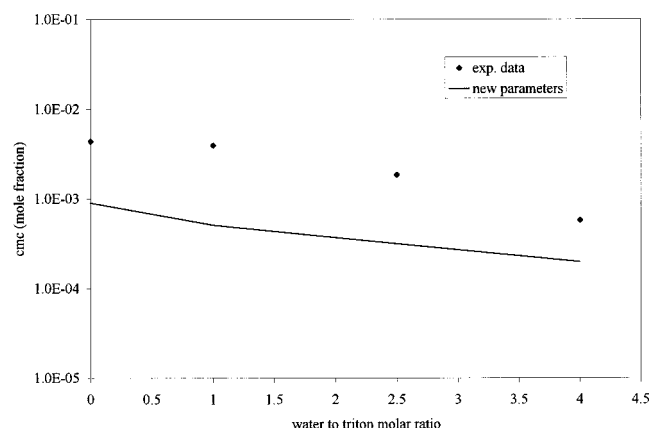
Figure 7. Experimental and predicted cmc values of Triton X-100 in cyclohexane as a function of the water to Triton X-100 molar ratio at 30 °C. Experimental data from Zhu et al.[14]

(ii) Prediction of cmc's for Surfactants in Organic Solvents. Figure 3D presents cmc predictions with the new parameters for polyoxyethylene alcohols in alkanes. The improved performance of the UNIFAC-Lyngby model with the new parameters over all of the other models (Figure 3A−C) is clear.

(iii) Predictions in Binary Solvent Systems. Figure 7 presents cmc predictions for Triton X-100 in cyclohexane containing small quantities of water. The formula of Triton X-100 (polyoxyethylene tert-octyl-phenyl ether) is $CH_3C(CH_3)_2CH_2C(CH_3)_2C_6H_4(OCH_2-HC_2-)_{9.5}OH$. The trend of the predictions agrees with the experimental results, i.e., as the water/Triton ratio increases, the cmc value decreases, which is due to the fact that, in the presence of water, the polyoxyethylene chain is more hydrated, thus facilitating the aggregation of the molecules. UNIFAC predicts the correct trend, and the agreement is better for the higher water/Triton ratios.

Conclusions

The UNIFAC-Lyngby model has been shown to successfully predict the critical micelle concentrations of nonionic surfactants in water, organic solvents, and binary solvent systems. A new group, the ethylene oxide (EO) one, has been introduced, rather than considering it as the sum of a CH_2 and a CH_2O groups, the need for such a change is indicated, for example, by the fact that PEO is soluble in water but PMO is not. Use of this group provides better predictions of cmc's of surfactants containing EO chains. New interaction parameters for the EO group with the CH_2, OH, H_2O, and ACH groups have been evaluated using a database of activity coefficients for nonsurfactant molecules.

Acknowledgment

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