Critical Micelle Concentrations of Nonionic Surfactants in Organic Solvents: Approximate Prediction with UNIFAC

Maria Victoria Flores,* Epaminondas C. Voutsas,† Nikolaos Spiliotis,‡ Gill M. Eccleston,† George Bell,§ Dimitrios P. Tassios,† and Peter J. Halling,*

*Department of Pure and Applied Chemistry, University of Strathclyde, Thomas Graham Building, 295 Cathedral Street, Glasgow G1 1XL, Scotland, United Kingdom; †Thermodynamics and Transport Phenomena Laboratory, Department of Chemical Engineering, National Technical University of Athens, 9 Heroon Polytechniou Street, Zographou Campus, 157 80 Athens, Greece; ‡Department of Pharmaceutical Sciences, University of Strathclyde, 27 Taylor Street, Glasgow G4 0NR, Scotland, United Kingdom; and §Department of Mechanical and Chemical Engineering, Heriot-Watt University, Riccarton, Edinburgh EH14 AS, Scotland, United Kingdom

Received August 29, 2000; accepted April 13, 2001

The objective of this study was to model the critical micelle concentration (cmc) of nonionic surfactants in nonaqueous systems using the UNIFAC group contribution method. For the prediction of the cmc the phase separation approach was used, where the micellar phase is approximated as a second liquid phase resulting from the liquid-liquid equilibrium between the solvent and the surfactant, with the necessary activity coefficients predicted by UNIFAC. The limited amount of literature data for reverse micelle formation in nonaqueous systems was used to test the predictions, varying surfactant type, solvent, and temperature. The most promising model was the modified UNIFAC of B. L. Larsen, P. Rasmussen, and A. Fredenslund (Ind. Eng. Chem. Res. 26, 2274 (1987)). Since most nonionic surfactants contain oxyethylene chains, a new set of parameters was evaluated for this group, leading to satisfactory predictions. The average deviation between the predicted and the experimental cmc’s was about 0.1 log units.

Key Words: critical micelle concentration; nonionic surfactant; UNIFAC.

INTRODUCTION

Surfactants are amphiphilic molecules that contain a nonpolar segment, commonly called “the tail,” and a polar segment called “the head.” This characteristic, 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 there will be a rather narrow size range.

In aqueous solutions, the hydrophobic tails of the surfactant associate, leaving the head groups (hydrophilic) exposed to the solvent. The simplest of such aggregates, with an approximately spherical shape, are called micelles. 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) (2–4). The concentration at which this change takes place is called the critical micelle concentration (cmc). Once the micelles are formed, further increase of the surfactant concentration does not significantly change the concentration of the free monomer. The surfactant added is incorporated completely 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 the so-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 so well defined. In fact the cmc is a transition region over a small composition range, so exact determination is difficult (5). However, experimental data show an apparent break between two lines.

The cmc of a surfactant in a given solvent is thus of great help in understanding and predicting behavior. Some approaches have been studied to predict cmc’s in aqueous solutions, but not in organic solvents. The early models are based on semi-empirical equations, which relate the cmc and the properties of the surfactants, using experimentally determined constants (6, 7). More recently, thermodynamic treatments have been employed to describe the phase behavior of surfactant solutions in an attempt to predict the cmc (8, 9). The thermodynamic models most commonly used are the phase separation model and the mass action model (3, 10). The phase separation model represents micellization as an equilibrium between two pseudophases: the micelles and the monomers in solution. The cmc can be calculated through the standard free energy of micellization. That simple model allows qualitative understanding of the micellar solution but it cannot provide information on the size of the micelle.
The mass action model, on the other hand, assumes equilibrium between the monomer itself and the micellar species formed by \( M \) molecules of monomer, \( M \) being the aggregation number. For this model, each aggregate with a different aggregation number is considered as a different species. Each one has a characteristic chemical potential for the surfactant monomer in the aggregate, varying with micellar size and shape. Both models assume activity coefficients equal to unity for the monomers in solution, because of their low concentration in the solution. As Chen (8) pointed out, a better approach is to look at the nonideality of the solution through the activity coefficients of the monomer molecule. Chen used the segment-based local-composition NRTL model (11) to determine activity coefficients and calculate the cmc for aqueous solutions of nonionic surfactants.

The UNIFAC method has proved to be a reliable method for predicting activity coefficients in liquid mixtures and thus many phenomena dependent on them (12). It is based on the UNIQUAC equation, which is a local composition model. Such models start from the core idea that the local concentrations surrounding a particular molecule or group will differ from their bulk average values: molecules or groups that interact favorably will be overrepresented, while those interacting unfavorably will be relatively excluded. UNIFAC adopts a group-contribution approach to the description of liquid mixtures, with the behavior of the molecules predicted from parameters for the chemical groups they contain and the interactions between them.

The process of surfactant 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 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 UNIQUAC and UNIFAC were designed to handle. The group parameters used in UNIFAC are derived principally from data for mixtures of small molecules that will not show strong aggregation.

It is the aim of this work to demonstrate the feasibility of using UNIFAC to predict cmc’s for reverse micelle formation by nonionic surfactants in organic solvents.

**RESULTS AND DISCUSSION**

**Selection of Test Systems**

We used UNIFAC group contribution methods to predict activity coefficients for each species present in a liquid mixture of a given composition. The activity coefficients are relative to the pure liquid standard state. The UNIFAC method considers the Gibbs energy of a solution as the sum of two terms: a combinatorial term that accounts for differences in the size and shape of the molecules and a residual term that accounts mainly for the effects that arise from energetic interactions between groups.

The molecules are represented as combinations of chemical groups, and the interaction parameters for each type of group have been compiled by regression of phase equilibrium data.

The majority of surfactants contain ionic charges, but since standard UNIFAC cannot handle charged groups, we restricted our initial study to nonionic surfactants. UNIFAC cannot account for specific intramolecular interactions, *i.e.*, proximity effects (14), either, except by defining a large group in which the interactions are internal. We have selected surfactants where other intramolecular interactions are expected to be weak, by an appropriate choice of polar head groups. The most studied solvent for surfactant aggregation is water. Chen (8) proposed a Gibbs energy model to represent the nonideality of surfactant solutions through activity coefficients. The model satisfactorily predicted cmc’s for surfactants containing oxyethylene groups in water. They also presented predictions with UNIFAC, and they showed that the predictions gave the correct trend but underestimated the cmc values. However, it is well known that standard UNIFAC is often poor at correctly predicting behavior in water-rich systems (15, 16). Hence, we concentrated on aggregation of nonionic surfactants in nonaqueous solvents, forming reverse micelles. There is relatively little good experimental cmc data for these systems, but we tested predictions against all that is available.

**Procedure**

The thermodynamics of aggregation tell us about the general shape of the activity against the concentration plot. Above the cmc the activity is almost independent of concentration because, as noted earlier, the concentration of free monomers remains...
constant once the micelles are formed. Below the cmc, concentrations are often sufficiently small that ideal dilute behavior is a good approximation, with a linear dependence of activity on concentration. Hence, in the region of the cmc, the two straight lines are joined by an abrupt bend. Another possible view of surfactant aggregation is as a pseudophase separation process on a molecular scale. The surfactant can be seen as driven out of the solvent to form a separate phase, but the nature of the molecule prevents this phase from being extensive. Activity coefficients predicted by UNIFAC will sometimes indicate that phase separation can lead to a lower free energy state.

A first test was to prove whether UNIFAC was able to reproduce such shapes of surfactant activity against surfactant concentration plot. Figure 1 shows an example of the predicted surfactant activity as a function of mole fraction. As can be seen, UNIFAC does predict distinctive nonideal behavior. The predicted activity at first increases approximately linearly with the concentration of the surfactant. However, there is then a region of sharp curvature at a relatively low mole fraction. Overall, the shape of the curve is qualitatively close to that expected for an aggregating surfactant solution. The region of sharp curvature could be taken as a quantitative prediction of the cmc, but we find it better to use a different approach based on phase separation.

As noted, a common thermodynamic model of micellization considers it as separation of a pseudophase. Thus the chemical potential of the surfactant in the aggregates is taken to have a fixed value, independent of the size of the aggregate or the total amount of the “micellar phase” present. We proceeded to test whether UNIFAC would predict a phase split in the systems of interest.

Figure 2 presents the full plot of the activity of \( n \)-dodecylpentaoxyethylene glycol (C\(_{12}\)H\(_{25}\)(EO)\(_{5}\)) in hexadecane versus its mole fraction at 20°C and 1 atm. This is a classical activity plot for a partially miscible system, where the activity curve has a maximum and a minimum. The two coexisting phases are identified using the usual isoactivity criterion: activities equal in both phases for both the surfactant and the solvent. All activities were predicted with UNIFAC, and the program searches for the solution that gives equal activities, subject to a mass balance constraint. The compositions of the two stable liquid phases predicted are shown by the arrows on the graph.

The molecular picture implied in UNIFAC is probably rather good for the solvent-rich phase. The concentration of the surfactant in this surfactant-poor phase can be taken as a prediction of the cmc. This is the method we have used for the following quantitative predictions. We used UNIFAC to calculate all the necessary activity coefficients. As presented in detail below, the resulting predictions are reasonably good. First, it is useful to consider further the reasons why the UNIFAC model might be expected to have problems describing micellization and why it is nevertheless quite successful.

The other predicted phase is surfactant rich, but also contains some solvent; if water is present, it is also predicted to be concentrated in this phase. Since micelles are considered as large aggregates of surfactants, excluding solvent from their interior, many authors suggest that these structures can be approximated as the pure liquid surfactant and, thus, the monomer activity equals unity. This approach has been recently used by Chen (8) for the modeling of cmc of polyoxyethylene alcohol nonionic surfactants in water with the NRTL activity coefficient model. However, another viewpoint suggests that these structures may exclude solvent from their core but solvent molecules exist on the surface of the aggregate as an integral part of the micelle. Thus, the surfactant-rich phase predicted by UNIFAC may have some relationship to reality. However, it should be emphasized that UNIFAC is only able to model a bulk phase, not
FIG. 3. Surfactant activity as a function of surfactant mole fraction. Predictions were done as one-phase system with original UNIFAC (19) for \( n \)-dodecylpentaoxyethylene glycol in hexadecane at 20 °C. (---) Tie line of predictions in the two-phase region. (-----) Experimental cmc (20).

The micellar structures actually formed. Nevertheless, the modeled phase might be quite similar to the surfactant-rich system that could (hypothetically) be produced by ultracentrifugation of the micellar dispersion. The precise composition of the micellar pseudophase cannot be defined, so a quantitative comparison with experimental values is impossible.

We do not attach much significance to the absolute values of activity calculated. Errors in these are probably dominated by the inability of UNIFAC to describe correctly the complicated nature of the pure liquid surfactant standard state. This state is used as a reference for the calculation of activities. However, the results of calculations for this standard state do not affect the shape of the activity profile or the phase split prediction. Because the standard state values are the same for all surfactant concentrations, they cancel out.

**Prediction of cmc for Surfactants Containing Oxyethylene Groups**

Having established that UNIFAC can predict qualitatively the type of nonideality found with surfactants, we wanted to see how well the predicted cmc’s agreed with the experimental values. Figure 3 illustrates how a cmc prediction is made as the composition at phase separation and compares the value with the experimental cmc. We should point out that the programs often have difficulty in finding a good solution for the phase split close to the cmc. This is a common problem close to a critical point. Hence, calculations were usually made for higher total surfactant content. The program then reliably predicts a phase split, and the composition of the surfactant-poor phase gives the cmc prediction directly. This is equivalent to the composition at the intersection of the line of single-phase predictions with the constant activity tie line in the two-phase region, as illustrated in Fig. 3.

Table 1 lists a range of surfactants and solvents that were tested. In every case UNIFAC predicted phase separation and hence a value for the cmc. However, we could see that original UNIFAC overestimates the cmc values (Fig. 4A). Larsen et al. (1) and Gmehling et al. (17) have presented modified UNIFAC models that have been found to give better predictions in a variety of systems. With surfactant aggregation, the former was found to give a better agreement with experimental results (Fig. 4B).

For the above predictions, the standard UNIFAC groups were used to describe the surfactant molecules. In particular, the

![Table 1](image)

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Experimental cmc (mole fraction)</th>
<th>Predicted cmc1 (mole fraction)</th>
<th>Data source</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{12}H_{25}(EO)_{6} )</td>
<td>Hexadecane</td>
<td>20</td>
<td>158.0 \times 10^{-4}</td>
<td>99.0 \times 10^{-4}</td>
<td>Ref. 20</td>
</tr>
<tr>
<td>( C_{12}H_{25}(EO)_{5} )</td>
<td>Hexadecane</td>
<td>20</td>
<td>191.4 \times 10^{-4}</td>
<td>158.7 \times 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>( C_{12}H_{25}(EO)_{4} )</td>
<td>Hexadecane</td>
<td>10</td>
<td>244.0 \times 10^{-4}</td>
<td>269.2 \times 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>( C_{12}H_{25}(EO)_{6} )</td>
<td>Decane</td>
<td>20</td>
<td>106.4 \times 10^{-4}</td>
<td>81.4 \times 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>( C_{12}H_{25}(EO)_{6} )</td>
<td>Decane</td>
<td>45</td>
<td>112.5 \times 10^{-4}</td>
<td>117.1 \times 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>( C_{12}H_{25}(EO)_{14} )</td>
<td>Cyclohexane</td>
<td>20</td>
<td>174.0 \times 10^{-4}</td>
<td>242.5 \times 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>( C_{12}H_{25}(EO)_{6} )</td>
<td>Cyclohexane</td>
<td>10</td>
<td>61.3 \times 10^{-4}</td>
<td>51.4 \times 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>Triton X-100</td>
<td>Cyclohexane</td>
<td>30</td>
<td>43.5 \times 10^{-4}</td>
<td>10.0 \times 10^{-4}</td>
<td>Ref. 21</td>
</tr>
<tr>
<td>Triton X-35</td>
<td>n-Heptane</td>
<td>25</td>
<td>150.0 \times 10^{-4}</td>
<td>493.0 \times 10^{-4}</td>
<td>Ref. 22</td>
</tr>
</tbody>
</table>

1 Predicted values were calculated with modified UNIFAC (1) and the new parameters for the oxyethylene group (EO).

![Fig. 4](image)

**FIG. 4.** Comparison between predicted and experimental cmc values for the systems shown in Table 1. (A) Original UNIFAC (19). (B) Modified UNIFAC (1). (C) Modified UNIFAC (1) and the new parameters for oxyethylene group (numerical values are shown in Table 1). cmc is expressed as mole fraction.
polyoxyethylene chains were represented as collections of methylene and oxyethylene groups. We had reasons to believe that the oxyethylene group might in fact show quite distinctive behavior (Voutsas et al., in preparation). Hence we evaluated a new set of interaction parameters for oxyethylene groups. The correlations with the experimental results are much improved using the newly evaluated parameters (Fig. 4C).

Figure 5A shows the experimental and UNIFAC predicted cmc’s for n-dodecyl surfactants with different numbers of oxyethylene headgroups (4–6). As can be seen, the trend is consistent with the observed experimental results. As the number of headgroups increases, the interactions between them favor their aggregation in a hydrophobic environment. In Fig. 5B, the effect of temperature is shown, and again the calculations follow quite well the experimental results: an increase in temperature always leads to higher cmc values.

The predictions and experiments agree in that aggregation of n-dodecylhexaoxyethylene glycol, C₁₂H₂₅(EO)₆, is less favored as the hydrocarbon solvent molecules get larger (Fig. 6A). The same trend, though less pronounced, was found for n-dodecyltetraoxyethylene glycol, C₁₂H₂₅(EO)₄, in decane and hexadecane (Fig. 6B).

Predictions for Systems Containing Water

Figure 7 and Table 2 show predictions and experimental results for Triton X-100 in cyclohexane containing small quantities of water. The trend of the predictions agrees with the experimental results. As the water/Triton X-100 ratio increases, cmc values decrease. It seems that UNIFAC can predict the fact that in the presence of water, the polyoxyethylene chain is more hydrated, facilitating the aggregation of the molecules. Although UNIFAC can predict the correct trend, the agreement is better for higher water/Triton X-100 ratios. In the absence of water, the differences between the predicted and the experimental results are rather large. UNIFAC underestimates the cmc value by approximately five-fold.

Prediction of cmc for Monoglycerides

Kon-no et al. (18) presented data for the cmc of monoglycerides in nonaqueous solutions (Table 3). Figure 8 shows the experimental and predicted cmc as a function of temperature, for 1-monoolein in cyclohexane and in n-heptane. For these two systems, it was reported that relatively large aggregates are formed. The concentration at which the surfactant deviated from
ideality was taken to be the cmc. The predicted trend of the cmc is consistent with the experimental values, but UNIFAC systematically overestimates the values. We might expect problems in UNIFAC modeling of monoglycerides, because it cannot take into account the proximity effects between the two adjacent hydroxyl groups. Hydrogen bonding between them might be expected to make exposure of the headgroup to nonpolar solvents less unfavorable. This would suggest that aggregation would be less favored, and that the cmc would be higher than predicted by UNIFAC. Unfortunately, this is opposite to the observed deviation.

For the other monoglycerides presented in Table 3, UNIFAC did not predict phase separation, and the shape of the activity–concentration plot does not suggest strong aggregation (Fig. 9). In fact, the reported aggregation numbers in these cases are extremely low (lower than 1.5). The concentration at which the solutions started to deviate from ideality were referred as “critical concentration for aggregate formation,” instead of cmc. Probably UNIFAC and experimental results agree that no true micellization occurs in these systems.

**TABLE 3**
Experimental Systems Used for the Predictions and Their cmc Values

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Surfactant</th>
<th>cmc Values (mole fraction)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30°C</td>
<td>40°C</td>
</tr>
<tr>
<td>Benzene</td>
<td>1-Monocaprin</td>
<td>$2.0 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>1-Monolaurin</td>
<td>$1.5 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>1-Monomyrustin</td>
<td>$1.3 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>1-Monopalmitin</td>
<td>$8.5 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>1-Monostearin</td>
<td>$6.1 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>1-Monoolein</td>
<td>$8.2 \times 10^{-4}$</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>1-Monoolein</td>
<td>$4.5 \times 10^{-4}$</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>1-Monoolein</td>
<td>$4.6 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Note. The cmc values came from Ref. 18.

**FIG. 8.** Predicted and experimental cmc values for monoolein as a function of temperature. (●) Experimental cmc (18). (—) Predicted cmc with modified UNIFAC (1). (A) 1-Monoolein in n-heptane. (B) 1-Monoolein in cyclohexane. cmc is expressed as mole fraction.

**FIG. 9.** Predicted activity as a function of the 1-monostearin mole fraction in benzene, at 30°C. Predictions were done with modified UNIFAC (1). Experimental cmc (mole fraction), $6.1 \times 10^{-4}$ (18).

**CONCLUSIONS**

The UNIFAC group contribution method has been shown to describe satisfactorily the nonideal behavior of nonionic surfactant in organic solvents. Critical micelle concentrations can also be predicted. Only approximate cmc values can be obtained using the original UNIFAC of Hansen et al. (19). However, more accurate values of cmc can be predicted provided the right parameters and UNIFAC model are used.

The UNIFAC group-contribution method has the advantage of being a well-known method widely used to predict activity coefficients for modeling activity-dependent phenomena. Thus, it can be a practical and easy tool for predicting critical micelle concentrations for anyone familiar with the idea of group-contribution methods. More experimental data are needed to investigate the complete capabilities of the method in nonaqueous media. Further work is in progress on UNIFAC predictions of micellization in aqueous media.

**ACKNOWLEDGMENT**

This research was supported by EC Biotechnology Project PL98-0363.

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