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# Quantitative Effect of Nonionic Surfactant Partitioning on the Hydrophile–Lipophile Balance Temperature

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Phase behaviors of water/nonionic surfactants/isooctane systems are determined experimentally in temperature–global surfactant concentration diagrams. The surfactants are monodistributed polyoxyethylene glycol *n*-dodecyl ether. They are used as model mixtures of two, three, or five compounds or as constituents of a commercial surfactant. It is found that the phase diagrams of these systems are bent gradually toward the highest temperatures as the global surfactant concentration decreases. Each phase diagram is well-characterized by the curve of the HLB (hydrophile–lipophile balance) temperature versus the global surfactant concentration. For any fixed global surfactant concentration, this temperature is the middle temperature of the three-phase region; it can be calculated from an additive rule of the HLB temperatures of the surfactants weighted by their mole fractions at the water/oil interface. These mole fractions are determined through the pseudophase model using surfactant partitioning. Calculations require the knowledge of the critical micelle concentration, the partition coefficient between water and oil, and the HLB temperature of each surfactant of the mixture. This treatment can be used to correctly predict the variation of the HLB temperatures of the surfactant mixtures studied versus the global surfactant concentration. Furthermore, these calculations show that the observed curvature of the phase diagrams at the lowest global concentrations is due to the most favorable partitioning toward the oil of the lowest ethoxylated surfactant molecules.

## Introduction

The phase behavior of water, oil, and surfactant mixtures is a subject of considerable research because of its scientific interest. When the surfactants used are nonionic, the phase behavior depends markedly on the temperature. At low temperatures, an oil in water microemulsion coexists in equilibrium with an upper excess oil-rich phase (such a system is designated as Winsor I or 2), whereas at high temperatures, a water in oil microemulsion coexists with a lower water-rich phase (such a system is designated as Winsor II or 2). At intermediate temperatures, a bicontinuous middle-phase microemulsion is in equilibrium with an excess upper oil phase and an excess lower water phase (Winsor III or 3). When the concentration of the surfactant is increased, the volume of the middle phase increases until a “one-phase” microemulsion (Winsor IV or 1) is formed.

The temperature at which the type of microemulsion inverts from 2 to 2 under an increase in temperature is called the phase inversion temperature (PIT) or HLB (hydrophile–lipophile balance) temperature ( $T_{HLB}$ ).<sup>1–6</sup> At this temperature, the hydrophilic and lipophilic affinities of the surfactant just balance, resulting in a minimum interfacial tension between the oil and water phases<sup>7–9</sup> and maximum solubilization.<sup>10,11</sup> Many authors emphasize the importance of this particular temperature for useful

applications in the emulsification process,<sup>3,12,13</sup> such as in the preparation of miniemulsions,<sup>14–16</sup> and the selection of the appropriate surfactant emulsifier.<sup>3,17</sup> It is also used in the preparation of microemulsion.<sup>18</sup> Furthermore, in some cases, the determination of the  $T_{HLB}$  value of a given emulsion or microemulsion is sufficient enough to define it.<sup>19,20</sup>

When a nonionic surfactant, which is monodistributed in the ethylene oxide units, is used, the  $T_{HLB}$  is independent of the surfactant concentration. On the other hand, at a fixed composition of a surfactant mixture, the  $T_{HLB}$  of blends of the monodistributed nonionic surfactants or commercial nonionic surfactant systems is largely skewed toward the highest temperatures as the global surfactant concentration decreases.<sup>21,22</sup> This behavior is mainly

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ascribed to the selective partitioning of each surfactant into the three phases of the system.<sup>6,23</sup>

For a long time, Shinoda et al.<sup>1–5</sup> have been conducting a systematic study of the effect of temperature on systems containing nonionic surfactants, more particularly on the stability and solubilization of emulsions. Kunieda et al.<sup>6,21,22</sup> have also studied the effect of temperature on the phase behavior of multisurfactant and commercial surfactant systems in order to evaluate their HLB based on the occurrence of a three-phase triangle in which oil, aqueous, and surfactant phases are in equilibrium. The surfactant solubilities in water were neglected for these systems.

More recently, Yamaguchi et al.<sup>24,25</sup> have presented a new method to analyze the three-phase behavior of the nonionic surfactant and small amphiphile systems, in which small amphiphiles are markedly soluble in both water and oil, whereas the solubilities of the nonionic surfactant in the excess water and oil phases are negligible. All of these studies have been performed at a constant temperature.

In previous papers,<sup>26–28</sup> we analyzed the effect of the partitioning on the phase behavior of polydistributed nonionic surfactant mixtures or on the surfactant mixtures containing polydistributed nonionic, anionic, and cationic species. We quantitatively determined the partitioning of all of the species in water, oil, and the interface by using the pseudophase model. However, all of these investigations were carried out at 25 °C, while often in practical cases, the temperature varies. Consequently, our investigations were extended to the systems subjected to variations in the temperature. For this purpose, we have already measured the partitioning coefficients of a series of monodistributed nonionic surfactants (polyoxyethylene dodecyl ether) at different temperatures.<sup>29</sup> We also measured the critical micelle concentrations as a function of the temperature for the same series of surfactants.<sup>30</sup>

In this paper, we present a method that can be used to determine quantitatively the phase behavior of the systems composed of water/oil/nonionic surfactant mixtures as a function of the temperature. This method takes into account the partitioning of all of the surfactants of the mixture between the three coexisting phases.

In the first part, we carefully measure the  $T_{\text{HLB}}$  of the monodistributed surfactants and then the  $T_{\text{HLB}}$  of the model mixtures of these surfactants. In the second part, we propose a quantitative treatment of the partitioning effect based on the pseudophase model, by developing a new strategy imposed by the variation in the temperature. Finally, we use the proposed treatment in order to account for the phase behavior of the systems containing the model mixtures of the surfactants or commercial surfactant mixtures.

## Experimental Section

**Materials.** The surfactants used are monodistributed polyoxyethylene glycol *n*-dodecyl ethers ( $\text{C}_{12}\text{E}_i$ )



where *i* is the ethylene oxide number (EON).

These surfactants were supplied by Nikko Chemical Co. (Tokyo, Japan), and their purity grade is very high. Analysis by gas chromatography reveals the existence of a single peak confirming the homogeneity in ethylene oxides for each of them.

The commercial nonionic surfactant is also a polyoxyethylene *n*-dodecyl ether with an average EON equal to 6. It was kindly supplied by Seppic Co., and it will be noted as  $\text{C}_{12}\text{E}_{(6)}$ . The distribution of the ethylene oxide units of its oligomers determined by chromatography is as follows: EON 1, 7.0 mol %; EON 2, 7.6 mol %; EON 3, 8.2 mol %; EON 4, 9.7 mol %; EON 5, 11.4 mol %; EON 6, 12.7 mol %; EON 7, 13.0 mol %; EON 8, 11.7 mol %; EON 9, 9.5 mol %; EON 10, 4.1 mol %; EON 11, 2.5 mol %; EON 12, 1.8 mol %; EON 13, 0.8 mol %. The average EON determined from this distribution is 5.9, which is not far from 6, the average value. Because this polydistributed nonionic was initially prepared by reacting pure normal dodecanol with ethylene oxide gas, we found the presence of a small amount of unreacted alcohol in its composition.

The isooctane is of the spectroscopic grade. The water is twice distilled.

**Procedures.** The phase behavior of each system is determined in the temperature–surfactant concentration diagram.

For each surfactant (or mixture of surfactants at fixed compositions), the mother solutions (aqueous or organic) were first prepared separately. Dilutions from these mother solutions performed in test tubes yielded solutions containing the desired concentrations of the surfactant in an equal volume of oil and water (10 mL). The tubes were sealed with polyethylene stoppers and shaken to facilitate the diffusion between the phases. Then, they were placed in a temperature-controlled water bath ( $\pm 0.05$  °C), and their contents were allowed to settle. In practice, the equilibrium is considered to be reached when the appearance and volume of each phase do not change for several days.

When equilibrium is achieved, the phase behavior of a given system (2, 3,  $\bar{2}$ , or 1) is recorded as a function of the surfactant concentration and temperature. Then, the bath temperature is increased to the next value, and the same operations are repeated (homogenization by shaking, settling, and observation). The bath temperature is changed until the three-phase domain or “one-phase” domain is completely crossed for the range of concentrations studied.

To have an accurate graphic representation of the phase diagrams, we have chosen an incremental step of 1 °C for the temperature and 0.5 or 1 (wt %) for the concentration.

For all of the systems studied, the oil/water volume ratio was fixed at unity.

## Results

**$T_{\text{HLB}}$  of the Monodistributed Surfactants.** The phase behavior of the three systems, each of them composed of water, isooctane, and a monodistributed nonionic surfactant ( $\text{C}_{12}\text{E}_4$ ,  $\text{C}_{12}\text{E}_5$ , or  $\text{C}_{12}\text{E}_6$ ), was experimentally determined. The phase diagrams as a function of the temperature and total surfactant concentration are shown in Figure 1a.

As expected, the phase boundaries of these diagrams look like a horizontal fish submerged in two-phase regions, the 2 region below and  $\bar{2}$  region above. The body of the fish contains the three-phase region; its tail encloses the “one-phase” microemulsion. As an example, the four separated phase regions are indicated for  $\text{C}_{12}\text{E}_5$  in Figure 1a. Furthermore, the height of the three-phase body grows with an increasing EON of the surfactant.

Knowledge of the point where the three-phase body meets the “one-phase” region is very important, because the surfactant concentration at this point represents the

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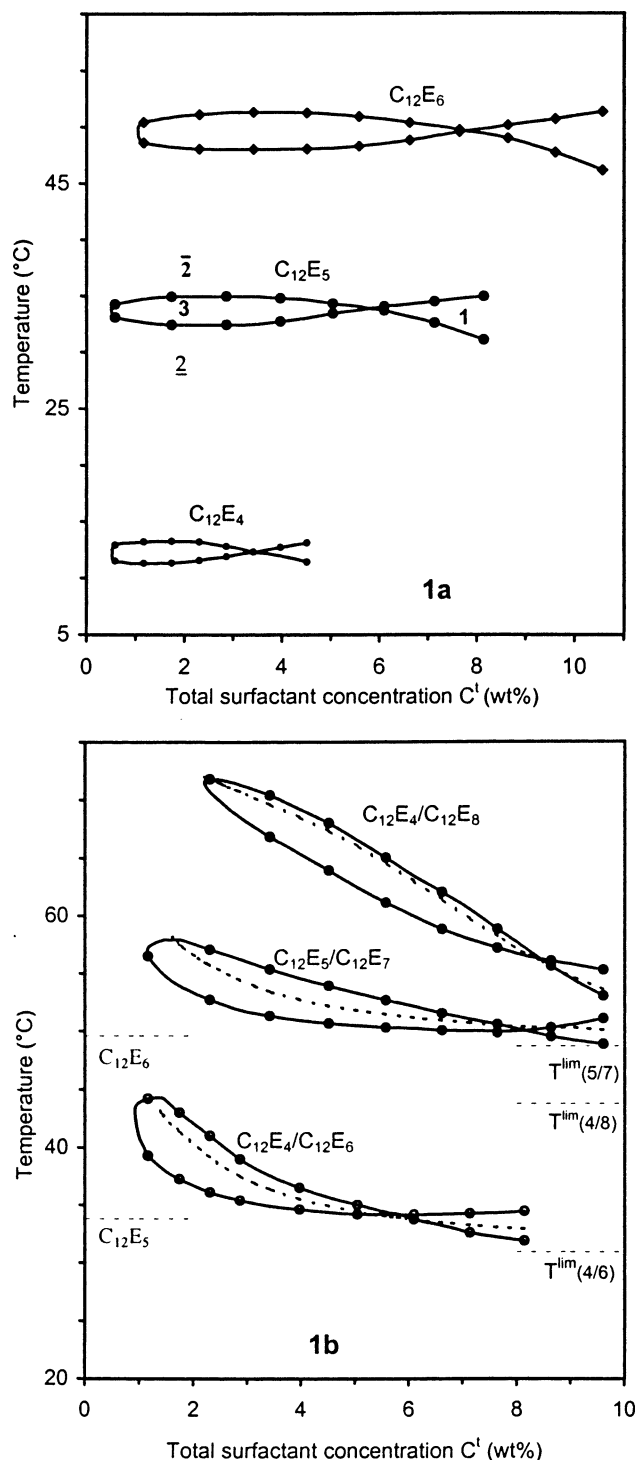
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**Figure 1.** Phase diagrams of the monodistributed surfactants (a) and binary mixtures (b). (---) Calculated curve  $T_{HLB} = f(C^I)$ .

lowest amount required to completely solubilize water and oil together. At this point, the temperature is the actual PIT ( $T_{HLB}$ ); it coincides with the middle temperature of the three-phase domain.

We found the following values of  $T_{HLB}$  for the three surfactants:

$$T_{HLB}(4) = 12.3\text{ }^{\circ}\text{C} \quad T_{HLB}(5) = 33.8\text{ }^{\circ}\text{C} \\ T_{HLB}(6) = 49.6\text{ }^{\circ}\text{C}$$

It is well-known that a linear relationship exists between

$T_{HLB}(i)$  and  $HLB(i)$  as follows:<sup>21</sup>

$$T_{HLB}(i) = A HLB(i) + B \quad (1)$$

where  $HLB(i) = 20[44.02i/(44.02i + 186.54)]$  for the nonionic surfactant used.<sup>31</sup> The three previous values of  $T_{HLB}(i)$  were then plotted in a  $T_{HLB}(i)$ – $HLB(i)$  diagram, to deduce the parameters  $A$  and  $B$  from their alignment. Then, the  $T_{HLB}$  values of the other monodistributed surfactants were calculated by using eq 1.

**$T_{HLB}$  of the Model Mixtures of the Surfactants.** We determined the phase behaviors of two binary mixtures ( $C_{12}E_5/C_{12}E_7$ ) and ( $C_{12}E_4/C_{12}E_8$ ) (Figure 1b), two ternary mixtures ( $C_{12}E_5/C_{12}E_6/C_{12}E_7$ ) and ( $C_{12}E_4/C_{12}E_6/C_{12}E_8$ ) (Figure 2a), and a five-surfactant mixture ( $C_{12}E_4/C_{12}E_5/C_{12}E_6/C_{12}E_7/C_{12}E_8$ ) (Figure 2b) in the temperature–concentration diagrams.

All of these systems were selected in order to keep the average EON of each system equal to 6. Moreover, all of the components in these systems have an equal mole fraction in the total surfactant mixture, except the ternary system ( $C_{12}E_4/C_{12}E_6/C_{12}E_8$ ) with (0.25/0.5/0.25) as the mole fraction of each component, respectively.

As with the monodistributed surfactants, the phase diagrams of these systems also look like a fish. However, this fish is no longer lying horizontally; it is bent gradually toward the highest temperatures as the surfactant mixture concentration decreases. However, the highest temperature measured does not reach the  $T_{HLB}$  of the most ethoxylated surfactant of the mixture.

In the concentration range studied in this paper, as the surfactant mixture concentration is increased,  $T_{HLB}$  decreases toward a lower limit temperature, which is relatively close to the  $T_{HLB}$  of  $C_{12}E_6$  (Figures 1b and 2a).

The same behavior is encountered for the binary mixture ( $C_{12}E_4/C_{12}E_6$ ). Its lower-limit temperature is close to the  $T_{HLB}$  of  $C_{12}E_5$  because the average EON in this surfactant mixture is equal to 5.

On comparison of the phase diagrams of ( $C_{12}E_5/C_{12}E_7$ ) and ( $C_{12}E_4/C_{12}E_8$ ) in Figure 1b and the phase diagrams of ( $C_{12}E_5/C_{12}E_6/C_{12}E_7$ ) and ( $C_{12}E_4/C_{12}E_6/C_{12}E_8$ ) in Figure 2a, it can be observed that an increase in the difference in the ethylene oxide chain length of the surfactant mixtures leads to an increase in the curvature of the phase diagram.

**Modelization of the Partitioning Effect.** It was already reported that the  $T_{HLB}$  of a surfactant mixture is directly related to the surfactant composition at the water/oil interface.<sup>21</sup> This temperature has been expressed as a linear function of the  $T_{HLB,i}$  of the surfactants in the mixture, weighted by their mole fractions ( $X_i$ ) at the oil/water interface

$$T_{HLB} = \sum_{i=1}^n X_i T_{HLB,i} \quad (2)$$

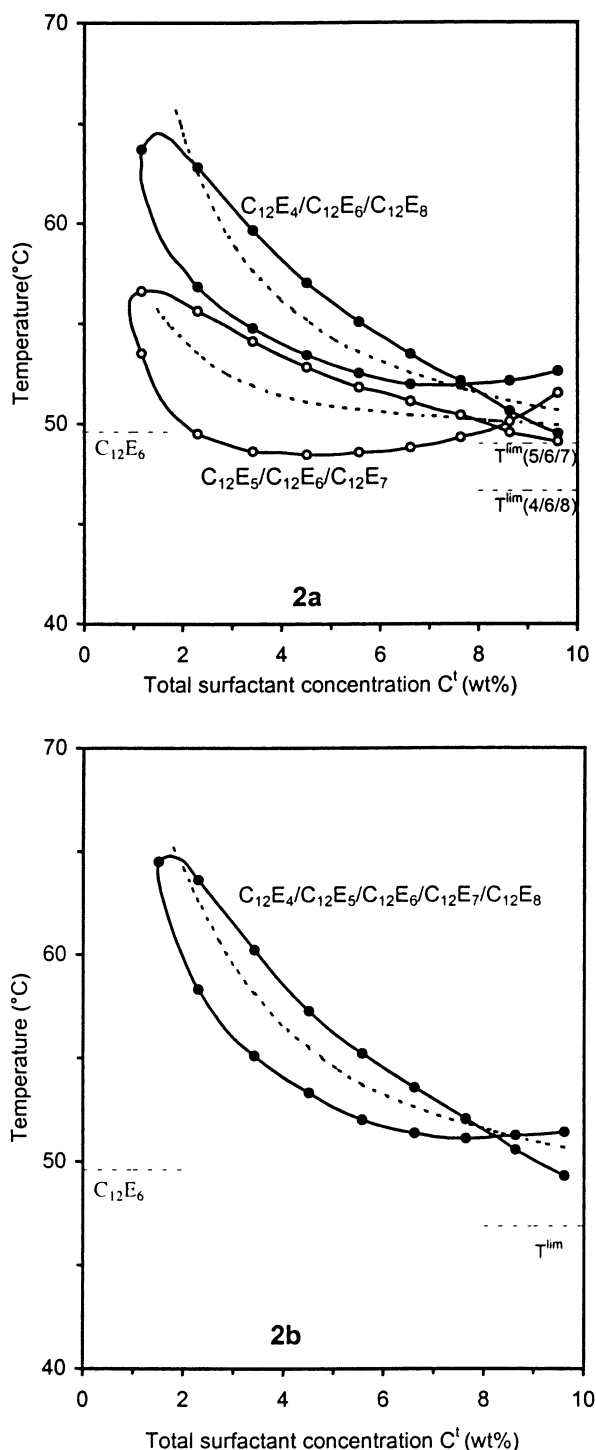
where  $n$  is the number of surfactants in the mixture.

By using this relation, the  $T_{HLB,i}$  of each surfactant can be measured separately, but the  $X_i$  cannot be directly determined. Kunieda et al.<sup>6</sup> determined them after an experimental analysis of the surfactants only in the excess oil phase, neglecting the partitioning of the surfactants into the excess aqueous phase.

In this paper, this assumption can be applied for the surfactants with short ethylene oxide chains, but it does not hold for those with long chains. Indeed, we pointed out in a previous paper<sup>29</sup> that the partition coefficient

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**Figure 2.** Phase diagrams of the ternary surfactant mixtures (a) and five compound mixture (b). (---) Calculated curve  $T_{HLB} = f(C)$ .

between water and oil is greater than the unity for the surfactants with more than 10 ethylene oxide units; therefore, their solubilities in the aqueous phase are greater than those in the oil phase, and consequently, they cannot be neglected.

To determine the  $X_b$ , we used the pseudophase model, which has been successfully applied for the surfactant mixtures.<sup>26–28</sup>

**A New Strategy for Using the Pseudophase Model.** It has been shown that the fractioning of the nonionic surfactants between the excess phases and microemulsion can be accurately predicted by considering the interfacial

region between oil and water as a pseudophase entirely composed of the surfactant and consequently devoid of either oil or water.<sup>26–28</sup> This pseudophase is in equilibrium with the oil and water excess phases, and it is assumed that the microdomains of water and oil inside the microemulsion have the same composition as these corresponding excess phases. The surfactant solutions in oil, like the surfactant solutions in water, are assumed to behave ideally. Then, for a mixture of  $n$  surfactants, the concentration of any surfactant  $i$  in the aqueous phase can be written as

$$C_i^w = \alpha_i X_i C_{mi} \quad i = 1, 2, \dots, n \quad (3)$$

In this relation,  $\alpha_i$  is the mole fraction of the surfactant in the system, and  $C_{mi}$  is its critical micelle concentration at the temperature of the system. The ratio between the concentration of the surfactant  $i$  in the aqueous phase and its concentration in the oil phase is defined as the partition coefficient of the surfactant between water and oil

$$K_i = C_i^w / C_i^o \quad (4)$$

This coefficient depends on temperature.

If  $n_i^t$  is the total inventory of the surfactant  $i$  in the system, then by mass balance

$$n_i^t = n_i^w + n_i^o + n_i^p \quad (5)$$

where the superscripts w, o, and p refer to water, oil, and pseudophase, respectively. Neglecting the volume of the pseudophase, the total volume of the system is

$$V^t = V^o + V^w \quad (6)$$

Using eqs 3–6, it can be showed after some elementary calculus that

$$\left[ C^p + C_{mi} \left( \frac{Z}{1+Z} \right) \left( 1 + \frac{1}{ZK_i} \right) \right] X_i = \alpha_i C^t \quad (7)$$

$$i = 1, 2, \dots, n$$

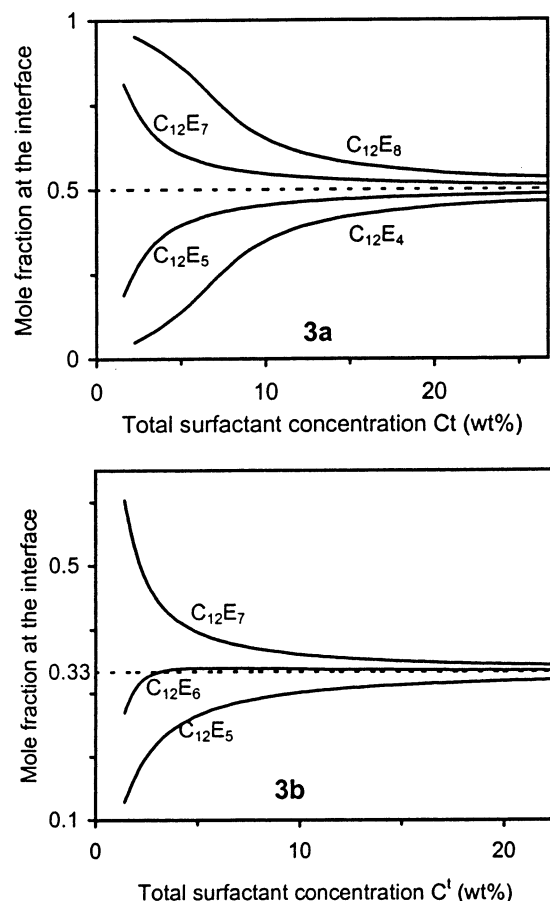
with

$$\sum_{i=1}^n X_i = 1 \quad (8)$$

where  $C^p$  and  $C^t$  are the total inventory of the surfactant mixture in the pseudophase and in the initial total system, respectively, and  $Z = V^w / V^o$  is the water/oil volume ratio.

Equations 2, 7, and 8 form a system of  $n + 2$  equations, which have to be solved to obtain the  $n + 2$  unknowns,  $nX_b$ ,  $C^p$ , and  $T_{HLB}$ . Because  $C_{mi}$  and  $K_i$  implicitly depend on the temperature in a nonlinear way,  $T_{HLB}$  cannot be calculated from the previous equations. Therefore,  $T_{HLB}$  is fixed in order to have  $nX_b$ ,  $C^p$ , and  $C^t$  as the unknown parameters. Then, at each given temperature ( $T = T_{HLB}$ ), the  $C_{mi}$  and  $K_i$  values necessary for the calculations are directly extracted (interpolated or extrapolated) from the databases previously established for the monodistributed nonionic surfactants used here.<sup>29,30</sup>

In practice, for a given surfactant mixture at a fixed composition, the temperatures used for solving the previous system of equations were taken as follows: starting at the lowest temperature, which will be determined in the next section, the temperature is programmed to increase step by step until the  $T_{HLB}$  of the most ethoxylated



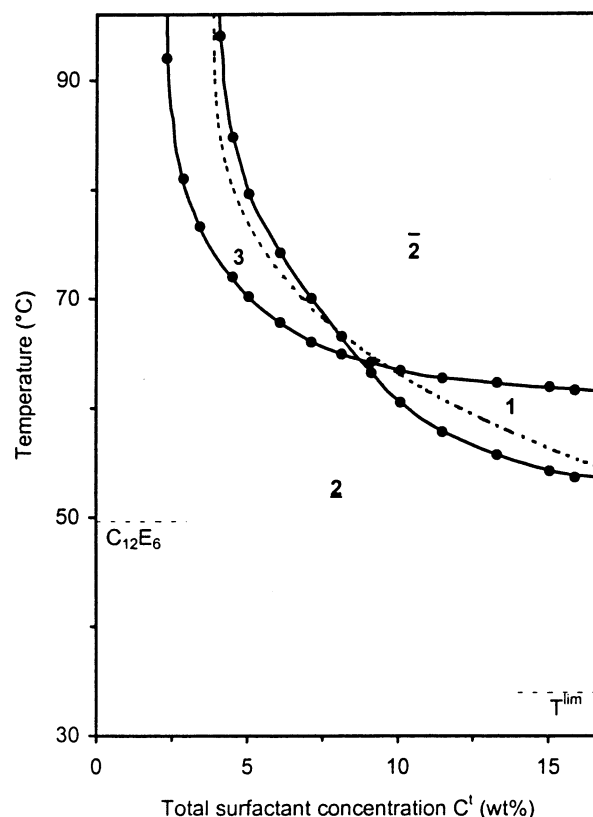
**Figure 3.** Variation in the calculated mole fraction of the surfactants at the water/oil interface for the  $C_{12}E_5/C_{12}E_7$  and  $C_{12}E_4/C_{12}E_8$  mixtures (a) and for the  $C_{12}E_5/C_{12}E_6/C_{12}E_7$  mixture (b).

surfactant of the mixture is reached. The process is interrupted when it begins to provide meaningless values for  $X_i$ ,  $C^p$ , and  $C^i$ . The results are used to plot  $T_{HLB}$  as a function of  $C^i$ .

**Application to the Model Mixtures of the Surfactants.** A comparison between the calculated  $T_{HLB} = f(C^i)$  curve and the experimental data corresponding to the model mixtures of the surfactants is presented in Figures 1b, 2a, and 2b. The agreement between the theory and experiment is satisfactory, taking into account the difficulty of the task.

To illustrate the effect of partitioning on the phase behavior, some examples of the calculated interface composition are given as a function of the surfactant concentration. It can be seen that, in a binary surfactant mixture at low concentrations, the less ethoxylated surfactant is much less concentrated than the more ethoxylated one (Figure 3a), and therefore, the  $T_{HLB}$  of the system is close to that of the more ethoxylated surfactant. As the global surfactant concentration continues to decrease, this tendency is strengthened and consequently  $T_{HLB}$  increases. The highest temperature is determined as the last temperature giving real values for  $X_i$ ,  $C^p$ , and  $C^i$  in solving the  $(n+2)$  equations, as pointed out above. In any case, it cannot reach the  $T_{HLB}$  of the more ethoxylated surfactant in the mixture, in agreement with relation 2.

On the other hand, as the total surfactant concentration increases, the proportion of the less ethoxylated surfactant increases, while that of the more ethoxylated surfactant decreases, which leads to a decrease in the  $T_{HLB}$  of the



**Figure 4.** Phase diagram of the polydistributed  $C_{12}E_{(6)}$ . (---) Calculated curve  $T_{HLB} = f(C^i)$ .

system. At high concentrations, the two mole fractions tend toward the values they have in the surfactant mixture, so that the lower limit for  $T_{HLB}$  can be written as follows:

$$T_{limit} = \sum_{i=1}^n \alpha_i T_{HLB_i} \quad (9)$$

This relation can be used instead of relation 2 when the quantity of the surfactants, which have partitioned into the two excess phases, becomes negligible compared with the total surfactant amount at the interface.<sup>21</sup> However, for most of the surfactant mixtures, this limit cannot be reached experimentally because of the formation of a liquid crystalline phase.

Furthermore, the comparison between the two binary mixtures of Figure 3a shows that the partitioning effect becomes stronger as the difference between the ethylene oxide chain lengths of the surfactants increases. Therefore, the mixture composition is reached less rapidly. This feature can explain the difference in the curvatures of the phase diagram.

For ternary surfactant mixtures, the same behavior is encountered (Figure 3b). Partitioning in the pseudophase is more pronounced for the more ethoxylated surfactant at low concentrations, and the mole fractions of the surfactants at the interface tend toward their corresponding values in the mixture as the surfactant concentration is increased.

**Application to the Polydistributed Surfactant.** The nonionic surfactants commonly used in practical applications are commercial surfactants, which are mixtures of numerous monodistributed ones. It is very useful to understand their phase behavior as a function of the temperature and concentration. Because our treatment of the  $T_{HLB}$  of the model surfactant mixtures was satisfac-

tory, we extended it to the commercial nonionic surfactant  $C_{12}E_{(6)}$ , previously presented in the Experimental Section.

The phase diagram of  $C_{12}E_{(6)}$  looks similar to those of the model mixtures, with a more pronounced curvature at low concentrations (Figure 4). Because the 13 oligomers making up this commercial mixture are of the same family as the monodistributed ones studied above, the already mentioned values of  $K_b$ ,  $C_{mb}$ , and  $T_{HLB}$  have been used. The broken curve in Figure 4 corresponds to the calculated  $T_{HLB}$  curve of  $C_{12}E_{(6)}$ , determined by our quantitative treatment using these values. This curve lies well within the three-phase region and the "one-phase" region. The slight deviation from the middle of these regions can be ascribed to the presence of some impurities, such as unreacted alcohol for example, which are not taken into account in our treatment.

### Conclusion

The quantitative treatment of the partitioning effect proposed in this paper correctly predicts the variations of the  $T_{HLB}$  as a function of the surfactant concentration not only for model surfactant mixtures but also for commercial surfactant mixtures. This treatment is a genuinely quantitative method because the calculations are based on well-identified physicochemical parameters such as  $C_{mb}$ ,  $K_b$ , and  $T_{HLB}$ .

The effect of surfactant partitioning between the excess phases is much stronger at low concentrations. The most ethoxylated surfactants impose their behavior at the

interface, and consequently, the  $T_{HLB}$  values are shifted toward the highest temperatures. This emphasizes the importance of the knowledge of this partitioning effect, because the choice of small amounts of surfactants are often made for economical and environmental reasons in industrial applications.

At high surfactant concentrations, the interface composition tends toward that of the initial surfactant mixture, and therefore, the partitioning effect becomes less marked. However, in practice, this limiting behavior cannot be attained, so that, in most cases, a blend of the surfactants cannot be described by an average EON.

Although the monodistributed surfactants used in this paper have a greater affinity for oil than water and consequently their partitioning in the aqueous phase is much weaker than that in the organic phase or at the interface, our model was designed to be effective based on whatever the hydrophilic character of the surfactant (in other terms, whatever their EON). For surfactants with EON higher than 11, partitioning in water becomes greater than that in oil, and if it is neglected, the prediction of the phase behavior can be erroneous. That is why, for the commercial surfactant used here whose oligomers have EON ranging from 1 to 13, it was absolutely necessary to take into account the partitioning in water of all of the oligomers.

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