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Hydrocarbon Extraction into Surfactant Phase with Nonionic Surfactants. II. Model

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Abstract

The solubilization kinetics of an extraction process of oil with an aqueous micellar solution of a nonionic surfactant has been modeled. The model is directly related to the phase diagram, allowing a simple form which explains the main effects. The theoretical results show the adsorption process of surfactant at the phase interfaces to provide the main resistance to the mass transfer processes. The values of adsorption rates, and of some of the diffusion coefficients obtained, compare well with the earlier experimental results.

INTRODUCTION

In previous work (*1*) we reported the results of an experiment describing the extraction in an oil-water-surfactant system. An aqueous micellar solution of tetraethylene glycol dodecyl ether was contacted with decane, and the development with time of different micellar and liquid crystalline phases was followed. Henceforth, Ref. *1* will be referred to as Part I. In this publication a theoretical model will be constructed to describe the process of extraction after an introductory discussion of the phenomena involved.

After initial contact of the aqueous solution and the oil, four layers were observed, labeled I to IV in Fig. 1. The lowest layer (I) was the aqueous micellar solution and the upper phase (IV) was oil. Layers II and

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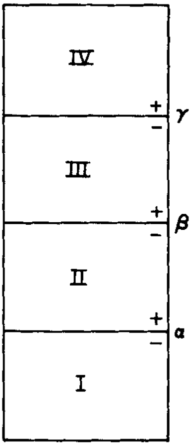

FIG. 1. The arrangement of the four phases: micellar phase (I), birefringent phase (II), surfactant phase (III), and oil (IV); the three interfaces are labeled from below as α, β, and γ.

III were a birefringent layer and the surfactant phase, respectively. The concentration of the aqueous micellar phase and the relative ratio of this phase to oil were chosen from the equilibrium phase diagram, determined in Part I, to be such that the surfactant phase resulted. The importance of such a contacting process lies in the fact that the surfactant phase contains equal parts of oil and water but less than 18% of surfactant. Consequently, a maximum amount of solubilization results with a minimum amount of surfactant. With our experimental results a new factor, the formation of a liquid crystalline phase at the oil/water interface, was brought to our attention. Although such a phase may be expected, considering the phase equilibria in amphiphilic systems (*6*), only one case of the transitory appearance in kinetic studies (*7*) has been reported earlier. However, it was shown in Part I that the birefringent phase (II) was actually a mixture of an aqueous phase and the expected lamellar liquid crystalline phase. The unexpected result was that the four-phase system did not form the single surfactant phase as originally conceived with the help of the phase diagram as the effect of precipitation of the aqueous phase in IV which eventually sealed off the oil.

To help to set Fig. 1 in proper relation to the phase diagram and to be able to construct a valid kinetic model, the interfaces between different layers are labeled from α at the bottom to γ at the top. Since the two concentrations above and below an interface are different, these have been indicated by + and − subscripts. Thus, α_- indicates concentration in Phase I in contact with α_+, the concentration in Layer II, at their mutual interface α.

The oil phase IV is enriched with water and surfactant. As seen in the phase diagram, excess amounts of water will be precipitated and, consequently, it was suggested in Part I that the small amount of water precipitated there forms a thin film which seals off the oil in IV at γ and stops the contacting process from reaching equilibrium. Since the amount of water tolerated in IV is small and the water and surfactant are molecularly dispersed, the diffusion coefficients of these molecules are high. It is assumed that the oil is water saturated and the concentrations in IV are the same as that of γ_+, Fig. 2. γ_+ is in contact with γ_-, which is in the surfactant phase, and both γ_+ and γ_- are on the same tie-line. No precipitates are visible in III as seen with microphotography and birefringence, and the layer is consequently assumed to be a pure surfactant phase. The end of Phase III is in contact with lamellar liquid crystals, and the concentrations at the β interface are marked as β_+ and β_- in Fig. 2. For simplicity, the path between γ_- and β_+ in Phase III is marked with a straight line, which is often argued to be the first approximation (*8*). The position of β_- has been verified with low angle x-ray diffraction as discussed in Part I. The lamellar liquid crystalline

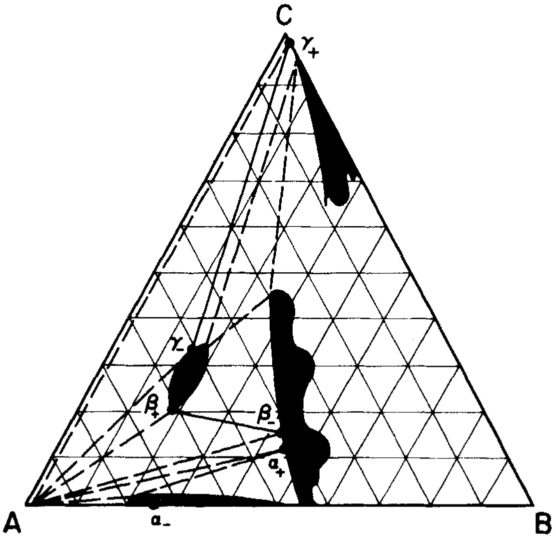

FIG. 2. The position of the concentrations at interfaces are shown on the equilibrium phase diagam.

phase and water droplets make up the birefringent Layer II, as discussed in Part I. Consequently, the composition in Layer II is made up of saturated lamellar liquid crystals dispersed with water. The equilibrium tie-lines are shown by dashed lines in Fig. 2. The lamellar layer ends at α_+, below which the system would give rise to a micellar phase.

In Part I, a number of previous investigations by different researchers were discussed showing that the solubilization of fats and oils by an aqueous micellar solution in many cases gives rise to the formation of a lamellar liquid crystalline phase at the interface (*6*) and that it is governed not by the diffusional resistance but by an "adsorption" phenomenon at the interface (*2–5*). As discussed previously, the formation of Phase II is a verification of the formation of a liquid crystal. The second condition is also verified in the experiments reported in Part I (Fig. 2, Part I) because the aqueous micellar phase was depleted with time at a constant rate. If the mass transfer had been diffusion controlled, the depletion rate would have been linear in the inverse square root of time. If this adsorption of water and oil were governed by linear or Langmuir isotherms, then the concentrations in Phase I would change with time and so would the rate of depletion of this phase. However, the latter was found to be constant and, hence, it is justified to assume that the ratio of water and surfactant going from Phase I to Phase II is also the ratio of their concentrations at α_-. Since the depletion of Phase I is not diffusion controlled, one finds that the variation in concentration in Phase I is insignificant and that the concentration is equal to that at α_- which is also its initial concentration. The position α_- is marked in Fig. 2. The pair of points α_+ and α_- are disjointed because there is neither an equilibrium at α nor is there a concentration variation through I.

MODEL

As shown in the experiments of solubilization and in the detailed theory provided for one interface by Shaeiwitz (*4*), a great number of physical mechanisms come into play during the transfer of amphiphilic substances across an interface: adsorption, desorption, breakdown and reformation of structures such as micelles, lamellar forms, etc., diffusional effects, interfacial mass transfer resistances, etc. In addition to the complexity from all these potential mechanisms, the system studied here has three interfaces. Consequently, it becomes very difficult to provide a detailed description. Even if such a description were available, the details would obscure the main mechanisms and fail to provide a consistent model which avoids some easily realized complications such as the fact that the continuous structures in Phase II, and possibly in Phase III, may not be immobile and that the dislocation patterns may have a considerable influence. Instead, the gross structure is assumed to be formed from below and depleted through the top.

The flux of oil and water was modeled on the assumption of quasistatic behavior. This is justified because of the large times involved. Hence, the fluxes may be written as $j = D\Delta c/l$, where D is the diffusion coefficient, Δc is the concentration difference across a layer, and l is the thickness of the layer. This form for diffusion of oil and water can be used in Layers II and III since the surfactant is assumed to be stationary. It cannot be used in Phases I and IV because it suggests that material enters through the ends of the system shown in Fig. 1. Fortunately, there are no diffusive fluxes in these two phases as argued earlier.

There are two stages in the experiment reported in Part I. In the first stage, which lasts for about 800 h, there are four phases as shown in Fig. 1, and the transport process is quite active. In the second stage, i.e., beyond 800 h, the transport process is extremely slow or nonexistant, partly because the aqueous micellar Phase I had completely disappeared and partly because the oil is effectively sealed off by that time as seen from the unchanged oil level. Consequently, it is only the first stage, shown in Fig. 1, that is of interest and is analyzed below.

Using superscripts I and IV to designate layers and mass fraction O, W, and S for oil, water, and surfactant, respectively, one has the material balance for Phase I as

$$\frac{\rho^{\mathrm{I}} dl^{\mathrm{I}}}{dt} = -R\left(1 + \frac{{}^{W}\alpha_{-}}{{}^{S}\alpha_{-}}\right) \tag{1}$$

where R is the rate in mass/(time-interfacial area) at which the surfactant leaves Phase I and the amount of water that accompanies it is proportional to concentrations at α_-. The amount of oil in this phase is very small and is neglected in the material balance. As the ratio between water and surfactant that enter Phase II is the same as in Phase I, with some amount of enrichment with oil, the resultant mixture at α_+ occupies the two-phase region (between the lamellar liquid crystalline phase and the water) immediately above the α_- composition. That is, the mixture splits into a lamellar liquid crystalline phase and water. The latter is trapped as droplets in a very viscous medium. The surfactant in Layer II is assumed to be immobile, and just as the liquid crystals build up from the bottom by adsorption from the aqueous micellar Phase I, these are depleted from the top by desorption/dissolution into the surfactant Phase III. Whereas the former process brings into Layer II material $R(1 + ({}^W\alpha_-/{}^S\alpha_-))$, the latter process takes out $Q(1 + ({}^W\beta_-/{}^S\beta_-))$, where Q is the rate of uptake of surfactant from the lamellar liquid crystals in layer II into the surfactant Phase III. The oil diffuses through Phase III into II at a rate $(\rho^{III}D_O^{III}/l^{III})\,({}^O\gamma_- - {}^O\beta_+)$. However, some oil is transferred from β_- to β_+ but not enough of it, and consequently some of the oil moving down is adsorbed at the β_+ interface. The rate at which oil leaves Phase II at β_- by adsorption is $Q({}^O\beta_-/{}^S\beta_-)$ and the amount of oil needed to form phase III at β_+ is $Q({}^O\beta_+/{}^S\beta_+)$. Thus, the amount of oil adsorbed at β_+ from the oil moving down is $Q[({}^O\beta_+/{}^S\beta_+) - ({}^O\beta_-/{}^S\beta_-)]$. The excess oil flows into Phase II, the rate of which is

$$\frac{\rho^{III}D_O^{III}}{l^{III}}({}^O\gamma_- - {}^O\beta_+) - Q\left(\frac{{}^O\beta_+}{{}^S\beta_+} - \frac{{}^O\beta_-}{{}^S\beta_-}\right)$$

Thus, the material balance in Phase II is

$$\frac{\rho^{II}dl^{II}}{dt} = R\left(1 + \frac{{}^W\alpha_-}{{}^S\alpha_-}\right) + \frac{\rho^{III}D_O^{III}}{l^{III}}({}^O\gamma_- - {}^O\beta_+) - Q\left(\frac{{}^O\beta_+}{{}^S\beta_+} - \frac{{}^O\beta_-}{{}^S\beta_-}\right)$$
$$- Q\left(1 + \frac{{}^W\beta_-}{{}^S\beta_-}\right) \qquad (2)$$

Similarly, it can be said that there is an upward diffusion of water in Phase II. The droplets are trapped in a viscous medium but the molecularly dispersed water is mobile. The flux takes place from Phase I through Phase II into Phase III. This loss of water from Phase I is assumed to be very small compared to the adsorption mechanism given in Eq. (2), but is important when Phase III is considered. Some enhancement of this flux can also take place in Phase II. As for the oil, the amount of water taken up by adsorption at β is $Q({}^W\beta_-/{}^S\beta_-)$, whereas the amount needed to make β_+ is $Q({}^W\beta_+/{}^S\beta_+)$. Consequently, if $(\rho_{LC}^{II}D_W^{II}/l^{II})$. $({}^W\alpha_+ - {}^W\beta_-)$ is the flux of water, then $(\rho_{LC}^{II}D_W^{II}/l^{II})\,({}^W\alpha_+ - {}^W\beta_-) - Q[({}^W\beta_+/{}^S\beta_+) - ({}^W\beta_-/{}^S\beta_-)]$ is the excess that passes into Phase III after adsorption at β_+. The material balance in Phase III becomes

$$\rho^{III}\frac{dl^{III}}{dt} = \frac{Q}{{}^S\beta_+} + \frac{\rho_{LC}^{II}D_W^{II}}{l^{II}}({}^W\alpha_+ - {}^W\beta_-) - Q\left(\frac{{}^W\beta_+}{{}^S\beta_+} - \frac{{}^W\beta_-}{{}^S\beta_-}\right) \qquad (3)$$

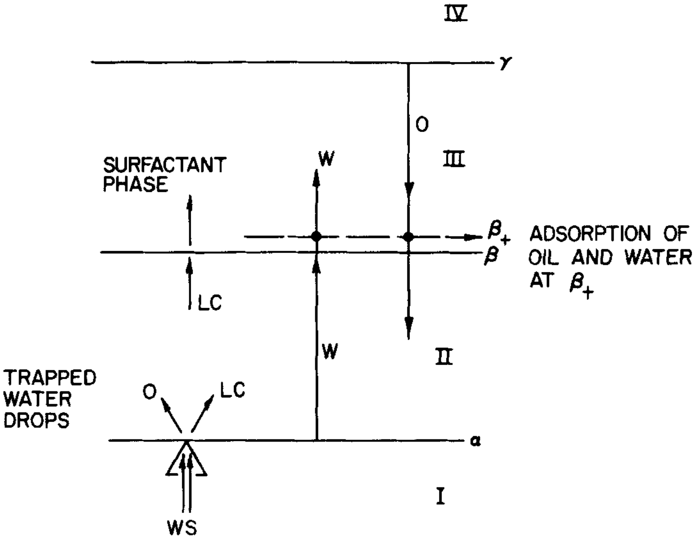

FIG. 3. Schematic view of the transport process.

The overall scheme is shown in Fig. 3. The weight fractions at α, β, and γ are obtained from Fig. 2. The linear equation, Eq. (1), can be fitted to the data for l^{I} with least squares to obtain R. Equations (2) and (3) are coupled with the unknowns D_O^{III} and D_W^{II}, each appearing once but Q appearing in both. The parameters are difficult to estimate because Eqs. (2) and (3) cannot be integrated and Q appears in both equations. An initial guess for the set of parameters was made, and the next guess was obtained by local linearization about those parameters by adapting and modifying the usual nonlinear regression (*10*). l^{II} and l^{III} and their derivatives with respect to the parameters were obtained numerically for every iteration. The dependent variable was taken as the vector $\begin{pmatrix} l^{II} \\ l^{III} \end{pmatrix}$.

The analysis which minimizes the sum

$$\left[\sum_i \left(l_{i,\text{exptl}}^{II} - l_{i,\text{predicted}}^{II}\right)^2 + \sum_i \left(l_{i,\text{exptl}}^{III} - l_{i,\text{predicted}}^{III}\right)^2\right]$$

where i refers to the ith data point, converged very rapidly. The values obtained were $R = 7.78 \times 10^{-4}$ g/(cm$^2 \cdot$ h), $Q = 1.704 \times 10^{-4}$ g/(cm$^2 \cdot$ h), $D_O^{III} = 2.411 \times 10^{-7}$ cm^2/s, and $D_W^{II} = 1.306 \times 10^{-6}$ cm^2/s. The density values

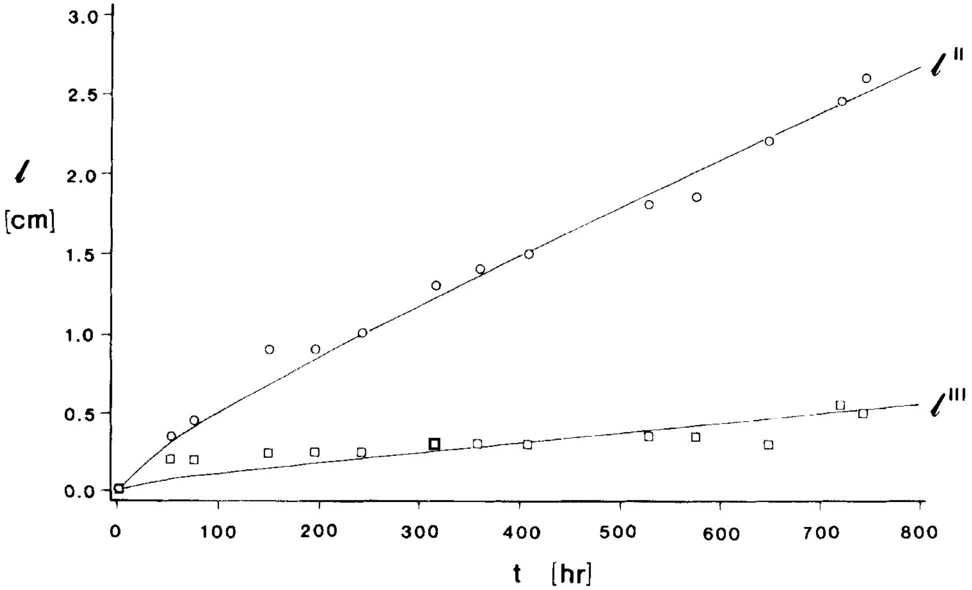

FIG. 4. Comparison of the experimental data with the results from the theoretical model.

used were $\rho^{I} = 0.9925$, $\rho^{II} = 0.9709$, and $\rho^{III} = 0.9163$, and that for the liquid crystals was $\rho^{II}_{LC} = 0.9418$ g/cm^3. These were computed with the following densities: water 1.0, decane 0.73, and surfactant 0.97 g/cm^3. In Phase II it was assumed that water-to-liquid crystals ratio was 1:1.

More data points than those reported in Part I (Fig. 2) were used. The data points and the solutions are plotted in Fig. 4.

DISCUSSION

Some effort has been made to reduce the number of unknown constants and to simplify the formulation in the proposed model. The diffusion coefficients of oil and water in liquid crystals is of the order of 10^{-7} to 10^{-6} cm^2/s and 0.8–3 × 10^{-6} cm^2/s, respectively (*11*). The diffusion coefficient of water was independently determined here as 1.306 × 10^{-6} cm^2/s. The diffusion coefficient of oil in the surfactant phase was found to be 2.411 × 10^{-7} cm^2/s, in contrast to the reported self-diffusion coefficient values of 1–7 × 10^{-6} cm^2/s (*12*). The adsorption rate for surfactants from the micellar form to the liquid crystalline form was found to be

7.78×10^{-4} g/(cm$^2 \cdot$ h) and from the liquid crystalline form to the structure peculiar to the surfactant phase to be 1.704×10^{-4} g/cm$^2 \cdot$ h). In contrast, Shaeiwitz et al. (*4*) report $1{\sim}2 \times 10^{-4}$ for the dissolution of palmitic acid in sodium dodecyl sulfate. Thus, it is seen that the results obtained here, while including many approximations, agree reasonably well with known data. In other words, the basic mechanisms have been preserved.

It is worth noting the main assumptions made in the model. The first is that the rate of adsorption of water from Phase I to Phase II to that of surfactant is proportional to their concentrations in Phase I. This explains in a simple way the constant rate of depletion of Phase I. This mechanism has also been used to explain the depletion of Phase II into Phase III, i.e., the surfactant-containing phase depletes as a whole if there is an adequate supply of make-up oil and water. It has been suggested from time to time (*2–4*) that when surfactant molecules are transferred from one interface to another and undergo structural changes, it is the latter that is rate controlling. For instance, the structural change is demicellization when the surfactant molecules are in micellar form at the interface. Recently, Roy et al. (*13*) looked at the transport of micelles through porous membranes. According to their experiments, micelles do appear to break down into single amphiphiles and then diffuse through pores and eventually reconstruct themselves on the other side. However, the transport is seen to be independent of concentration, suggesting that the process is not diffusion controlled even in such an adverse case. Although Shaeiwitz et al. (*4*) found some cases where the transport is diffusion controlled, such cases appear to be rare. It appears that structure-breaking/structure-forming resistances are generally the largest. Additional experiments are being done to investigate this feature.

Lastly, note this interesting feature. Traditionally, spontaneous emulsification has been seen to occur due to diffusion (*8, 14*). An instance is seen here where the mass transfer is adsorption limited but spontaneous emulsification still takes place, as seen in the form of trapped water droplets in Phase II.

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