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Hydrocarbon Extraction into Surfactant Phase with Nonionic Surfactants. I. Influence of Phase Equilibria for Extraction Kinetics

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Hydrocarbon Extraction into Surfactant Phase with Nonionic Surfactants. I. Influence of Phase Equilibria for Extraction Kinetics

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Abstract

The kinetics of absorption of decane into a "surfactant phase" in a oil–water–surfactant system capable of forming microemulsion was estimated by studying the relative changes in phase volumes when appropriate amounts of decane were brought into contact with an aqueous solution of tetraethylene glycol dodecyl ether at 30°C. The extraction rate was strongly retarded by the fact that the mass transfer path included a liquid crystalline phase. Extraction rate was obtained for a direct contact between the hydrocarbon with water and solubilized surfactant at a ratio which on equilibration produces the surfactant phase. This extraction path provides maximum solubilization of oil with minimum surfactant.

INTRODUCTION

The energies for the stabilization of various phases of oil–water–surfactant systems, capable of showing microemulsion phases, are generally taken to be small since the interfacial energies are "ultralow." Consequently, such systems provide a potential method for the extraction of oils with very low energy requirements (*1*). The studies on the kinetics of mass transfer in such systems are few: Shaeiwitz, Chan, Cussler, and Evans

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(*2*) studied the mass transfer of solid fatty acids from a spinning disk into an aqueous micellar solution and found a large number of cases where the mass transfer was limited by adsorption of micelles at the interface. The results indicated the slow stage of the process to involve desorption of the micelle from the fatty acid/water interface. Carroll (*3*) and Carroll and Ward (*4*) also observed that the rate-limiting step in solubilization of oil was the adsorption of micelles at the interface, assuming dissociation of the micelle to occur prior to the adsorption step. The authors showed the contribution from diffusion of hydrocarbon molecules through the water to the micelles to be without significance for an aliphatic hydrocarbon. Tondre and Zana (*5*) determined the solubilization rate of water and hydrocarbon into a microemulsion system with sodium dodecyl sulfate/pentanol as stabilizers under conditions of rapid mixing. They found the dissolution rates larger than the reciprocal of the time for intimate mixing, and concluded the diffusion-controlled collisions between oil (or water) droplets and microemulsion droplets to be the rate-determining step.

Hence, what is generally lumped as adsorption at the interface has been estimated to be a more complex process involving restructuring of micelles delivered to the interface into an adsorbed layer. The situation is similar to crystal growth when the mass transfer process brings the material that crystallizes from the solution to a crystal surface; however, these molecules must fit into a lattice site in order to be a part of the crystal (*6*). Consequently, the restructuring provides a resistance to the transport at interfaces whose kinetics can be best referred to in general as the kinetics of phase change at the interface.

We would, with this article, like to draw attention to the fact that the interface between an aqueous solution of a surfactant and a liquid carboxylic acid of necessity must include a liquid crystalline structure as shown by the great number of systems investigated by Ekwall and collaborators (*7*).

Since this effect has not been investigated, and since both the process of extraction and mass transfer mechanisms are of value, we have undertaken a study to explore the effect of the formation of a liquid crystal at the interface. Extraction is effected by mixing oil with an aqueous nonionic surfactant such that the surfactant phase (*8–11*) results. Such an extraction method is extremely effective since to make the surfactant phase with approximately equal amounts of oil and water, only 6 to 8% of the surfactant are needed. That is, a large amount of oil is solubilized using very little surfactant. In addition, the separation of the oil may be obtained by a simple temperature reduction of about 20°C (*1*).

The experiments were made by contacting oil with an aqueous micellar solution of a composition and in a relative amount to give the isotropic liquid surfactant phase when combined. Observations were made on the amount of phases that appeared. In this manner, the path taken by the system during mass transfer could be identified on the phase diagram and the roles played by different phases clarified. This also necessitated that the phase equilibria be determined first.

EXPERIMENTAL

Materials

The decane was Aldrich 99% pure, Gold Label. The tetraethylene glycol dodecyl-ether was Nikkol (>98%). The water was twice distilled.

Contacting Measurements

Aqueous solutions of the surfactant were placed in the bottom of a test tube and the hydrocarbon gently poured on top of it with care to retain the interface in an unbroken state. The volume of the different layers was measured directly on the thermostatted test tube.

Phase Equilibria

The phase boundaries were found by direct titration with one of the components at different compositions by noting points of clarity and turbidity for the isotropic liquid phases. The lamellar liquid crystalline phase was found, and its borders were observed by microscopy in polarized light.

The phase equilibria were found by observation of the number of phases of several series of samples in the multiphase regions. In this way the three-phase areas were separated from the two-phase regions because the presence of a liquid crystalline phase could easily be detected in a optical microscope with polarized light.

Low-Angle X-Ray Diffraction

A small amount of sample from the top of the birefringent layer was drawn into a fine glass capillary, then sealed in a flame for x-ray determinations of interlayer spacings in a Kiessig low-angle camera from

Richard Seifert. Ni-filtered Cu radiation was used, and the reflections were recorded by a Tennelec position sensitive detection system, PSD-1100.

RESULTS

The results are presented in the following order to facilitate the comprehension of the relation between the phase equilibria and the extraction kinetics. The phase boundaries in the pertinent part of the system are introduced, followed by the changes in phase boundaries with time in the contact experiments. After that, the phase equilibria are introduced and the essential barrier to extraction is presented.

Phase Regions

The phase regions (Fig. 1) in the part of the system with lower surfactant content are pertinent for the extraction experiments. This part of the system shows five isotropic phases:

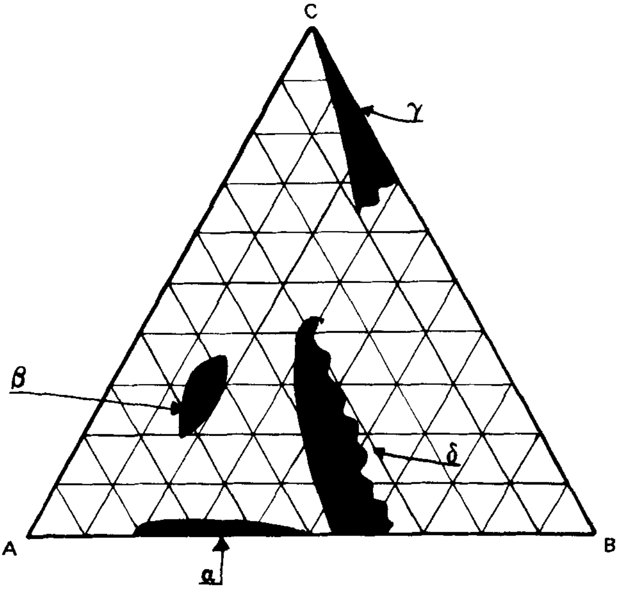

FIG. 1. In the system water (A), tetraethylene glycol dodecyl ether (B), and *n*-decane (C), the following phases were involved in the investigation: A = water with molecularly dispersed surfactant and hydrocarbon, α = aqueous micellar solution, β = "surfactant phase," δ = lamellar liquid crystal, γ = hydrocarbon/surfactant solution with solubilized water.

(1) Water with molecularly dispersed surfactant and hydrocarbon (A)
(2) Aqueous micellar region (α)
(3) Surfactant phase (β)
(4) Decane/tetraethylene glycol dodecyl ether solution with solubilized water (γ)
(5) A lamellar liquid crystalline phase (δ)

Extraction Experiment

3.00 g of a solution with 25.08 wt% tetraethylene glycol dodecyl ether (TEGDE) and 74.92% water was prepared, and 1.169 g of decane was placed on top of it. The gradual change of layers involved is given in Fig. 2. The volume of the observable aqueous micellar phase was approximately linearly reduced with time in 800 h and replaced by a birefringent layer.

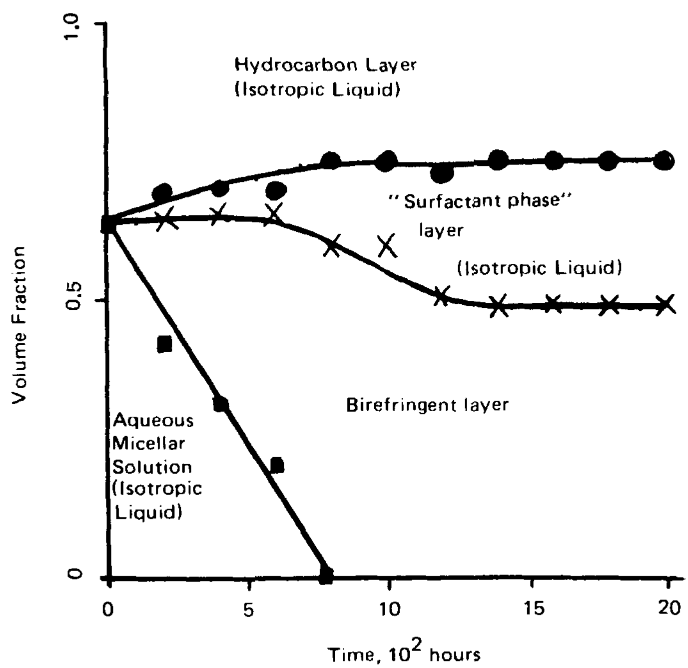

FIG. 2. Relative variation of different layers versus time. Initially, 1.169 g of *n*-decane was placed on top of 3.00 g of aqueous micellar solution 74.92% water and 25.08% surfactant. The initial height of the hydrocarbon layer was 1.54 cm.

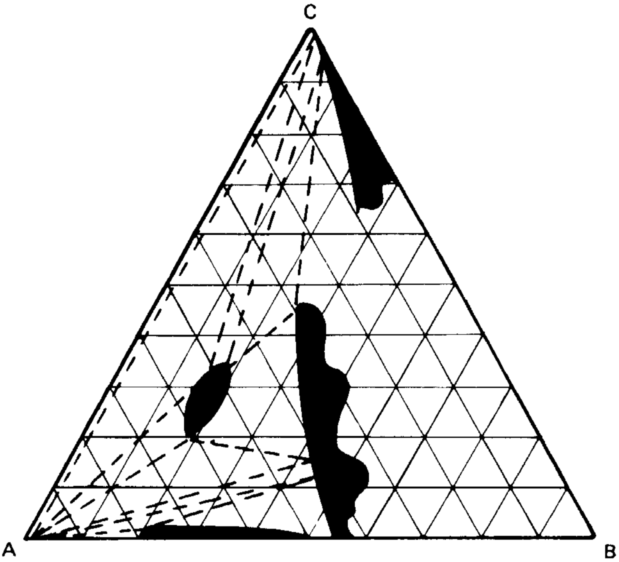

FIG. 3. The system from Fig. 1 with tie-lines marking two- and three-phase areas.

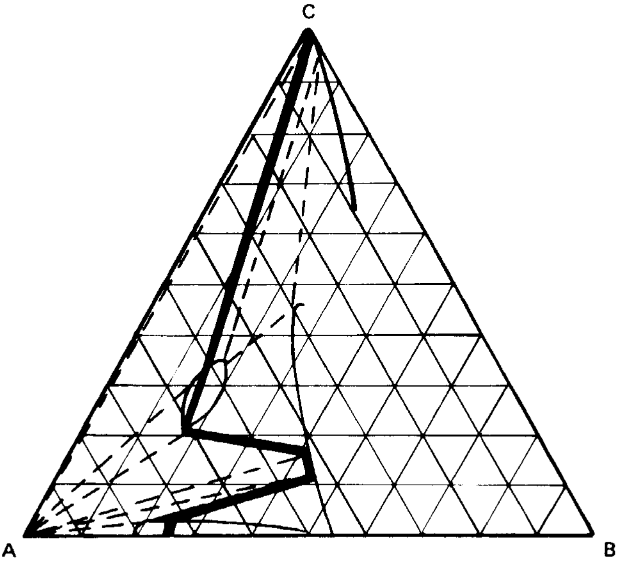

FIG. 4. The wide line marks the transport path from the micellar solution and *n*-decane (cf. Fig. 1).

After 800 h the volume of the birefringent layer was not increased; a slight reduction was found. In a time range of less than 600 h, the increase of the surfactant phase was small, showing a more rapid increase in a time range of 600–1400 h, and after that it was constant. The hydrocarbon phase was slightly reduced up to 800 h and remained constant after that.

Phase Equilibria

The phase equilibria (Fig. 3) show two three-phase areas between the aqueous micellar region and the surfactant, involving the water and the liquid crystalline phase in addition to the two phases mentioned. It should be observed that the surfactant phase (β, Fig. 1) and the aqueous micellar solution (α, Fig. 1) were not in equilibrium with each other. The two-phase area between the surfactant phase β and the decane/tetraethylene glycol dodecyl ether solution (γ, Fig. 1) was narrow, limited by two three-phase regions including the lamellar liquid crystalline phase and the water, respectively.

DISCUSSION

The results gave sufficient information to establish the route of mass transport in the system as marked in Fig. 4. The hydrocarbon/surfactant solution (γ) was in equilibrium with the surfactant phase, and the surfactant phase, in turn, was in equilibrium with the lamellar liquid crystalline phase (δ). The latter was in equilibrium with the micellar solution (α).

A sample removed from the top part of the liquid crystalline phase gave an interlayer spacing of 66 Å. A comparison with earlier results (*12*) indicated a composition close to the limit of $\beta + \delta$ (Fig. 1) with the least hydrocarbon in the surfactant phase/liquid crystal two-phase area. This result supports the transport route from the surfactant phase to the lamellar/liquid crystal as indicated in Fig. 4.

The overall transport pattern from Fig. 2 consists of an initial transport of hydrocarbon through a concentration gradient in the surfactant phase to the liquid crystalline phase. The amount of surfactant phase was small prior to depletion of the micellar solution at 800 h. The transport in this direction was complemented by transfer of water and surfactant from the micellar phase, and a first observation of Fig. 2 indicates the entire content of the micellar phase is combined with the hydrocarbon to form mainly the lamellar liquid crystal.

A simple mass balance calculation shows this interpretation not to be

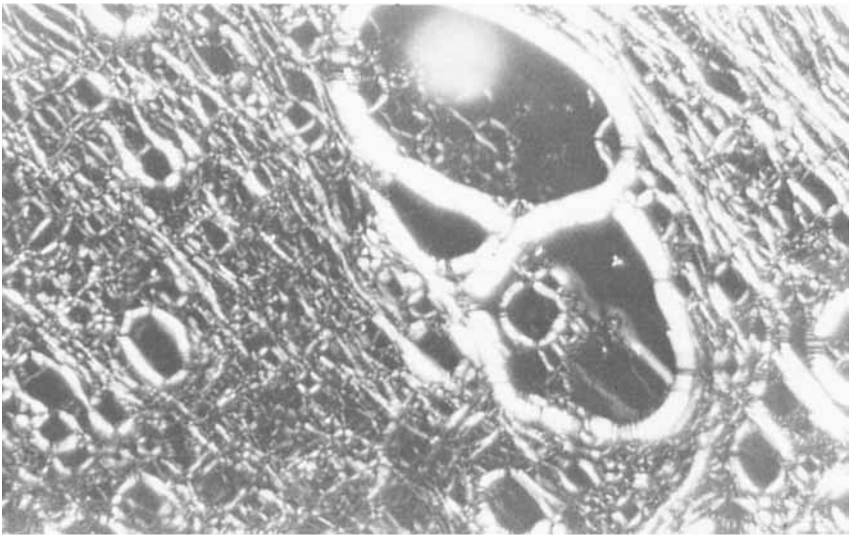

FIG. 5. A photomicrograph of a sample in polarized light shows the fine dispersion of the water in the liquid crystalline phase.

correct. To account for the surfactant content in both the aqueous micellar solution and the surfactant phase, one is left with approximately half the amount of surfactant needed if the birefringent layer were only lamellar liquid crystal. Hence, the birefringent layer on top of the aqueous micellar solution cannot be a single phase. The phase equilibria in Fig. 3 suggest a dispersion of water (A) and liquid crystal forms the layer. The two- and three-phase areas are easily accessible to the original micellar solution (α, Fig. 1) on addition of oil without a change in its water/surfactant ratio.

This interpretation is supported by a photomicrograph (Fig. 5) showing isotropic droplets dispersed in a liquid crystalline matrix. Spontaneous dispersion of this kind has been reported by Miller et al. (*13*).

With this assumption and by assuming reasonable average compositions in the surfactant phase (53% water, 18% surfactant, and 29% hydrocarbon) and the liquid crystal (42% water, 41% surfactant, and 17% surfactant), the volume ratio variation of all phases in the system during the experiment were calculated. The results (Fig. 6) show the separation of water (phase A) and the liquid crystal to be parallel, but the water phase was of larger magnitude than the liquid crystalline phase due to continuous transport of surfactant, hydrocarbon, and water into the surfactant phase.

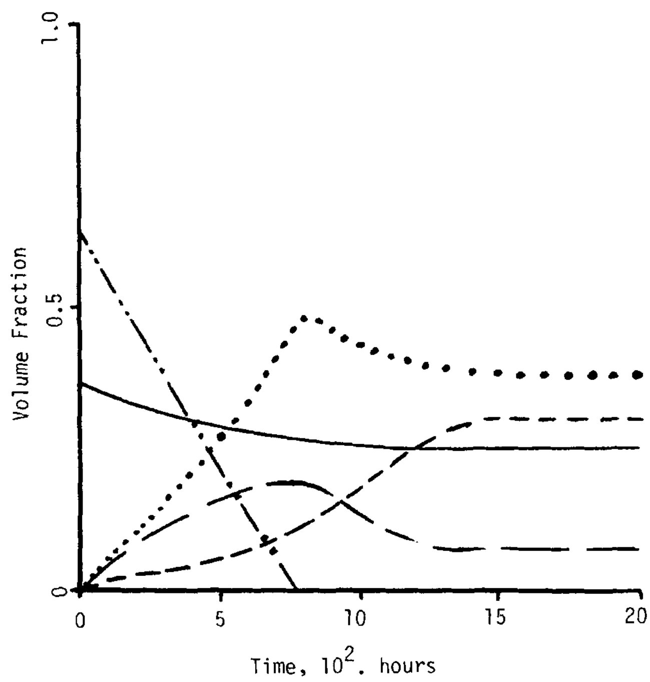

FIG. 6. The relative volume of all involved phases was calculated as a function of time: (——) *n*-decane, (– –) lamellar liquid crystal, (- -) surfactant phase, (– · ·) aqueous micellar solution, (· · ·) water.

The fraction of liquid crystal in the binary mixture, Fig. 6, was continually reduced to the time (≈1500 h) (Fig. 7) when the growth of the surfactant phase ceased.

A second interesting feature was that, when contacted this way, the oil and aqueous micellar solution did not equilibrate. When the two were chosen in a ratio which leads to only the surfactant phase at equilibrium, the oil is virtually unchanged and the liquid crystals remained even at 2000 h after the initial contact. The reason may be the fact that according to the phase equilibria in Fig. 3, the path taken by the system on the phase diagram must pass through the three-phase region with *water* as one of the phases, even though enrichment of pure oil with surfactant and water causes the surfactant phase to precipitate. Consequently, some water also precipitates in the oil phase, eventually giving rise to a thin water film separating and, hence, isolating the oil from the rest of the system. One reaches the important conclusion that in contacting processes, the phases

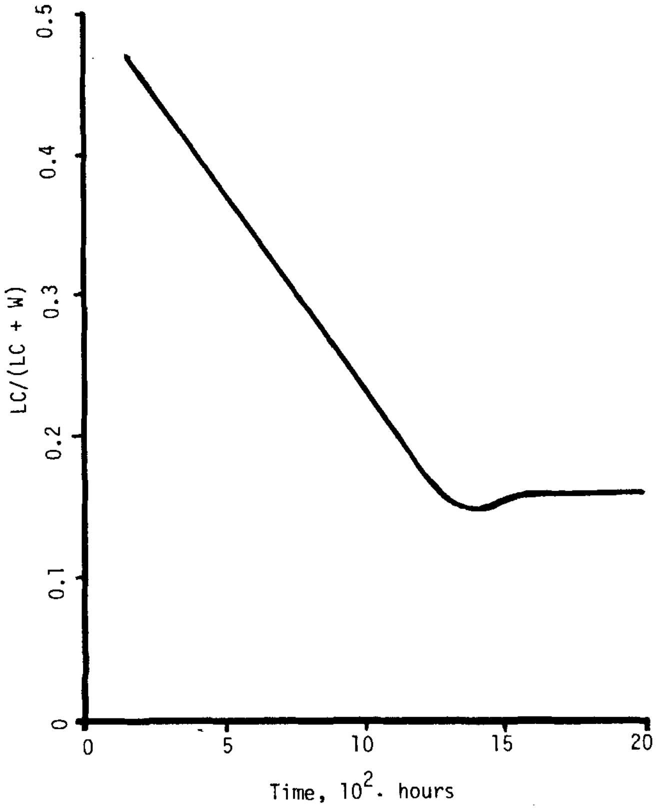

FIG. 7. Volume fraction of liquid crystal (LC)/liquid crystal (LC) + water (W) versus time.

predicted by equilibrium may never be attained due to the nature of contact.

Similarly, we demonstate here the importance of the equilibrium phase diagram on the extraction process. The three-phase regions in the aqueous end of the phase diagram produce liquid crystals and slow the rates. The three-phase region of oil, water, and surfactant creates a water phase in the oil and the liquid crystal, and stops the extraction process altogether.

One other feature of the contacting process is the constant rate of change of the thickness of the aqueous micellar phase. If the rate of mass transfer from the micellar phase is limited by diffusion, then the change in the square of the thickness would have been proportional to time. Since this is not the case, mass transfer in the system is assumed to be limited by adsorption of micelles at the interface, based on previous work (*3*, *4*). In this process of adsorption, the restructuring of single amphiphiles from spherical micelles into the lamellar phase is probably the most difficult and rate limiting as discussed earlier.

A surfactant transport rate independent of diffusion has recently been reported by Ruckenstein et al. (*14*). During diffusion through porous membranes, the diffusion rate will be independent of concentration when the surfactant is transported in the form of micelles.

Finally, from the above discussions it is possible to provide the concentration changes from the top to the bottom, as shown in Fig. 4. Since the oil is cut off after it precipitates both the surfactant and water, the oil–surfactant phase tie-line lies near one extreme of the water–oil–surfactant phase three-phase region. The surfactant phase is also in equilibrium with pure water throughout. The lower end of the birefringent phase, containing water dispersed in liquid crystals, is in equilibrium with the aqueous micellar phase.

With this sketch of the contacting process, a more formal study of the kinetics can be undertaken. This will be taken up in Part II.

Acknowledgments

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