Single-Component Mass Transfer in a Cosurfactant-Water-Surfactant System

A mass transfer system has been designed to allow transport of only one component and over small changes in concentration. One of the phases was always lamellar liquid crystals, the other was micellar or its inverse structure. It can be argued that the kinetics of phase transformation at the interphase would be important in such systems; in fact, the measurements of individual phase volumes show overshoots that are not explained by classical mass transfer mechanisms. It is suggested that the intermediate structures that are formed during transport are not thermodynamically favored, and consequently the condition of local equilibrium does not hold. Using developments for such systems in diffusion in polymers, the breakdown of local equilibrium has been shown to be adequate in explaining the observations qualitatively. A parallel development for adsorption has not been undertaken.

Zhuning Ma
Beijing Graduate School
East-China Petroleum Institute
Beijing, P. R. China

Stig E. Friberg
Department of Chemistry
Clarkson College of Technology
Potsdam, NY 13676

P. Neogi
Department of Chemical Engineering
University of Missouri
Rolla, MO 65401

Introduction

A significant number of extraction-purification schemes employ surfactants (Schamehorn and Harwell, 1989), and a particular kind of extraction scheme to be used to recover crude petroleum from underground reservoirs (Reed and Healy, 1977; Sharma and Shah, 1985, Neogi, 1987; Miller and Qutubuddin, 1987) is receiving considerable attention at present. In most cases, an aqueous solution or suspension of surfactants is used to contact oil or oil bearing materials (Friberg et al., 1985, 1986; Benton et al., 1986; Raney et al., 1985). The success of the extraction process depends both on oil-water-surfactant-phase equilibria and mass transfer kinetics. The scheme is also central to detergency (Raney et al., 1987; Carroll, 1981; Carroll et al., 1982; Tondre and Zana, 1980) as well as in the physiological detergency problem of dissolution of gallstones and cholesteric materials (Chan et al., 1976; Schaeiwitz et al., 1981).

One method for determining the dynamics in oil-water-surfactant-cosurfactant system has been to layer oil on a surfactant containing phase and measure individual phase volumes as they evolve in time. A difficulty arises as intervening phases appear at times, which sometimes disappear as equilibrium is reached (Friberg, Podzimek and Neogi, 1986), effectively prevent the system from attaining equilibrium under unstirred conditions (Friberg et al., 1985), or even give rise to phases not available on the phase diagram involving those components (Friberg et al., 1986). This makes the analysis, which is done using the diffusion path theory (Neogi et al., 1985; Raney and Miller, 1987), very tedious. Some of the existing experiments and analyses, however, show an interesting feature in that the interphase mass transfer in some cases follows a zeroth-order kinetics which cannot be explained using diffusion alone. When mass transfer takes place between the two phases where the surfactant aggregates have different shapes—for instance, between spherical (as in a micellar phase) and lamellar (as in lamellar liquid crystalline phase) phases, it is suggested not to be sufficient for the surfactant to reach the interface before it crosses over, and it has to restructure as well. It is this last step, the kinetics of phase transformation which is loosely called adsorption, which gives rise to the zero-order kinetics.

From the diverse nature of systems which show interfacial adsorption, it is difficult to find a common denominator for identifying systems which should show such behaviors. It does, however, appear that systems involving continuous lamellar liquid crystalline phase would be the prime candidates. Consequently, to investigate such features and in the absence of formation of intervening phases the experiments described below were designed. A special emphasis on the design has been placed such that to a good approximation only one component is transferred between phases, thus eliminating synergistic effects involved in structural changes when two or more species migrate.

Consider the phase equilibrium diagram in Figure 1, containing sodium dodecyl sulfate (SDS), water, and *n*-decanol ("oil"). The three single phases shown there are water-in-oil (w/o) microemulsion, micellar solution and lamellar liquid crystalline (LC) phase. If two fluids with compositions from w/o micro-

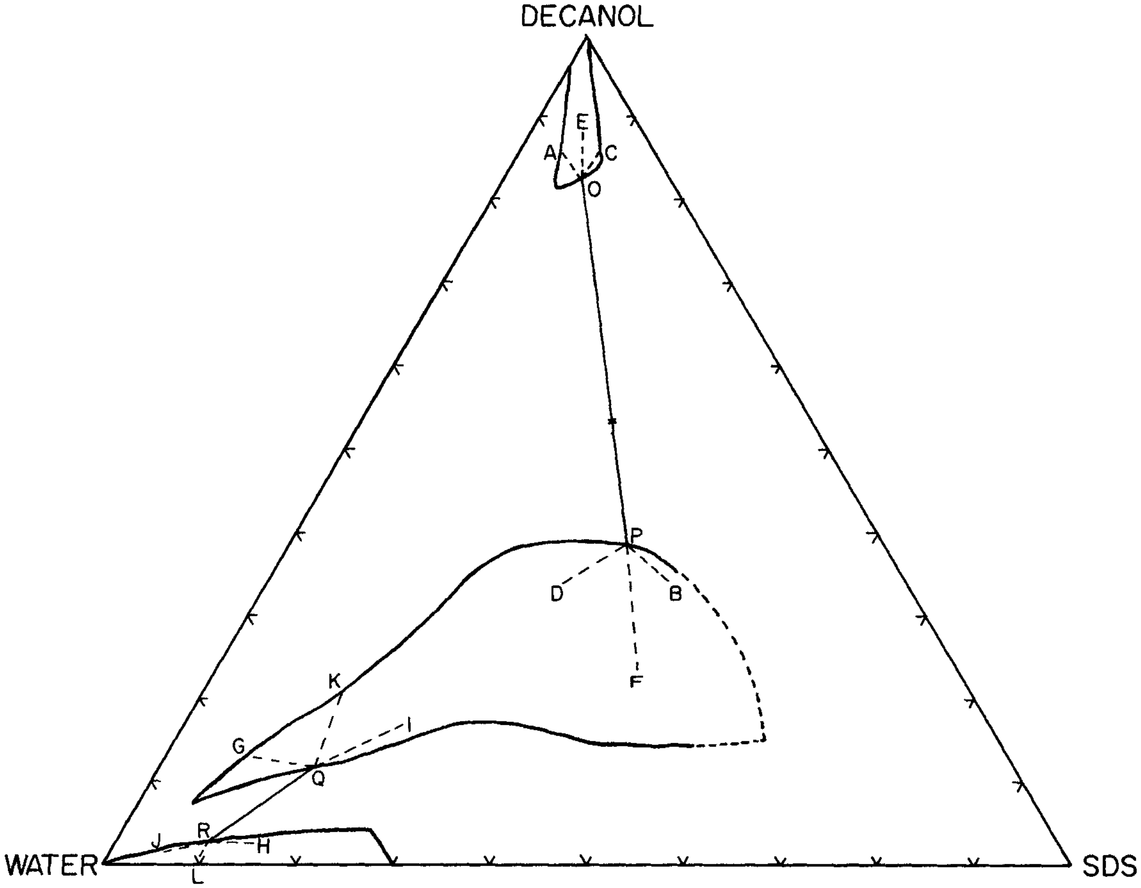

Figure 1. Phase behavior in SDS-*n*-decanol-water at 30°C.
It shows the compositions of fluid pairs contacted (see Table 1) and tie lines used and overall compositions.

emulsion and LC phase close to the tie line separating them are contacted, then the diffusion path will not take the system through a third phase. Similar conclusion is reached for a micellar solution and LC-phase combination.

Consider now a tie line, *OP*, between microemulsion phase and LC phase. The point *O* is joined to the decanol corner, and a point on the line is denoted with *E*. The ratios of water:SDS are the same at *O* and *E*, but *E* contains more decanol. Similarly, the line joining decanol corner with *P* can be extrapolated into LC phase, and a point *F* can be selected. Both *P* and *F* have the same water:SDS ratio, but *F* contains less decanol. The ratio between *E* and *F* used for contacting is used such that the overall composition lies on *OP*, in this case shown by a star in Figure 1. The consequence of contacting *E* and *F* are as follows: the diffusion paths in the single-phase regions are lines joining *E* with *O* and *F* with *P*, and the interphase equilibrium is denoted by the tie line, *OP*. This last assumption needs some justification. We know from material balance that, at equilibrium, the tie line, *OP*, will be operative; consequently, the assumption is good as equilibrium is approached. Further, the assumption also applies as *E* is made arbitrarily close to *O* and *F* to *P*. In practice, the progress of the experiments is monitored by measuring individual phase volumes. Consequently, if *E* and *F* are too close to *O* and *P*, respectively, the measurements become very difficult to take. Thus, these have been removed sufficiently far from the equilibrium compositions but not too far away. In the worst case, lines *EO* and *FP* may not be straight and the operating tie line may lie only in the neighborhood of *OP* but returning to *OP* near equilibrium. The key features of contacting *E* with *F* are that the material balance indicates that only *n*-decanol is transferred from *E* to *F* and that to a reasonable approximation the diffusion path is *EOPF* at all times.

For the w/o microemulsion–LC system, the component that is transferred can be designed to be water (*COPD* in Figure 1) or surfactant (*AOPB*). Similar studies can be made on LC-micellar solution systems as shown in Figure 1. The systems are summarized in Table 1.

Experimentally there are a number of difficulties to overcome, and all of these are due to the use of LC phase which is very viscous. It was very difficult to layer the LC such that its contacting surface was a horizontal plane. This was particularly true in the case of micellar solution-LC system where LC being

Table 1. Contacting Cases Studied

Top phase *t*	Bottom phase *b*	Component Transferred	Path on Fig. 1	Direction of Transfer
LC	w/o Microemulsion	Decanol	EOPF	$t \rightarrow b$
		SDS	AOPB	$b \rightarrow t$
		Water	COPD	$b \rightarrow t$
Micellar Solution	LC	Decanol	KQRL	$t \rightarrow b$
		SDS	GQRH	$b \rightarrow t$
		Water	IQRJ	$b \rightarrow t$

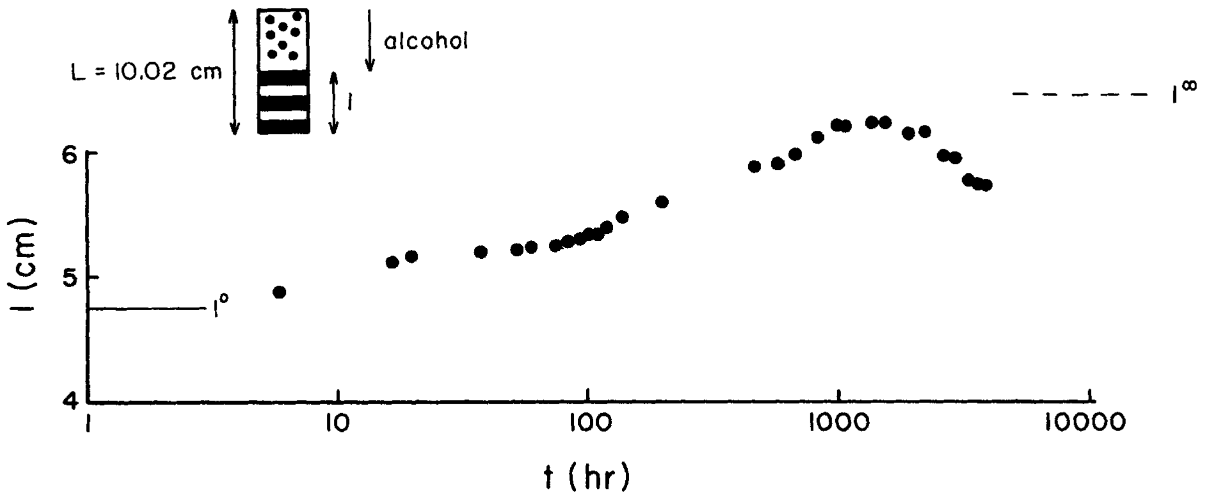

Figure 2. Height of LC phase with time.
Transport of decanol from w/o to LC.

the lighter fluid was needed to be layered on top of the micellar solution. This difficulty was overcome by first layering LC in a broken burrette, layering the micellar solution, and then sealing the top and inverting it. Like in the constrained systems, even the unconstrained system showed no changes in the total volumes with time.

It was also very difficult to drive out the air bubbles from the LC phase. After centrifuging extensively, the LC phase appeared translucent with the largest bubbles barely visible. On the other hand, the LC phase increased in volume in four out of the six experiments reported here. The additional LC phase formed was fully transparent. No migration of bubbles nor abrupt changes in the appearence of interface was observed; consequently, it was concluded that the presence of air bubbles had little or no impact on the experiments.

Experimental method

Sodium dodecyl sulfate, specially pure BDH, was twice recrystallized from absolute ethanol. The cosurfactant *n*-decanol from Aldrich, 99% pure, was used as supplied. Redistilled water was used.

Phase diagram

The phase diagram showing limits of water-in-oil microemulsion, lamellar liquid crystalline phase, and oil-swollen micellar solution were obtained for SDS-decanol-water system at 30°C by titration. Samples were extensively centrifuged and then checked carefully using polarized light, polarizing microscope, and small angle X-ray diffraction.

Two tie lines, *OP* and *OR*, were determined by refractometer, and the densities of the compositions *O*, *P*, *Q*, and *R*, were determined by densitometer. Then, the liquid with composition *A*, which contained lesser amounts of SDS than the compositon at *O*, was placed in contact with liquid of composition *B* which contained greater amounts of SDS than the composition at *P*. Using densities, the volumes were chosen such that the overall composition was on the *OP* tie line (shown with a star in Figure 1). The movement of the interface was measured using a cathatometer.

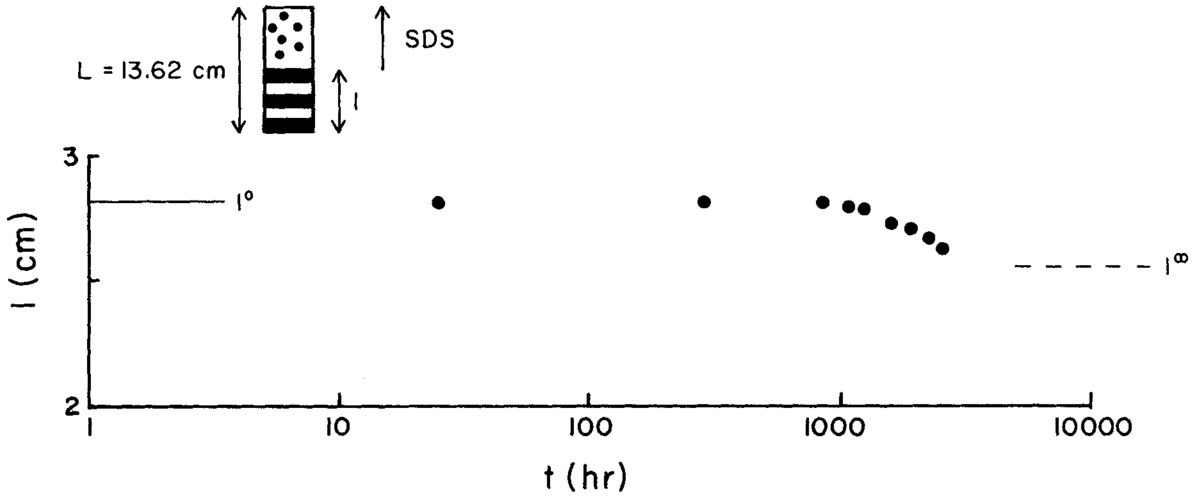

Figure 3. Height of LC phase with time.
Transport of SDS from LC to w/o.

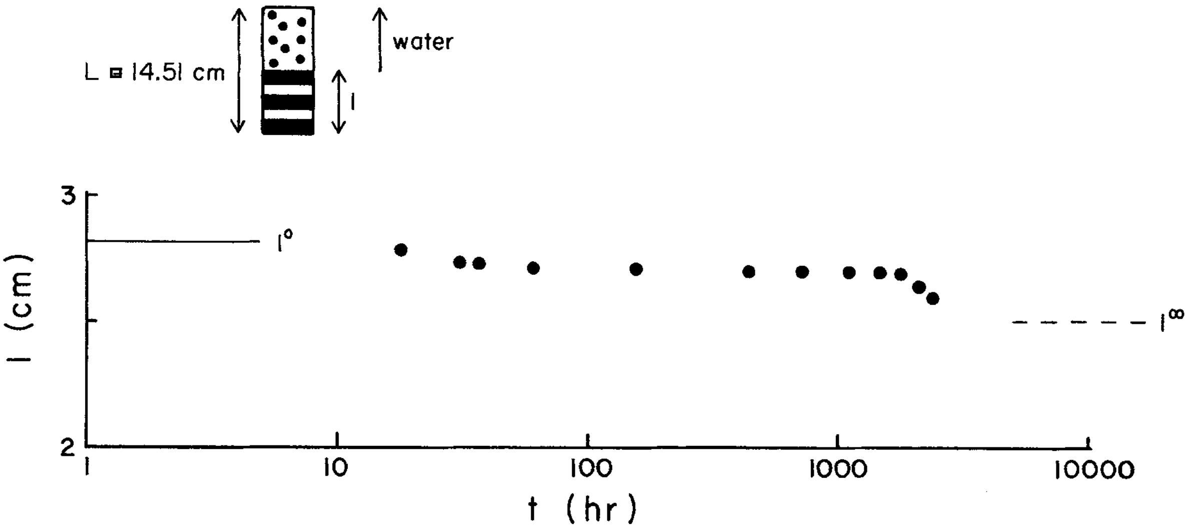

Figure 4. Height of LC phase with time.
Transport of water from LC to w/o.

Other systems shown on Figure 1 and Table 1 were studied similarly.

Towards a Mechanism

The results have been plotted in Figures 2–7. One interesting feature in these plots are overshoots and oscillations. In some these are marked, in others they are somewhat masked by the fact that they are superimposed on monotonic functions. In some the changes in levels are too small to be determined with accuracy, yet leaving enough room to suppose that small oscillations could be taking place in the system. The key aspect of oscillating response, it should be stressed, is that it cannot be explained with classical diffusion or adsorption. Because the liquids have been layered with the denser fluid below and the lighter fluid at the top, instabilities due to density differences are not expected. Interfacial instability and instabilities in general are marked by visible features (Miller, 1978), but no myelins/dendrites grew, no pitting nor cellular structures were observed, and the possibility that the systems were unstable was ruled out in absence of any visible flow. It is noteworthy that these structures would compare in length to the overshoots and thus would have been visible.

As designed, only one component is to be transferred across an interface, thus there is little cooperative action during transfer. If all three components were being transferred from say a micellar phase to LC phase, then whole micelles in proper proportions of the dispersion medium could get "adsorbed" at the interface, with the mass transfer resistance coming from the

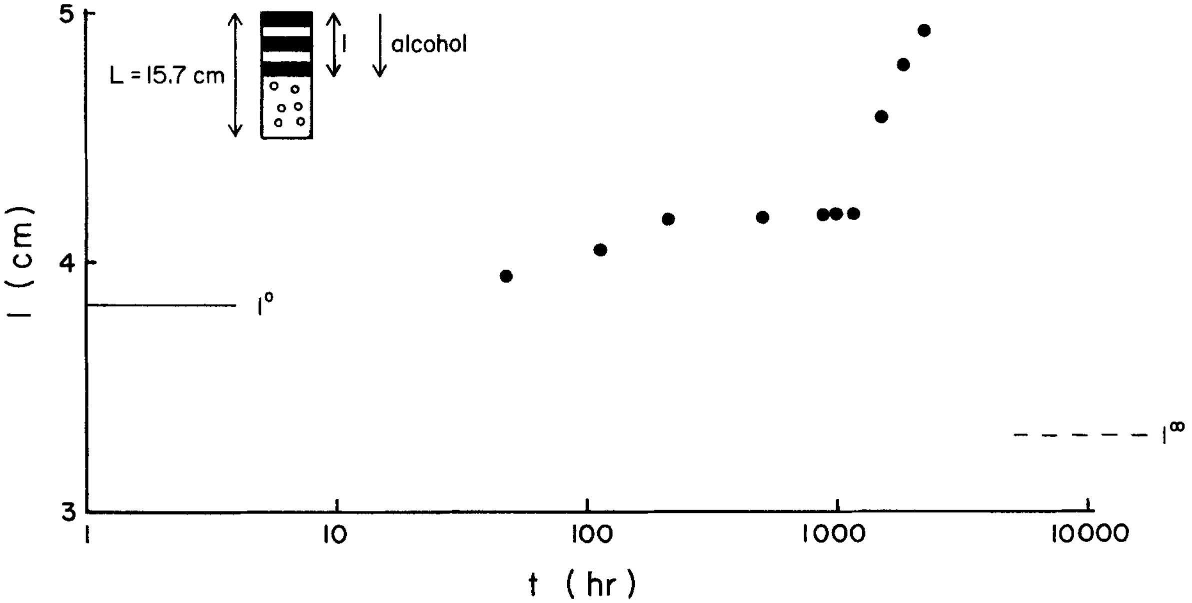

Figure 5. Height of LC phase with time.
Transport of decanol from LC to micellar solution.

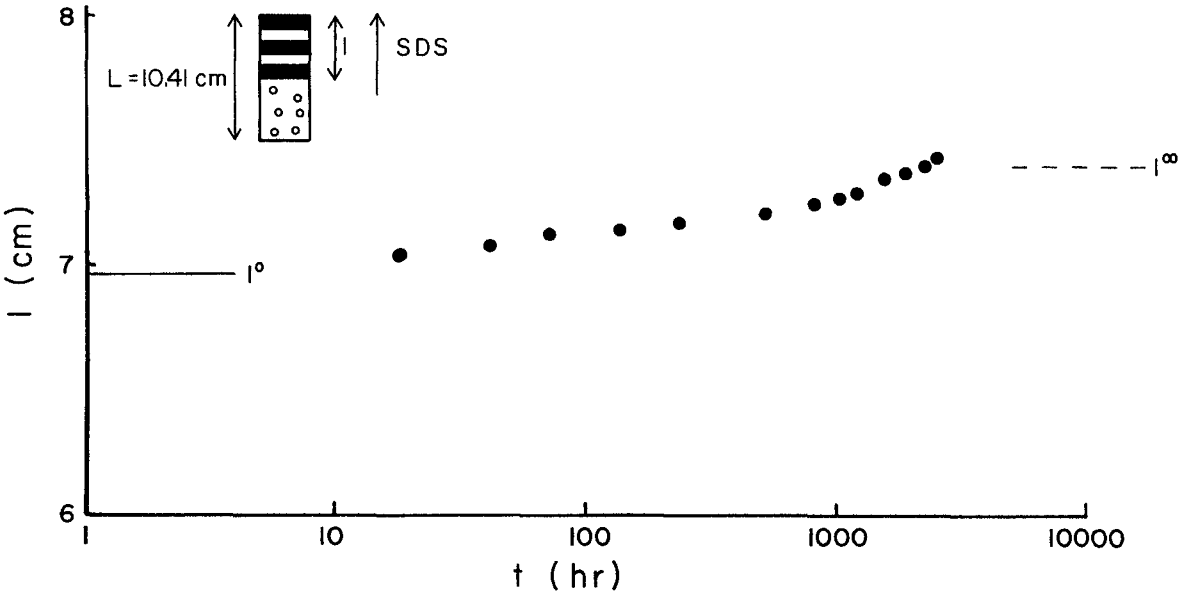

Figure 6. Height of LC phase with time.
Transport of SDS from micellar solution to LC.

restructuring of a whole micelle into a lamella. The same mechanism can work when a single component is being transferred; however, restructuring becomes significantly more difficult and arises from many interactions in the neighborhood of the interface. In that, the system here has been tailored such that the kinetics of phase transformation is made extremely slow to be a significant factor in overall rates.

Consider now a simple model where structural changes take place near an interface between a micellar solution and an LC phase. Because of the nature of difficulties faced in delivering primarily a single component across an interface via structured systems, the highly fluctuating shapes near an interface on an average will neither be spherical nor lamellar. Neogi and Friberg (1989), however, have shown that structures, where the

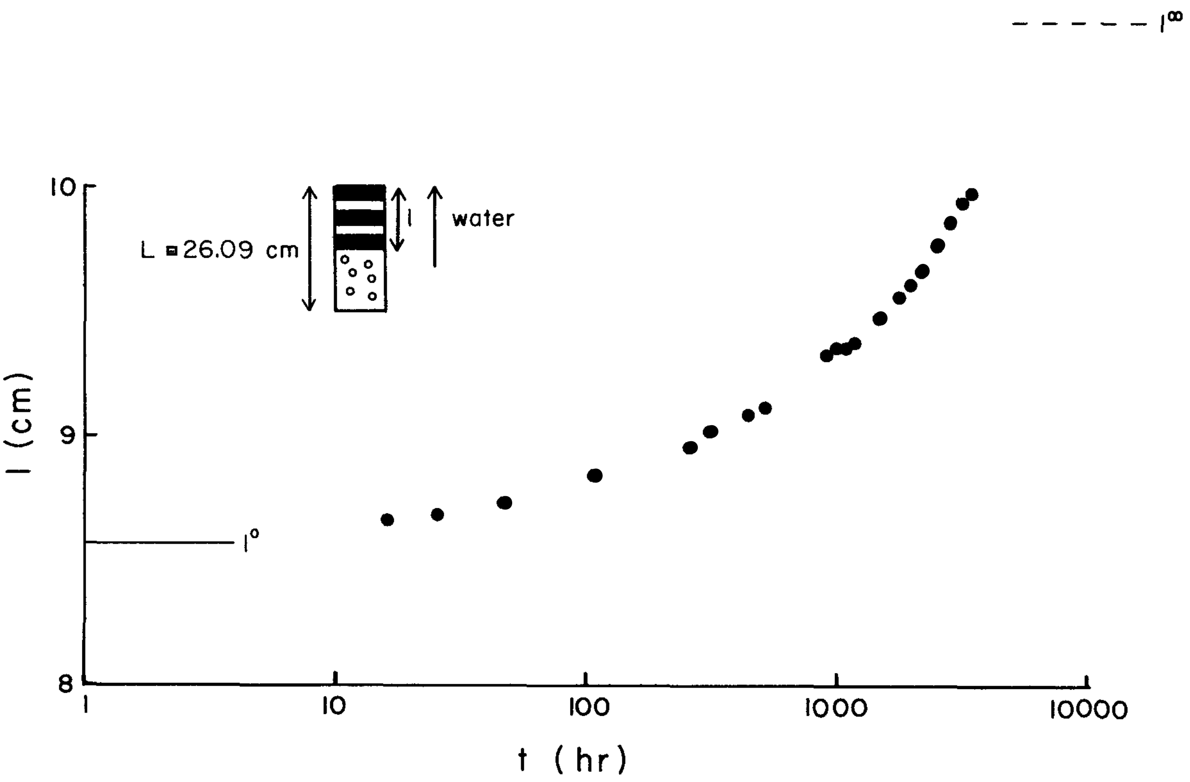

Figure 7. Height of LC phase with time.
Transport of water from micellar solution to LC.

curvatures vary along the interface, are not at thermomechanical equilibrium. Consequently, the concept of local equilibrium does not hold. To provide a thermodynamic description of structures of various shapes in surfactant systems, the physicists have postulated and used a parameter λ called the persistence length or Bancroft factor (de Gennes and Taupin, 1982; Widom, 1987). It is the distance through which a section of surface (here the surface occupied by the surfactant film) can be represented by a plane. Obviously λ decreases as the curvature increases, and hence λ can be used to characterize shapes. Other quantities similar to the role played by λ can also be defined. If λ or a similar quantity is taken to be an extensive property, then the change in entropy can be written as

$$TdS = -\sum_i \mu_i dn_i + Ad\lambda \tag{1}$$

where the affinity is

$$A = T\left(\frac{\partial S}{\partial \lambda}\right)_{n_i,T} \tag{2}$$

and from equilibrium considerations, A is to be positive becoming zero at equilibrium.

From previous considerations locally λ is different from its equilibrium value λ^o. If it is not too far away then from irreversible thermodynamics, a linear rate law

$$\frac{d\lambda}{dt} = -\ell_\lambda A/T \tag{3}$$

applies (de Groot and Mazur, 1962). By linearizing about the equilibrium, one can obtain the chemical potential of ith species in terms of λ and using the flux law that

$$\underset{\sim}{j}_i = -L\underset{\sim}{\nabla}\mu_i \tag{4}$$

one eventually obtains (Neogi, 1983)

$$\underset{\sim}{j}_i = -\int_0^t \mu(t-t')\underset{\sim}{\nabla}c_i(\underset{\sim}{x}, t')\,dt' \tag{5}$$

where

$$\mu(t) = D^i\delta(t) + \frac{D^o - D^i}{\tau}\exp(-t/\tau) \tag{6}$$

where D^i amd D^o are the initial and final diffusivities, $\delta(t)$ is Dirac delta function and τ is a relaxation time $\tau = -\ell_\lambda/(\partial^2 S/\partial\lambda^2)^o$, where the superscript denotes the fact that the derivative is to be evaluated at equilibrium. Fickian diffusion is a special case of Eq. 5. If the system is in contact with a reservoir where the chemical potential of the ith species remains a constant, the solubility or the skin concentration becomes

$$c^* = c^o + (c^i - c^o)\exp(-t/\tau) \tag{7}$$

Here c^i and c^o are the initial and final values.

One may now apply these to a simplified system to show that the mechanism here can capture the main features of the experimental observation. Consider a finite system where the flux is given by Eqs. 5 and 6. It is insulated at $x = 0$, where $\partial c/\partial x = 0$ and ends at $x = \ell^o$ where the concentration is given by Eq. 7 where c^o is that given by one end of the tie line in Figure 1. A second phase starts at $x = \ell^o$ where the diffusion and solubility is classical. Because of the nature of the problem, the second phase is at a concentration which is taken to be that given by the other end of the tie line. The conservation equation

$$\frac{\partial c}{\partial t} = -\frac{\partial}{\partial x}j_x \tag{8}$$

is solved using Eqs. 5 and 6, and the boundary conditions stated earlier under the assumption that the change in the thickness in this finite system is small. The result in Laplace transformed quantities are used in an overall balance for the change in the thickness ℓ form its initial value ℓ^o to get

$$\frac{\bar{\ell} - \ell^o/p}{\ell^\infty - \ell^o} = \frac{\bar{c}^* - c_o/p}{c^o - c_o}\left(\sqrt{\frac{\bar{\mu}}{p}}\right)\frac{1}{\ell^o}\tanh\left(\ell^o\sqrt{\frac{p}{\bar{\mu}}}\right) \tag{9}$$

where overbars denote Laplace transformed quantities and p is the transformation variable. ℓ^∞ is ℓ at equilibrium. The solution is identical to that obtained by Adib and Neogi (1987) for fraction mass sorped by a membrane M_t/M_∞. As their solution shows $(\ell - \ell^o)/(\ell^\infty - \ell^o)$ would show an overshoot followed by decaying oscillations superimposed on a monotonically changing response. *Two* such wave trains will arise if the second phase is also non-Fickian; the relative importance of the two will be determined by the parameters in the two systems. That is, unlike the system studied by Adib and Neogi (1987), it may very well be that the second overshoot is more important in such systems than the first as suggested, for instance, in Figure 2. One may instead also find an initial movement in the direction opposite to that demanded by equilibrium as in Figure 5. In contrast, almost Fickian diffusion, such as that shown in Figure 7 can also result when the relaxation times are small. Whereas we have not demonstrated these aspects using our model, it is important to stress that the present model predicts overshoots where classical mechanisms would show only monotonic changes: that is, the primary requirement for a model is satisfied and the physical basis appears to be reasonable. Further investigations into the model at present, which is not trivial, would not be profitable for the data do not cover the full range of behaviors with time, even though these were taken over periods exceeding two months. The values of ℓ^∞ were calculated using material balance.

At large time Eqs. 5–7 collapse into classical behavior. Mathematically it implies that, sufficiently behind and sufficiently ahead of the front, the mechanism is classical and hence conforms to the physical model such that the restructuring activities are confined to the region of the interface.

One may also consider adsorption-controlled mass transfer. In this, the classical theories of adsorption equilibrium and dynamics have to be redone to include the effects of λ, which appears to be difficult at this point in time. Therefore, we are unable to distinguish the cases of adsorption-limited transport from diffusion-limited (whether or not local equilibrium holds), the primary reason for undertaking the present investigation. Nevertheless, it has been possible to show that the kinetics of phase transition, in particular the cooperativity necessary to make the transition, plays a significant role. We note that, using material balances, the experimental data can be used to obtain the time-dependent adsorption rates as

$$R = \frac{dl_1/dt}{(1 - \ell_1/L)^2}\left[\bar{c}\left(\ln\frac{\ell_1}{\ell_1^o} - \frac{\ell_1}{L} + \frac{\ell^o}{L}\right) + (c_2^o - c_1^o)\left(1 - \frac{\ell_1^o}{L}\right)^2\right] \quad (10)$$

where subscripts 1 and 2 denote lower and upper phases, and $\bar{c}$ is the overall concentration of the species being transferred.

Conclusion

It is possible to design experiments in mass transfer in surfactant system such that effects of the kinetics of phase transformation are unmistakable. Here, cooperativity among different species being transferred have been eliminated. The effects on diffusion have been shown theoretically to be adequate in explaining the key experimental observations. (Analogous studies in adsorption could not be made).

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