Dynamics of Phase Separation between a Lyotropic Dilute Lamellar Phase and an Isotropic Phase

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We have studied the dynamics of the phase separation between a dilute lyotropic lamellar phase (smectic) and an isotropic phase in a quaternary (water, sodium dodecyl sulfate, pentanol, dodecane) system. Observation of the phase separation with small-angle light scattering on an oriented sample allows us to demonstrate the anisotropic growth of the isotropic phase inside the lamellar phase. Measurement of the variation of the largest characteristic distance as a function of time indicates that the kinetics of the phase separation follows a power law with a characteristic exponent $\frac{1}{3}$.

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It has been known for a long time that mixtures of a surfactant and water lead to a large variety of liquid-crystalline phases among which the lamellar phase is one of the most common. This lyotropic liquid-crystal phase consists of stacked layers of surfactant separated by the solvent (usually water). In most cases the maximum distance between the layers is of the order of a molecular length (10–20 Å). When such a phase is diluted by addition of the solvent, a phase separation occurs between the lamellar phase and an isotropic phase, either pure solvent or micellar. In some interesting cases, if strong long-range repulsive forces exist, lamellar phases can swell to several hundreds and even thousands of angstroms[1-3] without phase separation. Such dilute lamellar phases are models of special interest for our understanding of the interactions between living cells since the range of accessible distances is very large; they are one of the rare examples of colloidal smectics.

The problem of the stability of this dilute lamellar phase arises when one considers the addition of increasingly more solvent. From a theoretical point of view, a calculation[4] involving the competition between repulsive and attractive forces predicts that two different states can exist, one where the membranes remain bound and a phase separation with pure solvent occurs and another one where the membranes can swell without bound. These two different states are separated by a critical point (critical unbinding). Experimentally, the situation is less simple. As we shall see, the dilute lamellar phase does not coexist with pure solvent but rather with an isotropic phase containing surfactant. In the system that we have studied, this isotropic phase is distinct from the regular micellar phase.

In this paper we report on an experimental study of the dynamics of the phase transition between a very dilute lamellar phase (distance between layers of order 600 Å) and an isotropic phase. By means of small-angle light scattering, we study the phase separation process involving the nucleation and growth of the isotropic phase in the lamellar phase. The weakly first-order nature of the phase transition makes the phase separation slow enough to be followed experimentally. Using an appropriate cell we are able to orient the lamellar phase partially and then to follow the growth of the isotropic phase in this anisotropic medium. The growth is observed both in the plane of the lamellae and out of plane. The analysis of the light-scattering patterns indicates that the growth is anisotropic and proceeds faster in the in-plane direction than out of plane. The analysis of the kinetics indicates that at the early stage the typical size (L) of the isotropic phase domains follows a power law $L \propto t^{\beta}$ with the exponent $\beta = \frac{1}{3}$. This last result is similar to what has been observed in other types of phase separation in liquids involving two isotropic phases[5] or two nematic phases.[6]

The system consists of a quaternary mixture of water, dodecane, pentanol, and sodium dodecyl sulfate. The complete three-dimensional phase diagram at constant temperature and pressure has previously been published.[3,7] A section of the phase diagram at a water-surfactant weight ratio of 1.2 is shown in Fig. 1 (from Ref. 7), which represents the domain of existence of the phases as a function of the dodecane and pentanol concentrations for the region corresponding to large concentrations of oil and alcohol. Three different phases have been characterized.[7] Phase L_2 is a microemulsion phase whose structure in this part of the phase diagram is known to be micellar.[7] Phase D is a lamellar liquid-crystal phase composed of layers of water (thickness $\approx$ 18 Å) separated by oil (thickness varying from 15 to 600 Å); a mixed surfactant-pentanol film is situated between the oil and the water layers. Phase L_3 is isotropic but exhibits strong flow birefringence. At equilibrium, a sample of this phase is fully isotropic between crossed polarizers but upon shaking, even slowly, a transitory birefringence appears instantaneously which relaxes in a matter of a few seconds. Similar phase behavior has been found in binary systems of a nonionic surfactant and water,[8] but so far the structure of this L_3 phase has not been determined.[9]

Phases L_2, L_3, and D are separated by polyphase regions involving two- and three-phase equilibria, indicating that the phase transitions between these distinct phases are all first order. However, a large difference exists between the D-L_2 (region II_1 in Fig. 1) and D-L_3 (region II_2) phase transitions. The lamellar-to-micellar phase transition (D-L_2) is strongly first order in the sense that a quench (by means of temperature, for example) from one of the one-phase regions to the two-phase region II_1 results in a very fast (less than a second) phase separation leading to a very turbid inhomogeneous mixture that forms a well-defined interface in a few minutes. In contrast, the D-L_3 and L_3-L_2 phase transitions are extremely slow. It takes minutes after the quench before turbidity develops and hours or days before an interface appears. Moreover, when a sample in the two-phase region ($D+L_3$ coexisting) is gently sheared (by means of a slight agitation of the cell) it becomes homogeneous and birefringent. If the agitation is stopped, the sample relaxes toward its equilibrium state by a slow phase separation similar to that obtained by a temperature quench. The very slow phase separation together with the extreme sensitivity to shear flow and the flow birefringence property of L_3 lead us to conclude that the D-L_3 phase transition is weakly first order, at least compared to D-L_2. The effect of a shear flow is qualitatively similar to what has been observed in liquid-liquid phase separations.[10-12]

In order to study the dynamics of the D-L_3 phase transition and to make use of the extreme sensitivity of this phase transition to the shear flow, we have built a specialized cell shown schematically in Fig. 2. The cell consists of two sealed reservoirs A and B situated on each side of an optical cuvette C. A set of stacked stainless-steel plates allows a shear flow to be created in a well-defined direction. The plate separation is 400 μm and the plate thickness is 125 μm. A piston in reservoir A can be used to force the liquid through the plates into the optical cuvette. The sample is studied by small-angle light scattering: A laser beam passes through the cuvette and the scattering pattern is formed on a screen situated at a variable distance from the cell. The pattern is recorded on video tape and the image can be then digitized for analysis. The incident laser beam can be directed either parallel to the axis perpendicular to the plates (in-plane direction) or perpendicular to this axis (out-of-plane direction).

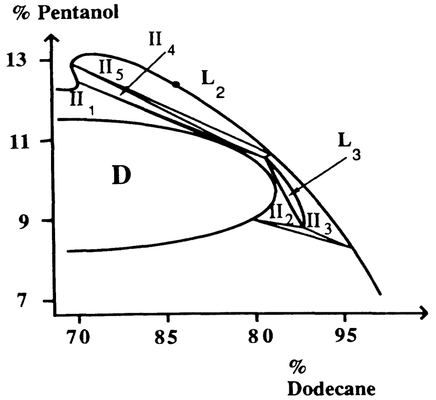


FIG. 1. Cut of the phase diagram of the quaternary system water, dodecane, pentanol, and sodium dodecyl sulfate at 23 °C and atmospheric pressure. The one-phase regions are D (lamellar), L_2 (isotropic liquid), and L_3 (isotropic liquid). The regions labeled II_i are two phase.

The cell is filled with a sample whose composition corresponds to a point in the two-phase region II_2 at which the coexisting D and L_3 phases have equal volumes. This two-phase mixture is placed in reservoir A and the phase is forced through the plates until the entire cuvette is filled with sample that has been sheared. The effect of the shear flow is twofold: It mixes the two phases and drives the sample into the lamellar phase D and it partially orients this stabilized lamellar phase as we shall demonstrate. Once the flow stops, phase separation begins and the isotropic phase L_3 is formed, allowing the dynamics of this phase separation to be studied by light scattering. The dynamics of phase separation is observed in the two directions (in plane and out of plane). Figure 3 shows three photographs of the pattern obtained after a typical time of a few tens of seconds in the in-plane [3(a)] and out-of-plane [3(b),3(c)] directions, respectively. The in-plane pattern is an isotropic ring of scattering that is visible after a few seconds; the diameter of the ring shrinks with time and the ring disappears in the main beam after a typical time of several minutes. As shown in Figs. 3(b) and 3(c), the out-of-plane pattern is anisotropic. At low shear rate [Fig. 3(b)] the pattern can be described as being composed of two broad scattering peaks centered on the vertical axes (the shear flow was applied along the horizontal axes). At higher shear rate the pattern is more complex: as shown in Fig. 3(c), the two broad scattering peaks split into four peaks off axis and the splitting is an increasing function of the shear rate. In all cases, with time these peaks move symmetrically toward the center of the pattern [$q=0$,

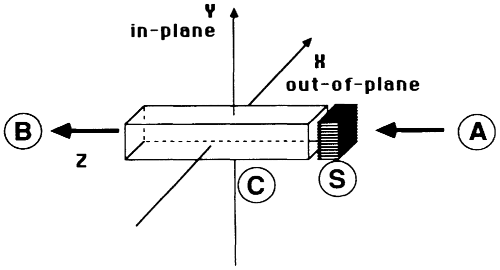
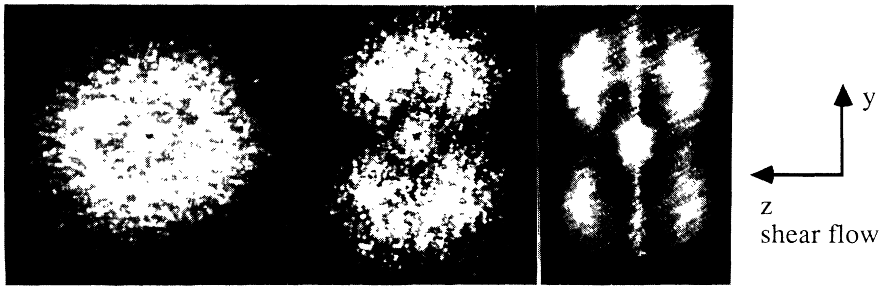


FIG. 2. Schematic drawing of the cell. A and B are reservoirs containing the sample. S is a stack of thin plates. C is an optical cuvette. The arrows indicate the direction of the shear flow. The in-plane and out-of-plane axes are indicated on the drawing (see text).



(a) (b) (c)

FIG. 3. Photos of the light-scattering pattern during the growth of the isotropic phase inside the partially oriented lamellar phase. (a) In-plane geometry (see Fig. 2), (b) out-of-plane geometry at low shear rate, (c) out-of-plane geometry at high shear rate.

where q is the wave number $q=4\pi/\lambda \sin(\theta/2)$, λ is the wave length of the laser, and θ is the scattering angle]. The in-plane and out-of-plane kinetics are exactly the same, the only difference being the shape of the scattering pattern.

The difference between the two observed patterns in the in-plane and out-of-plane directions is evidence of the anisotropy of the growth of the isotropic phase L_3 in the lamellar smectic phase D. The symmetry in the scattering pattern is typical of that seen in the scattering from oriented anisotropic objects in which the structure consists of stacks of planes. Figure 3(b) corresponds to a structure where the axes perpendicular to the planes are all aligned along the same direction (z axis of Fig. 2) and Fig. 3(c) corresponds to a structure where the axes are inclined to the left and right with respect to the z direction. If the normals to the planes are at an angle $\pm\rho$ measured from the z direction, the scattering consists of four peaks whose centers are displaced from the z direction by angles $\pm\rho$ (for small-angle scattering).[13] We believe that the orientation that underlies the out-of-plane pattern has been produced by the shear flow: similar shear-induced orientation has been observed for nematic phases.[14] When the isotropic phase starts to grow, the growth is faster in the direction parallel to the layers rather than perpendicular. The corresponding scattering pattern is then that of Fig. 3(b), which indicates that the scattering objects are elongated in the direction of the shear flow. As the shear flow is increased the axes of the domains no longer remain perpendicular to the shear flow but make an angle smaller than 90° and the scattering pattern is then that of Fig. 3(c). The growth of the isotropic phase is unaffected.

Having established that the growth is anisotropic, we proceeded to study the kinetics of the phase separation on unoriented samples in sealed well-thermostated cells [$T=(23.10\pm0.0)\,^\circ\mathrm{C}$]. In this case the pattern is independent of the direction of observation because no preferred orientation exists (powder sample). As before, the lamellar phase is obtained with a shear flow, produced by agitation of a magnetic stirrer inside a sealed cell. The scattering pattern is always an isotropic ring. To treat the data, we have digitized the scattering patterns and the intensity profiles are obtained by circular averaging.[5] The position of the maximum in the scattered intensity, q_m is then obtained as a function of time. The initial time is taken as the time at which the agitation is stopped. Figure 4 represents a typical set of data on a log-log plot. Clearly, at the early stage of the decomposition the kinetics can be interpreted as having power-law behavior ($q_m \propto t^{-\beta}$) with an exponent $\beta=0.3\pm0.06$. A similar analysis of the kinetics of the maximum intensity of the peak indicates a linear behavior with time ($I_m \propto t$). Similar values are obtained in other phase-separation studies in a large range of isotropic phase separations[5,11,12] and also in one anisotropic phase separation involving two nematic phases.[6] The increase in the slope at late times has also been observed in mixtures of isotropic fluids.[15]

The lamellar phase is a liquid-crystalline phase, liquid-like in the direction of the layers and crystalline in the direction perpendicular to them. It is therefore not surprising that the growth of an isotropic phase inside

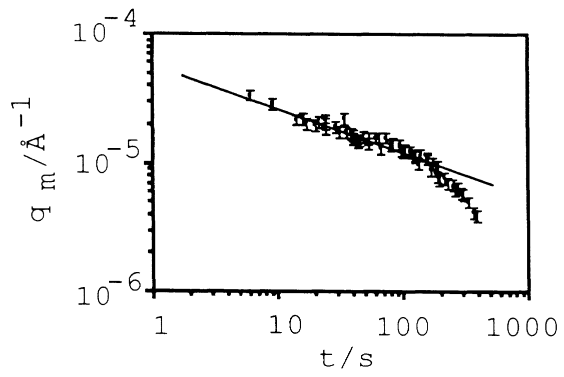


FIG. 4. Log-log plot of the variation of the position of the peak of scattering (q_m) as a function of the time (t). The straight line has a slope of $\frac{1}{3}$.

this smectic phase is anisotropic. One might argue that the anisotropy is produced by a difference between diffusion in the two opposite directions (in plane and out of plane). In another case of anisotropic phase separation, Fabre, Leger, and Veyssie[16] have measured the diffusion constant perpendicular ($D_\perp$) and parallel ($D_\parallel$) to the nematic director in a mixture that undergoes phase separation into two nematic phases. They suggest that this asymmetry in the diffusion constants may be responsible for the anisotropic growth.[6] In systems similar to ours, the diffusion constants may differ by a factor of 2.[17] It is possible that this difference contributes to the observed anisotropy in the growth of the isotropic phase. We believe it is more likely, however, that the asymmetry arises from differences in the elastic response of the medium in which the isotropic phase is growing. The growth of the isotropic phase perpendicular to the layers involves stress due to the distortion of the liquid crystal, making the growth less favorable in that direction. Differences in elasticity are known to be a major factor in the determination of the directions of growth in solids.[18]

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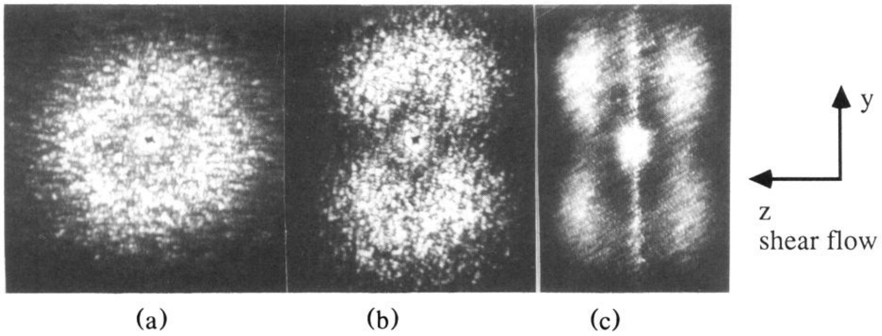

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