Evidence of a Phenomenon of Epitaxy at the Interface between a Lamellar L_α Phase and a L_3 Sponge

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In the quasiternary lyotropic system CpCl/brine/hexanol, the interface between the lamellar L_α and the "sponge" L_3 phase adopts geometries characteristic of a tilted anchoring of the lamellar layers on the sponge phase. Quantitative measurements of this new phenomenon are performed at equilibrium. Additionally, the evolution of the characteristic distances d_α and d_3 of the two phases in the biphasic region with swelling variation was determined by x-ray scattering. Our results support the hypothesis of an epitaxial matching between the two phases. [S0031-9007(96)00501-7]

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Surfactants may form with a remarkably large amount of solvent thermodynamically stable phases. Amongst them, the complex "sponge" L_3 phase has been studied for more than 10 years [1–4], and still exhibits surprising properties. It is now widely believed that a continuous membrane (bilayer of amphiphilic molecules) of complex topology divides the solvent into two entangled connected parts, the whole phase presenting neither privileged direction nor long-range order. As will be demonstrated here, this phase plays, nevertheless, a crucial role in the orientation of another membranar phase of lower symmetry, the L_α phase [5].

The system under study is the quasiternary cetylpyridinium chloride (CpCl)/brine/hexanol mixture. This system exhibits a lamellar L_α and a sponge L_3 phase of comparable compositions [1], and a first-order phase transition from L_3 to L_α occurs on increasing temperature [6]. The transition was observed by optical polarizing microscopy using a Mettler hot stage, the L_3 phase having been introduced in a glass capillary of rectangular section (300 μm thick) in order to avoid evaporation. At an early stage in the growth, the L_α droplets are small enough for the arrangement of the layers to be mainly dependent on the interfacial conditions. Reference [5] describes in passing the observations of very anisotropic droplets, in which some part the L_α layers and the L_α/L_3 interface make an angle $\alpha \neq 90°$. This is, at least locally, different from what occurs in thermotropic systems of similar symmetry [7]. We present here new observations of droplets that we recurrently obtain in the lyotropic system under study, with shape much simpler than those observed in Ref. [5], allowing a quantitative analysis. Extinction brushes parallel to the nicols directions, and a symmetry axis that is an axis of revolution, indicate that the layers are spherical and concentric [Figs. 1(a) and 1(b)]. The image analysis of the droplet profile shows that it is a part of a logarithmic spiral (LS) centered on the pole. Such a spiral, of equation $\rho = \rho_0 \exp(\theta/u)$ in polar coordinates, makes a constant angle $\arctan(1/u)$ with any circle centered on the origin [Fig. 1(c)]: hence not only is α nontrivial ($\neq 0°, 90°$), but it is constant over the whole droplet surface.

Quantitatively, the numerical analysis of the droplets shape provides the tilt angle α. However, repeated experiments for various swellings do not yield reproducible quantitative data for α from one droplet to another (typical values obtained for α vary between 10° and 60° for $P_{\text{br}} = 70\%$, and between 60° and 75° for $P_{\text{br}} = 90\%$). The main difficulty in these free-growth experiments is that the density difference between L_α and L_3 restricts the duration of the observations to 5–10 min, before the L_α droplets reach the upper face of the capillary and squeeze on it. Within this short time, they are likely not to be in an equilibrium configuration. In order to obtain information on this point, we compared the energy of perfect logarithmic spiral profiled droplets with another possible conformation, where the condition of a constant tilt angle over the whole interface is achieved without any elastic deformation of the layers, i.e., double-cone shaped droplets (DC) where the common axis of the cones is perpendicular to the layers.

Let us calculate the energies of the two types for a given volume V; the only contribution to be taken into account here is a surface term for the double cone, $E_{\text{DC}} = \gamma(2\pi/\cos\alpha)\,(3V/2\pi\tan\alpha)^{2/3}$, whereas an elastic deformation contribution is to be added for the logarithmic spiral:

$$E_{\text{LS}} = \gamma \frac{4\pi}{\sin a} \frac{e^{\pi/u}}{1 + 4u^{-2}} \left(1 + \frac{2}{u} \sinh \frac{\pi}{u}\right) \times \left(\frac{3V}{2\pi} \frac{1 + (3/u)^2}{1 + e^{3\pi/u}}\right)^{2/3} + 4\pi K \frac{1 + e^{\pi/u}}{1 + u^{-2}} \left(\frac{3V}{2\pi} \frac{1 + (3/u)^2}{1 + e^{3\pi/u}}\right)^{1/3},$$

where $u = \operatorname{cotan}\alpha$, γ is the surface tension for the involved tilt angle, and K is the elastic mean curvature constant. The comparison between these two expressions shows that, even for high values of γ, DC droplets are expected to have a lower energy that LS's in the domain of observation of the latter ($\alpha \approx 20°$ to 70°) [8]. Understanding why, despite their respective energies, we recurrently observe LS's and never DC's is probably a problem

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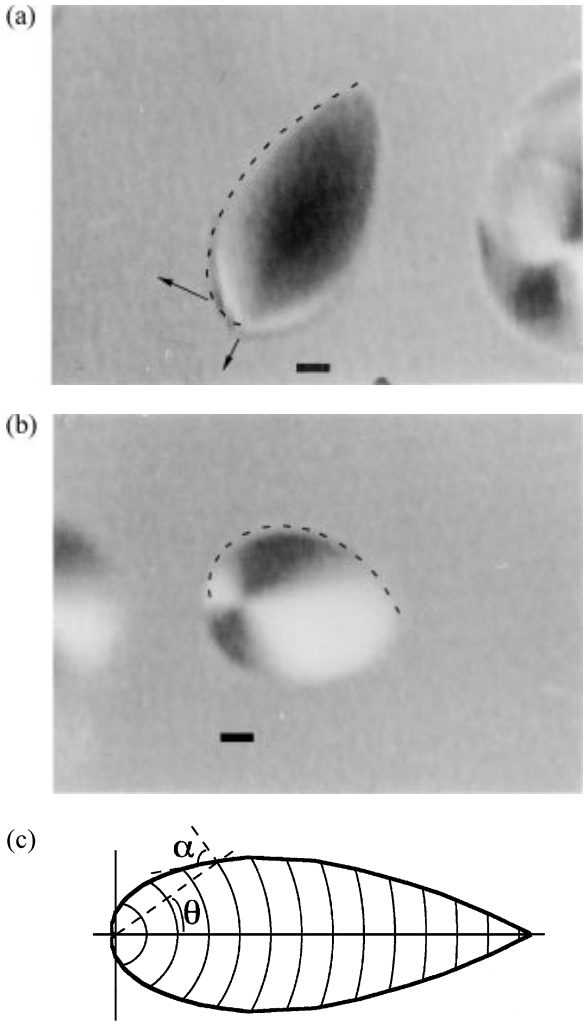

FIG. 1. (a) Droplet of L_α phase in L_3 (polarized microscopy, photography of a videoprinting), bar = 10 μm. Global composition: $P_{br} = 83\%$, h/c (weight ratio hexanol over CpCl) = 1.132 (the coexistence of the two phases ranges from 37–39 to 51–53°C). Dashed line: logarithmic spiral ($\alpha = 38°$), whose pole is at the center of the indicated axis. Notice that the profile departs slightly from this LS at the extremities; the zones of concern are of small size and their details approach the microscope limit of resolution: they were not studied here. (b) $P_{br} = 90\%$, $h/c = 1.132$. The LS ($\alpha = 62°$) goes through the middle of the white halo; its pole is at the center of the extinction figure. Notice that there are two black brushes instead of four (axial symmetry); this is due to a very weak birefringence of the lamellar phase in this swelling range. (c) Arrangement of the concentric layers in a logarithmic spiral droplet.

concerned with growth kinetics. A metastable conformation with concentric layers is likely to be induced during the nucleation, and the anchoring condition may then be strong enough to prevent a modification of the configuration that would necessarily involve large surface and elastic energies. From this remark, we may suppose that the two types of energy are roughly comparable in this metastable state. Taking $V = 10^{-15}\,\mathrm{m}^3$ and $\alpha = 60°$ from standard observations, and a typical value of $K \approx 10^{-13}$ N, we may deduce an order of magnitude of $10^{-7}\,\mathrm{J\,m^{-2}}$ (10^{-4} erg cm^{-2}) for γ, which is extremely weak [9]. The calculation we have presented does not, however, explain the fact that the tilt angle, even in a nonequilibrium situation, is constant over the whole interface. This property will be discussed in more detail in Ref. [10].

In order to study the tilt angle α at equilibrium, we have observed the interface in systems which are biphasic at room temperature. The biphasic mixture is placed in cylindrical capillaries (diameter between 0.7 and 2 mm), flame sealed, then held vertically. Because of the difference in density, the L_3 phase settles to the bottom part of the capillary within a couple of hours. Within one or two days, the top region, lamellar, organizes in a well-known [11, 12] leeklike way (concentric cylinders) due to the parallel boundary conditions of the lamellar layers on the glass. The sample then presents a uniform illumination in polarizing microscopy, except for an axial defect decorated with very fine and regular transversal striations, due to small focal conics allowing relaxation of the high curvature energy of this region. The texture and measurements presented herein do not evolve over months, indicating a stable texture.

It was observed that the interface was mainly conical (Fig. 2), except near the triple L_α-L_3-glass contact line and at its apex [Fig. 2(a)]. The angle of the conical part gives α directly; its variation with the swelling of the system is presented in Fig. 3 (there is no variation with the diameter of the capillary) [13]. The main effect is an increase of the tilt (decrease of α) as the system becomes more swollen.

Near the triple line, the surface properties of the three materials in contact impose the angle of the L_α-L_3 interface at the glass contact (Young conditions). In the most general case, this angle is not α; the fact that the lamellar phase creates defects in the zone where the conical interface is deformed by the triple line —and only there [Fig. 2(b)]— is a supplementary hint that the L_α-L_3 interface and the lamellar layers have a preferred angle. The defects have an axial symmetry and are hexagonally close packed, similar to the texture of toric focal conics studied by Fournier, Dozov, and Durand [14]. In thermotropic systems, toric defects allow the matching of layers from a parallel anchoring ($\alpha = 0°$) on the glass to a perpendicular one ($\alpha = 90°$) on the isotropic phase. In the present case, the interface is likely not to be flat, but deformed at the location of each toric defect, showing up as a logarithmic spiral profile of revolution, in order to satisfy the tilted anchoring conditions (Fig. 4).

In order to explain the evolution of the equilibrium tilt angle α with swelling, let us recall that the L_3 phase, though without long-range order, presents a typical intermembranar distance d_3 (measured as the position of the maximum of a broad peak in x-ray or neutron small-angle scattering). Moreover, the phase being isotropic, it imposes this characteristic distance d_3 to any imaginary

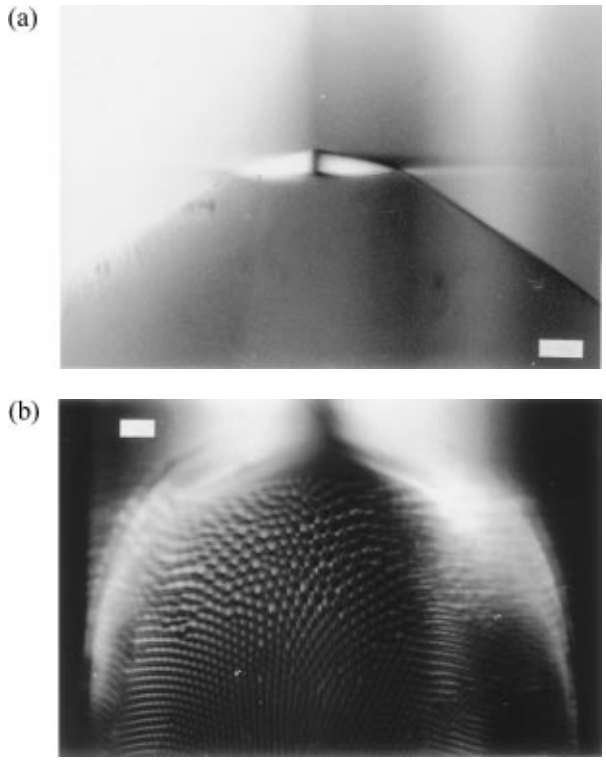

FIG. 2. (a) Interface between L_α (up) and L_3 (down) in a system of global composition $P_{\text{br}} = 81\%$ and $h/c = 1.1$ ($\alpha = 57°$), crossed polarizers. Bar = 100 μm. Notice the defect that cuts the apex in order to decrease the interfacial energy. (b) Idem, $P_{\text{br}} = 70.4\%$ ($\alpha = 69°$), focus on the defects tiling in the L_α crown near the glass-L_α-L_3 contact line, above the conical part. There are no detectable defects at the apex: α being larger, the surface of a cone of comparable basis is less important than for more swollen systems. The L_α-L_3 interfacial energy gaining by "cutting" the apex with a defect would be smaller than the cost of elastic energy.

cut surface. In a rough model where the L_α/L_3 interface would "cut" the sponge phase without modifying it at its vicinity, the L_α phase is likely to tilt in order to match its periodicity d_α to d_3; the matching avoids a discontinuity of the membranes at the interface, generally acknowledged as quite energetic in this region of the phase diagram [1–2, 4]. We may calculate from d_α and d_3 an expected matching angle α_m : $\alpha_m = \arcsin(d_\alpha/d_3)$. In order to test this hypothesis, x-ray experiments were performed on the L_α and L_3 parts of the biphasic systems under study. The corresponding d_α and d_3 are presented in Fig. 5; the calculation of α_m from these data is compared to α in Fig. 3. The two angles have comparable values: the matching model then gives a good order of magnitude for the tilt angle. We do not state here the way in which the matching between the L_α and L_3 membranes occurs and the geometrical and topological questions it raises; this point will be discussed in a forthcoming paper

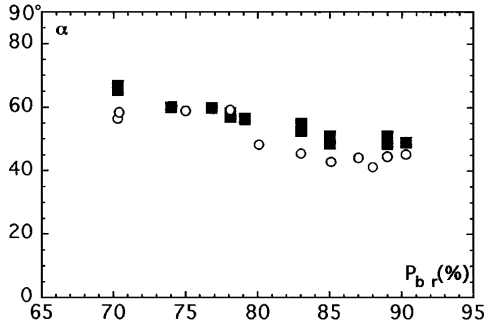

FIG. 3. ■: Measurement of α in cylindrical capillaries. ○: Calculation of α_m from experimental x-ray measurements of d_α and d_3 (Fig. 5 data). For both kinds of results, L_α and L_3 are the two parts of the biphasic mixture obtained for $h/c = 1.1$ (except for $P_{\text{br}} = 89\%$ and 90%, for which $h/c = 1.11$).

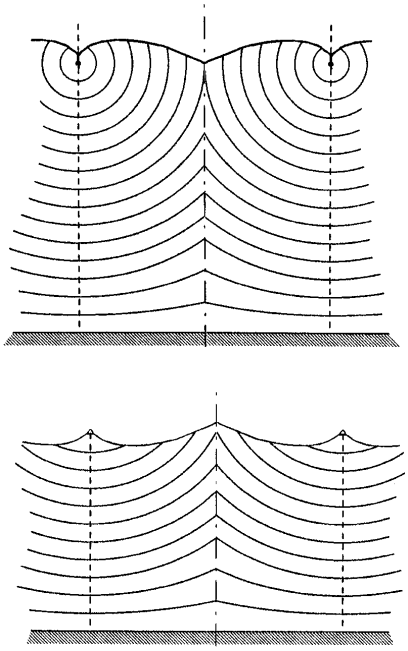

FIG. 4. Two possible ways for the L_α/L_3 interface to realize a constant tilt angle with a toric focal conic defect. In the second case, more probable, the circle line defect is virtual. When $\alpha = 0°$, as in thermotropics [7, 14], the two cases are degenerated in a flat interface.

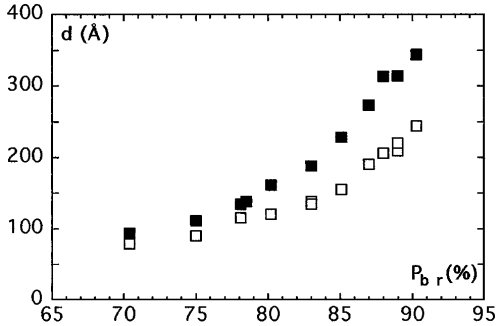

FIG. 5. Characteristic distances d_α and d_3 in the L_α (□) and L_3 (■) parts of the $h/c = 1.1$ biphasic mixture ($h/c = 1.11$ for $P_{\text{br}} = 89\%$ and 90%) of global brine weight fraction P_{br}.

[10]. Let us notice that this model of membrane continuity between L_α and L_3 phases is consistent with a very small value of γ, the interfacial energy being mainly due to rather weak curvature contributions.

The matching presented here is reminiscent of a phenomenon of epitaxy. Epitaxy is usually defined by the existence of a finite set of relative orientations at the interface between two media, due to a matching of lengths. It is the case here, and more precisely since one of the phases is isotropic, the only orientations in play are those of the lamellar phase at the interface. Other cases of epitaxy are documented in physics of surfactant and other supramolecular assemblies [15–19]. They are closer to the usual types of epitaxy since they involve ordered media on both sides of the interface. The present case is much simpler, as there is only one typical distance in the sponge phase, and in a sense keeps the essence of epitaxy.

Notice that another anchoring of the L_α is conceivable which avoids a discontinuity of the membranes at the interface: the case where membranes are parallel to the interface ($\alpha = 0°$). Here, the sponge phase must stop at the interface, and, as will be explained in Ref. [10], this is unfavorable from the point of view of the Gaussian curvature of the L_3 membrane. Of course, this argument is not valid when the L_α phase is in contact with an isotropic phase of a different structure. Observations via polarizing microscopy of L_α droplets surrounded by the L_1 (micellar) phase indicate that they are made of concentric spherical layers [20, 21]: The anchoring of the L_α phase is parallel when the phase in contact is not a phase of membranes. The membrane as a basic constituent of the two phases in contact is definitely a crucial point in making $\alpha \neq 0°, 90°$ possible.

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