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Pattern Formation in the Growth of Smectic A Liquid Crystals in Some Binary Mixtures

We report the formation of several unusual patterns in the growth of smectic A liquid crystals from the isotropic phase in some binary mixtures. If the composition is such that the interfacial tension anisotropy ($\Delta\gamma$) is weakly positive, the smectic A separates as ellipsoidal drops with flat layers. As the temperature is lowered, changes in the composition lead to a reversal of $\Delta\gamma$ and to the growth of a spherical cap at one end. Some spherical drops appear to have a variable angle between the layer normal and the interface, implying that $\Delta\gamma \simeq 0$. Flat drops which have concentric smectic A layers develop interfacial instabilities as the temperature is lowered. In some cases, a transformation of cylindrical or spherical structures to discs is observed.

1. INTRODUCTION

The smectic A liquid crystal consists of a periodic stacking of liquid layers.[3] The director is parallel to the layer normal and the medium is uniaxial. The lamellar phase which is exhibited in some concentration range of solutions of amphiphilic molecules

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SFI Studies in the Sciences of Complexity, Addison-Wesley, 1995

in water and/or alcohol also has the same symmetry. The growth of smectic liquid crystals from the isotropic phase was studied by Friedel and Grandjean long ago. They found that the A phase separates in the form of often highly decorated rodlike structures called batonnets. The structure arises because of the positive interfacial tension anisotropy in these materials, i.e., $\gamma_{\parallel} > \gamma_{\perp}$, where the subscripts refer to the mutual orientation of the interface and the layers. Such systems were studied in great detail by Fournier and Durand[4] who have also shown that the focal conic domains in the batonnets are in thermodynamic equilibrium.

Recently there have been several studies[1,2,5,6,7] of highly elongated cylindrical growths of smectic A liquid crystals that result when the interfacial tension anisotropy is negative. This type of growth occurs efficiently by absorption of molecules without nucleation of new layers. While, in the case of single component systems, these structures are metastable,[5] we have shown that in the case of two component systems, concentration gradients can actually stabilise such cylindrical structures.[6,7] There are some similarities between these cylindrical structures and the Myelene forms that are found in lyotropic lamellar systems. In the present paper we report some novel structures which occur when $\Delta\gamma$ is around zero.

2. OBSERVATIONS

We have studied in some detail the binary system consisting of octyloxy cyanobiphenyl and dodecyl alcohol. For low percentages of alcohol ($< 30\%$, say), the smectic A liquid crystal separates in the form of batonnets mentioned above. For $> 50\%$ of alcohol, we get the elongated cylindrical structures. In the following we discuss the growth of smectic A liquid crystals for intermediate compositions in which the interfacial tension anisotropy is quite small. When we cool a mixture with an alcohol concentration of $\sim 34\%$ at 0.1°C/min., the smectic A drops that separate are not much elongated, though they are made of focal conic domains. (See Figure 1(a).) For higher percentages ($\sim 40\%$) of alcohol, the smectic A separates usually as elliptical drops with flat layers or occasionally as spherulites (Figure 1(b)). The elliptic shape arises due to the positive interfacial tension anisotropy, but, unlike in mixtures with lower concentrations of alcohol, these are not decorated with focal conics. It is clear that in the coexistence range of smectic A and isotropic phases in this two component system, the smectic liquid crystal which initially separates from the isotropic phase will have a lower concentration of alcohol than the average and, hence, has positive interfacial tension anisotropy. But as the temperature is lowered and the smectic regions grow, the alcohol concentration in the isotropic phase increases and the interfacial tension anisotropy of the newly condensing smectic A liquid crystal progressively reduces and can even change sign, and then becomes increasingly negative. A variety of structures are formed in this regime. We describe them below.

a. The elliptic object develops a fine line all along the major axis. Then a hemispherical cap develops at one end. The orientation of the director can be easily visualised by dissolving anisotropic and dichroic dye molecules in the medium and making observations with a polarizer. (See Figure 2.) Apparently as $\Delta\gamma$ becomes increasingly negative, the layer at one end can fluctuate to develop a *hump*, which will not have an unfavourable energy. Layers now grow around this hump to form the structures shown in Figure 2(c) and 2(d). In one of the elliptical drops in Figure 2(a), a point defect is seen near one of the foci. The dark line in this case extends from this point to the farther periphery of the drop and a spherical structure develops at the latter end (Figure 2(d)) giving the appearance of a round-bottomed bottle. These observations were made between two glass plates which were treated with a polyimide solution (but not rubbed), and without any spacers. This treatment favours an orientation of the molecules parallel to the glass plates. Similar structures were found in 50 μm thick cells, but in that case the drops were not isolated as two or three of them would lie along any particular line of sight.

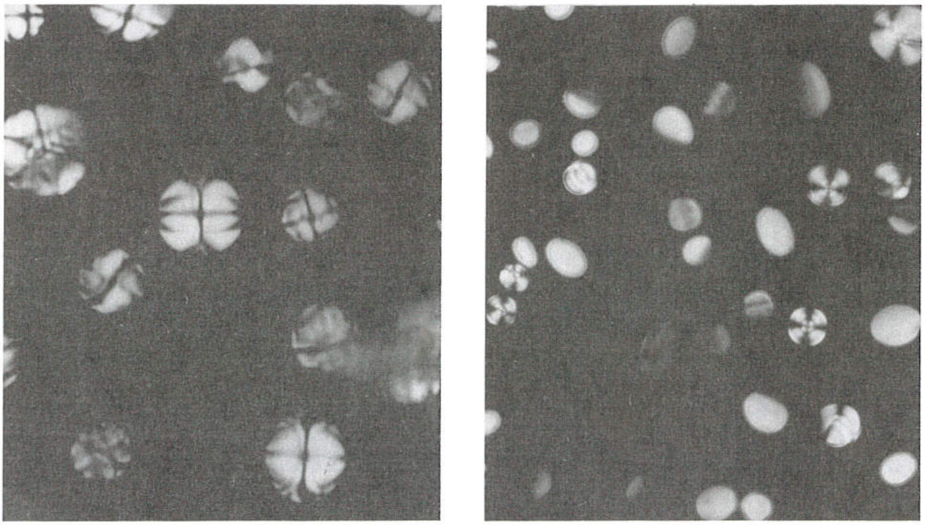

FIGURE 1 (a) (left) Smectic A drops made up of focal conic domains in a mixture with $\sim$ 34% of dodecyl alcohol. Sample thickness $\simeq$ 50 μ, crossed polarizers ($\times$400). (b) (right) Elliptic drops of S_A with flat layers in a mixture with $\sim$ 40% of alcohol. Crossed polarizers ($\times$300).

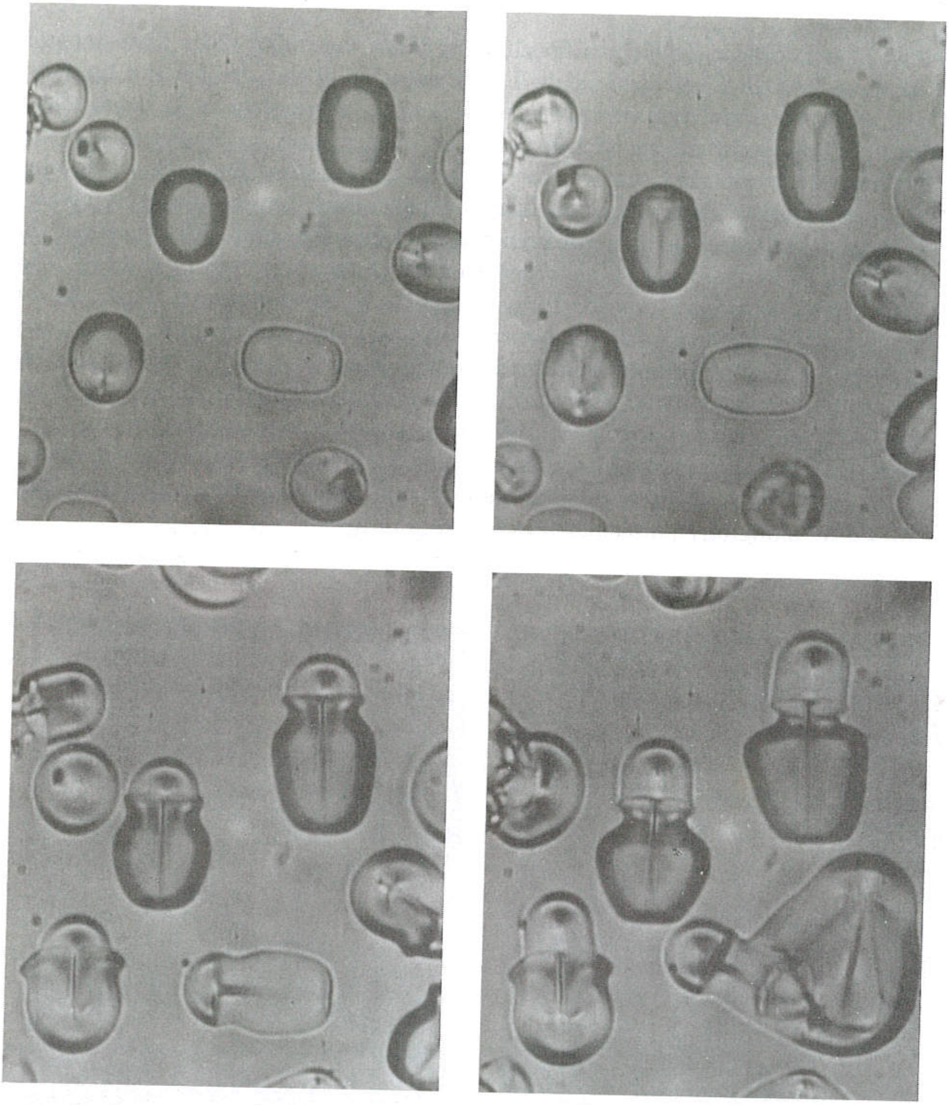

FIGURE 2 Smectic drops in a mixture with ~ 40% of alcohol and a polariser set parallel to the vertical edge of the photograph (×400). (a) (upper left) sample at 44°C; (b) (upper right) at 42.4°C, the elliptic drops have developed fine lines; (c) (lower left) at 41.7°C, well-developed hemispherical *caps* are seen at one end of the drops; (d) (lower right) at 40.7°C, the caps have slightly elongated. Note the round-bottomed shape of one of the drops.

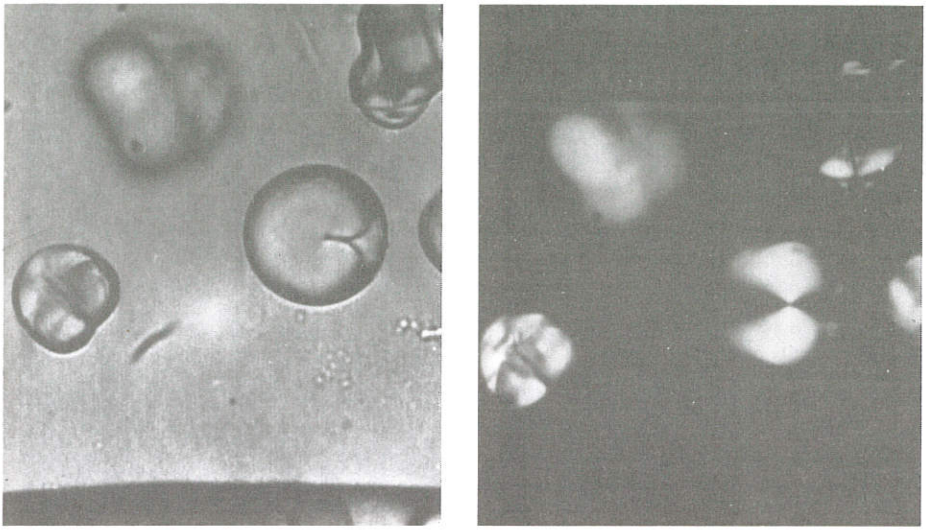

FIGURE 3 A nearly spherical drop with a radial line in a mixture with ~ 42% of alcohol. (a) (left) A polariser is set perpendicular to the radial line. (×400); (b) (right) with crossed polarisers, only two dark brushes are seen in a direction parallel to the radial line.

b. If the alcohol content in the mixture is slightly higher, $\sim 42\%$, the smectic A drop grows with a nearly spherical shape, but with a radial line defect (Figure 3). Between crossed polarizers set parallel and perpendicular to the line, only two dark brushes are seen (Figure 3(b)). The spherical shape shows that $\Delta\gamma$ may be close to zero in this case. Further, in a few drops which have defects whose location could be monitored, we have observed that the drops continuously *rotate* as they grow in size with the lowering of temperature. In one case we could observe the rotation for more than one hour.

c. In the case of a mixture with an alcohol content of about 45% taken between two plates treated with polyimide, often the A phase grows in the form of circular discs, in which the layers are concentrically arranged implying that $\Delta\gamma < 0$. As the temperature is lowered, the drops develop interfacial instabilities which may have 3-fold and higher (up to 20-fold) symmetry (Figures 4(a) and 4(b)). The process appears to be somewhat analogous to the case (a) discussed earlier: *humps* formed on the surface giving rise to radial lines. The alcohol concentration in the newly condensing material being greater, the humps usually grow into cylindrical stubs (Figures 5(c) and 5(d)). Similar growth processes have been seen in thicker (~ 50 μm) cells.

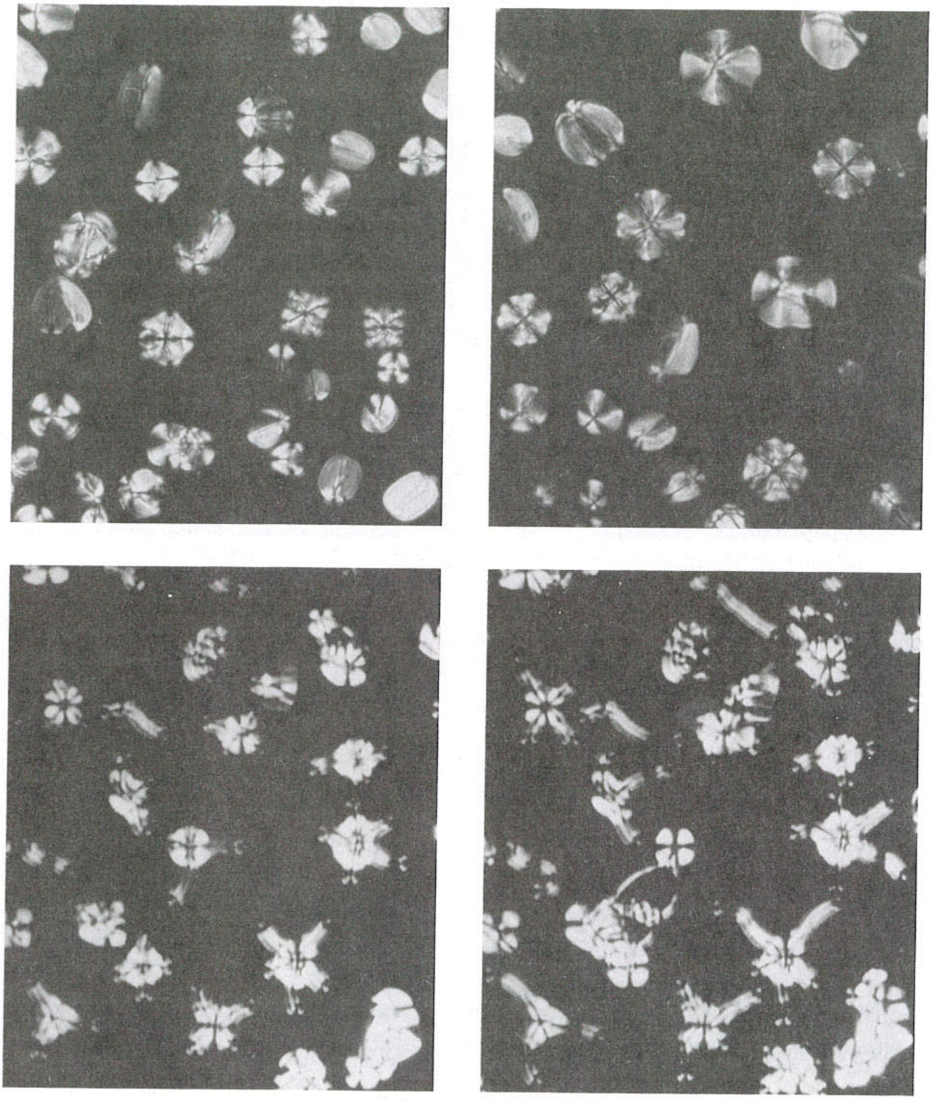

FIGURE 4 Smectic A drops that have developed multifold interfacial instabilities in a mixture with ~45% of alcohol. (a) and (b) (upper left and right) show two regions between crossed polarizers (× 300); and (c) and (d) (lower left and right) at lower temperatures, cylindrical growths are seen from such drops. In (d) a cylinder has split to form a disclike structure.

d. Often one of the cylinders elongates considerably and at some stage *splits* to form a disclike object which encloses well-aligned smectic layers (Figure 4(d)). As this structure forms, the material of the disc obviously comes from the main drop and simultaneously all the other cylindrical stubs disappear.

e. In a thick cell filled with a mixture having an alcohol concentration of ~ 47%, spherical drops with one cylindrical tail can often be seen on maintaining the temperature for several hours. On a slight warming of the sample, the cylinder splits to form a disc whose rim becomes circular (Figure 5(a) and 5(b)). Eventually the disc shrinks to form a sphere.

f. When the alcohol concentration is even higher, say, ~ 50%, $\Delta\gamma$ will be sufficiently negative and, as we mentioned earlier, long cylindrical structures grow as the temperature is lowered. As the alcohol content in the isotropic phase progressively increases, the negative concentration gradient needed for stabilising the cylinder cannot be sustained and the cylinders collapse to form compact objects.[6] If relatively thick cylinders collapse slowly at a fixed temperature,

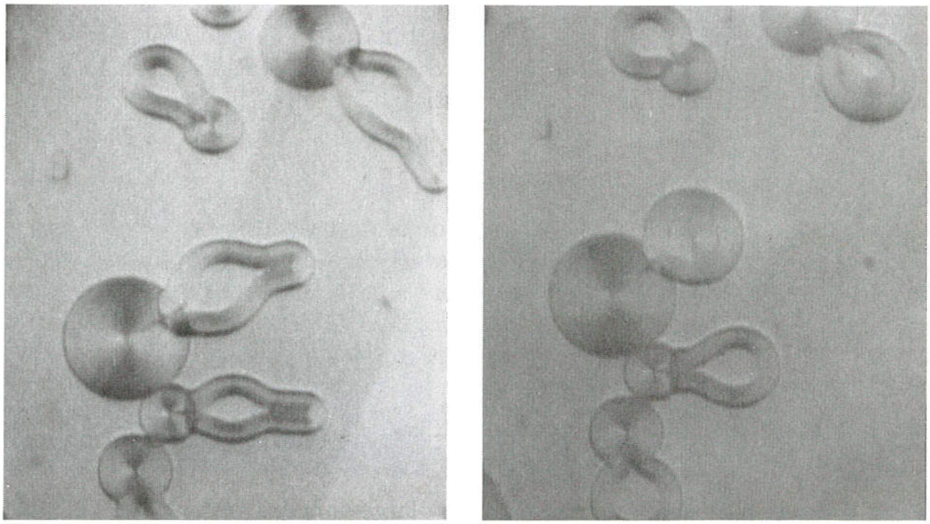

FIGURE 5 (a) (left) Spherical drops with cylindrical tails which have just split to form discs in a mixture with ~ 47% of alcohol. A polariser is set parallel to the vertical edge of the photograph (×400); (b) (right) about half a minute later, the rims of the discs have become more circular in shape.

they often form objects that consist of a large spherical object with one section chopped and, hence, forming a flat surface and a smaller spherical drop attached to it (Figure 6(a)). As time progresses, the small sphere grows at the expense of the large one whose shape changes to form a disc (Figure 6(b) and 6(c)). The disc later shrinks to form a smaller sphere which is finally swallowed up by the large sphere. In some cases, large spherical objects with one side *flattened* are also seen (Figure 6(d)).

3. DISCUSSION

The batonnets with focal conic domains studied by Friedel and Grandjean and more recently by Fournier and Durand minimise the total energy which has contributions from the curvature in the bulk and the interfacial energy with the constraint that smectic layers are orthogonal to the interface. In crystals the shapes are usually decided by dynamical processes and may not correspond to true minimisation of the interfacial energy. In smectic A which has a one-dimensional crystalline order, it is easier to attain equilibrium shapes. Fournier and Durand[4] have shown that the focal conics occurring in batonnets are indeed in an equilibrium configuration.

In our experiments, in which we add considerable quantities of a long chain alcohol, we can change the interfacial tension anisotropy. Indeed, if our starting composition is appropriate, the anisotropy can change sign during the growth of the smectic liquid crystals. This produces the variety of patterns that we have observed in the present study.

In systems that give rise to batonnets decorated with focal conic domains, the energy of the focal conic arises from curvature elasticity which increases linearly with size $[(\sim K/L^2) \cdot L^3 \propto L]$. (The presence of disclinations gives rise to only a logarithmic correction.) The interfacial energy is $\propto \bar{\gamma} L^2$. Hence, if there is anisotropy of γ $(\Delta\gamma > 0)$, focal conic domains occur within the elongated structures for a size[4]

$$L > l_o \sim \frac{K}{\bar{\gamma} - \gamma_\perp} \sim \frac{K}{\Delta\gamma}. \qquad (1)$$

Hence, if $\Delta\gamma$ is very small, we can have very large domains without focal conic defects as has been found in our samples (Figure 1(b)). This also probably means that both $\gamma_\parallel$ and $\gamma_\perp$ are considerably smaller in the mixture than in the pure component. Reduction of the interfacial tension by impurities is a well-known phenomenon.

As the smectic liquid crystals condense with lowering of temperature, the concentration of alcohol in the isotropic liquid increases. As a consequence, the alcohol

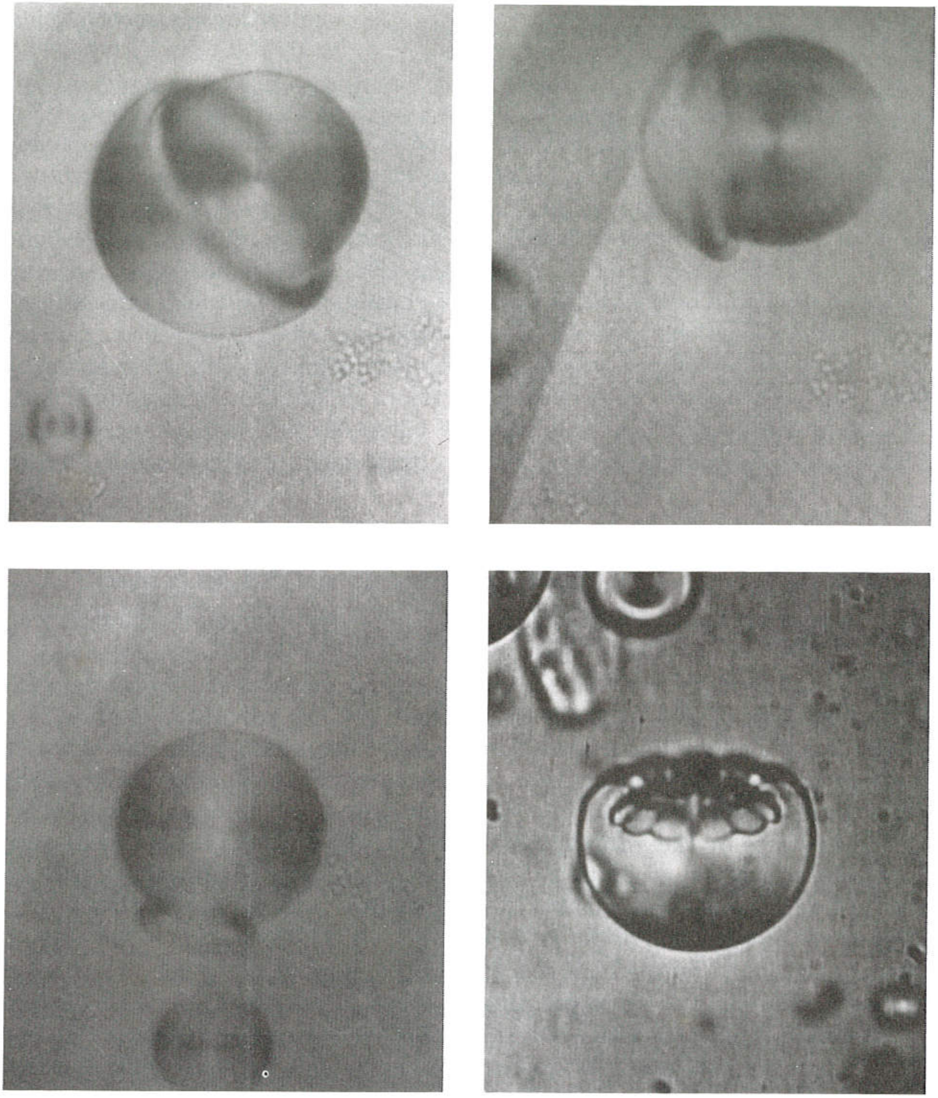

FIGURE 6 Spherical drops in samples with ~ 50% alcohol with flattened portions. (a) (upper left) A thick cylinder has slowly collapsed to form a pair of drops; (b) (upper right) after 35 minutes the smaller sphere has grown at the expense of the larger one; (c) (lower left) after another 15 minutes, the latter has shrunk to a disc; (d) (lower right) an isolated large drop with a flattened portion.

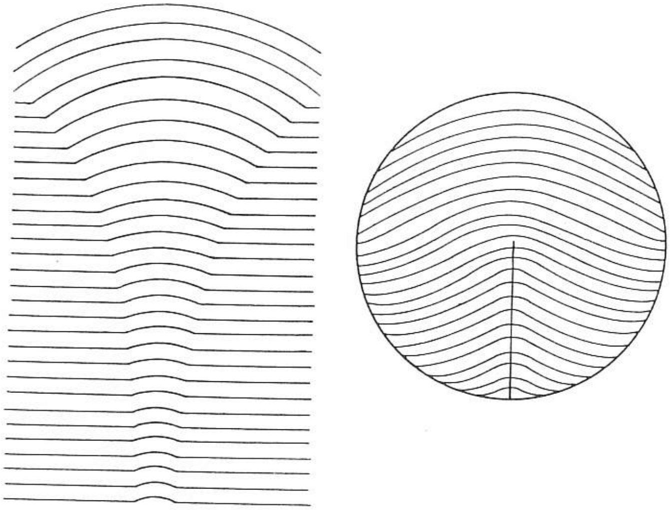

FIGURE 7 (a) (left) Schematic diagram of the arrangement of layers in smectic drops of the type shown in Figure 2(c). (b) (right) Schematic arrangement of layers in spherical smectic drops with a radial line seen in Figure 3.

content of newly condensing smectic A will also be larger and the interfacial tension anisotropy can eventually change sign. This favours the growth of smectic such that the layers are parallel to the interface. In the elongated and uniformly aligned drops, the process starts by the formation of a *hump* in the centre of a layer at one end. The strong anisotropy of elasticity of smectic phase (the compression coefficient $B \gg$ the curvature elastic constant K) results in the *hump* propagating through the layers to the other end of the drop (Figure 7(a)). The formation of the hump is, of course, facilitated by the high concentration of alcohol in the top layers, which also lead to a swelling of the layers. Indeed, X-ray measurements indicate that the layer spacing for mixtures with $\sim 40\%$ alcohol is about 10% larger than that in pure 8OCB. The new layers can now grow around the hump with spherical symmetry.

Qualitatively we can see that the formation of a hump can actually reduce the energy of the drop. For the sake of argument, assuming that the original drop consisted of a cylinder of length L and radius R of perfectly flat layers, if a hemispherical hump with a radius r develops such that the area of the layer is unaltered, the new lateral radius R' is given by

$$\pi R'^2 + 2\pi r^2 = \pi R^2. \tag{2}$$

The change in energy is

$$\Delta E \simeq 2\pi\gamma_{\perp} L(R' - R) + \frac{K}{2r^2} \cdot \pi r^2 L \tag{3}$$

which becomes negative for

$$r \geq \sqrt{\frac{K}{\gamma_\perp}} R\,. \tag{4}$$

For $K \sim 10^{-6}$ dyne, $\gamma_\perp \sim 10^{-2}$ dyne/cm and $R \simeq 10\mu\text{m}$, $r \simeq 3\mu\text{m}$.

Of course the energy will be lower for larger r. This leads to the formation of a *neck* near the top layers as seen in Figure 2. The final shape as seen in Figure 2(d) implies that the *flat* layers which are orthogonal to the interface grow at a faster rate than those that make smaller angles.

The other unusual object seen in our study is a spherical drop with a radial line when $\Delta\gamma \simeq 0$. The experimental observations indicate that the layers are arranged as shown in Figure 7(b). As we mentioned earlier, we see that many drops in which the line appears to be along the direction of observation rotate continuously as they grow in size. We feel that the radial line may also incorporate a screw dislocation with a relatively large Burgers vector which may be responsible for the rotation of the drop.

We have also seen that in some cases, at constant temperature some cylinders can split to form disclike objects sucking the material from the cylindrical stubs protruding from a parent spherical object. As we have argued elsewhere,[6] concentration gradients can stabilise a cylinder with respect to a sphere. As the concentration of alcohol in the surrounding liquid increases, the required type of gradient cannot be sustained. In this case the cylinder would usually be expected to collapse to a sphere. We can now compare the energy of a disc compared to that of a sphere with the same volume. A disc with lateral dimension of $2R$ and thickness $2r$ has an energy

$$F^{\text{disc}} = 2\pi\gamma_\parallel(R^2 + \pi r R) + (2\pi R)\frac{\pi K}{8} \ln \frac{r}{a} \tag{5}$$

where a is of the core radius of the line dislocation of strength $+1/2$ around the periphery and is of the order of a molecular dimension.

A sphere with the same volume will have a radius R_{sp} such that

$$R_{\text{sp}} = [(3/4) r R (2R + \pi r)]^{1/3}$$

and an energy

$$F^{\text{sp}} = 8\pi K R_{\text{sp}} + \gamma_\parallel 4\pi R_{\text{sp}}^2\,.$$

We can compare the energies of the two objects for the usual material parameters; viz., $K \sim 10^{-6}$ dyne, $\gamma_\parallel \sim 10^{-2}$ dyne/cm for different values of R and r. Calculations show that for a given value of r, $F^{\text{disc}} < F^{\text{sp}}$ for R less than some value R_o say. It is found that, for example, if $r \simeq 1$ μm, $R_o \sim 2.5$ μm. It is also seen that r/R_o decreases as r increases. If $r \simeq 4$ μm, $R_o \simeq 5.5$ μm. Hence, it would appear that thin discs, which form when a cylinder splits, become thicker by adding layers and, hence, finally become unstable with respect to spheres, as seen in the experiments.

We have also observed other structures in these systems. A more detailed paper on these structures will be published in due course.

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