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The cellular optical texture of the lyotropic nematic phase of the caesium pentadecafluoro-octanoate(CsPFO)/water system in cylindrical tubes

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The nematic phase of the CsPFO/water system, when held in a cylindrical glass tube, spontaneously forms a detailed 'cellular' texture with an axial $S = +1$ disclination. This texture is the lyotropic discotic analogue of that previously found for a calamitic thermotropic system.

1. Introduction

The mesomorphic properties of the polyfluorinated amphiphile system of caesium pentadecafluoro-octanoate(CsPFO)/water has attracted increasing attention over recent years [1–10]. The dominant type of mesophase formed by this system is lamellar rather than hexagonal or cubic. Presumably this is because of the greater rigidity of the polyfluorinated alkyl chain as compared with the corresponding hydrocarbon chain and hence the greater difficulty in creating the splayed arrangements of molecules present in spherical and cylindrical micelles. The phase diagram for the CsPFO/water system is well established [11, 12]. It exhibits isotropic micellar (L_I), nematic (N_D) and defected lamellar (L_α^H) phases. Of particular interest in this study is the narrow band of lyotropic nematic phase. Such N_D phases are rare and this system has been extensively studied and is thought to be composed of approximately circular discs of bilayer [1, 3, 11].

Whilst preparing samples of the nematic phase for an X-ray diffraction investigation, we discovered the remarkable optical texture (shown in figures 3 and 4) which is formed when the sample is constrained in a cylindrical tube. The sample appears to be irregularly subdivided by a number of transverse planes into 'cells' and there is a distinct line of disclination running along the central axis of the tube. Previous investigations [6] have shown that both the nematic and lamellar phases are prone to surface alignment in cylindrical tubes, but in this earlier work appreciably larger diameter tubes (1 mm) were used and the highly organized patterns described here were not observed.

2. Preparation of the sample

The sample investigated was an approximately 45% by weight, aqueous solution of CsPFO and it was held in a sealed 0·3 mm diameter Lindemann glass capillary tube. The lamellar to nematic transition temperature was approximately 50°C. When first introduced into the tube, the nematic phase adopts the confused schlieren texture shown in figure 1. The cellular texture is developed by holding the sample in this phase for several minutes, cooling it into the lamellar phase (figure 2) and then reheating it back into the nematic state (figure 3). The cellular texture may therefore be regarded as being

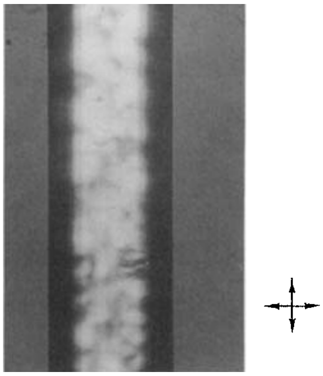

Figure 1. The confused varicose, schlieren texture of the CsPFO/water system in the nematic phase adopted by the sample when it is first introduced into a tube. (Crossed polarizers; the diameter of the sample tube is approximately 0·3 mm).

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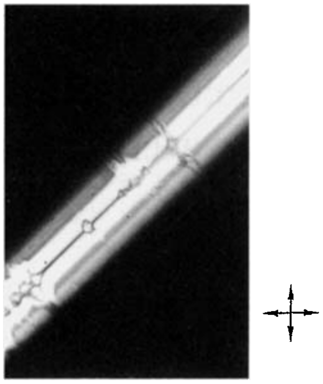

Figure 2. The highly aligned texture of the lamellar phase of the CsPFO/water system created by cooling the sample shown in figure 1 below the nematic → lamellar transition (Crossed polarizers).

to some extent paramorphotic, but once formed, it appears to be perfectly stable.

3. Explanation of the optical texture

When the sample is viewed between crossed polarizers with the axis of the sample tube aligned parallel to the polarizer, the transverse cell boundaries and the axial disclination are very apparent as black lines, figure 3(*a*). When a 1 λ, first order red plate is introduced at 45° to the specimen, additional information is given. As shown in the extreme left of figure 4, the sample now has a chequered appearance in which alternate segments appear blue and yellow. (These areas correspond respectively to regions where the birefringence of the sample either adds to or subtracts from the birefringence of the 1 λ plate, see for example Hartshorne and Stuart [13].) This indicates that the molecular directors are arranged in a pattern which approximates to the alternating chevron pattern shown in figure 5(*b*). However, if the structure contained parallel arrays as shown in this sketch, then each block would extinguish evenly at the appropriate orientation of the sample. This is not the case. When the sample tube is rotated on the microscope stage, the pattern becomes progressively distorted as shown in figure 4 and we infer that the pattern of molecular directors is actually that shown in figure 6. As shown in figure 7, this director field pattern explains the observed changes in appearance of the sample as it is rotated.

4. Discussion

The immediate conclusion that can be drawn from the optical evidence concerns the pattern of directors shown in figure 8(*a*). To infer from this a picture of the structure of the sample requires some additional knowledge about the nature of the molecular organization of the micelles. If we take it that the N_D phase consists of bilayer micelles, the director will correspond to the disc normal, the phase will be optically positive and the arrangement of the micelles in the sample is as shown in figure 8(*b*).

The central axis of the sample corresponds to an $S = +1$ disclination (with a radial pattern of the directors and a tangential pattern of micellar alignment) and the apparent division of the sample into cells results from the change of direction of curvature of the phase.

Although we did not realize it at the beginning of this study, this optical texture is similar to that previously found for a thermotropic nematic phase constrained in

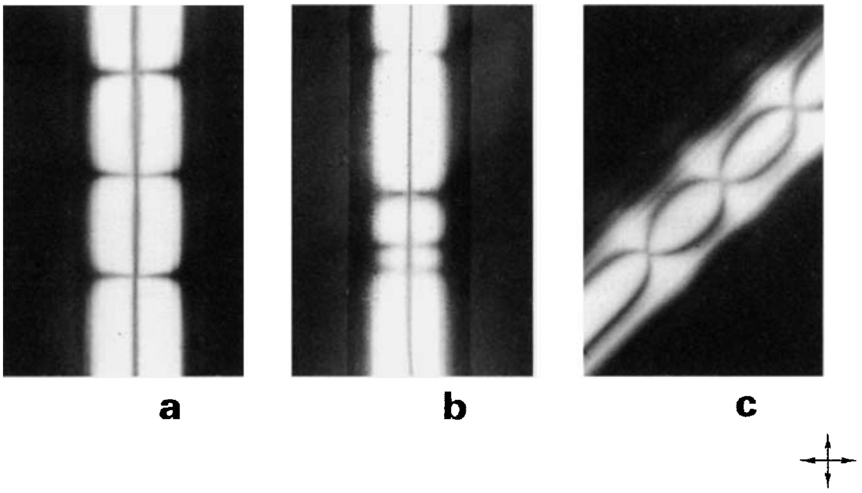

Figure 3. The cellular texture of the nematic phase of the CsPFO/water system formed by warming the lamellar sample shown in figure 2 back into the nematic phase. (Viewed between crossed polarizers). In (*a*) and (*b*) the sample tube is aligned parallel to one of the crossed polarizers. In (*c*) it is at 45°. (*b*) shows a more irregularly spaced section of the sample demonstrating that the 'cells' in this texture do not have to be the same length.

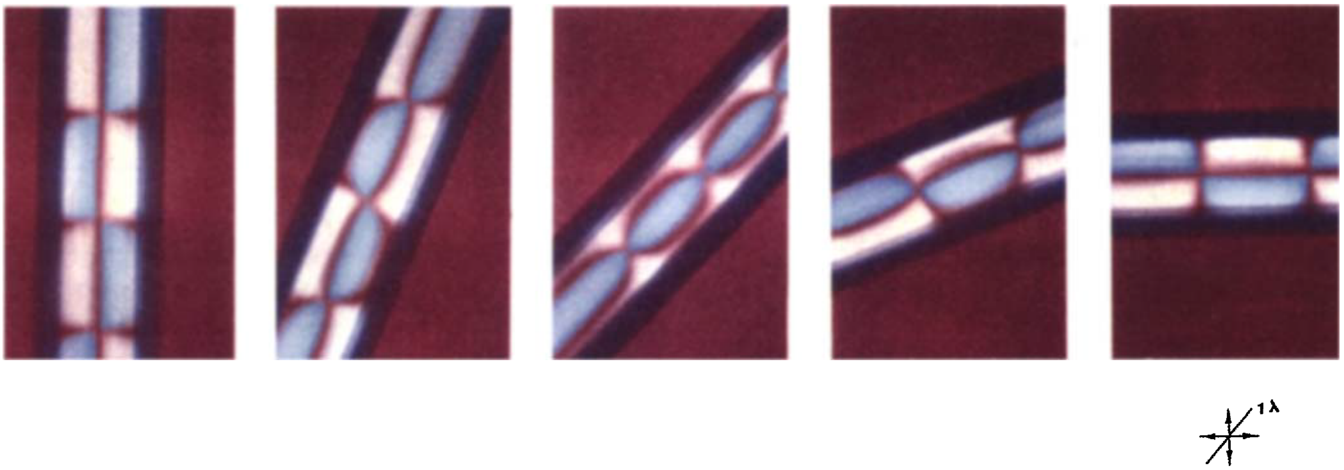

Figure 4. The cellular texture of the nematic phase viewed at different orientations between crossed polarizers with a 1 λ plate inserted at 45°.

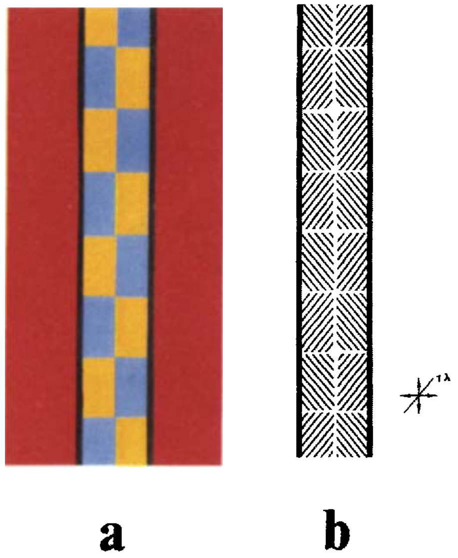

Figure 5. The explanation of figure 4 (far left). When viewed with the sample tube parallel to one of the crossed polarizers and with a 1 λ plate inserted at 45°, the sample appears as a chequer pattern of blue and yellow rectangles against the magenta first order red background (*a*). The blue regions occur where the birefringence of the sample adds to that of the 1 λ plate and the yellow regions indicate where it subtracts from it. This implies a structure with more or less diagonal blocks of director alignment as shown (*b*).

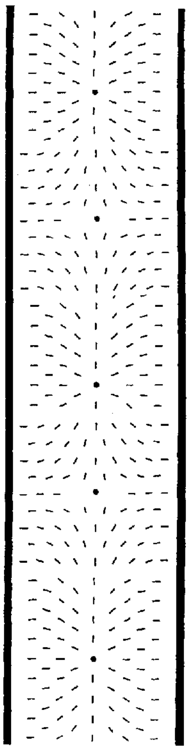

Figure 6. A more accurate representation of the director field than that shown in figure 5, with a curved rather than a straight line pattern and showing the alternation of the two types of point singularity along the axial $S = +1$ disclination. As shown in figure 7, this director field pattern explains the progressive change in appearance of the sample as it is rotated between crossed polarizers.

a cylindrical tube [14–17] and in fact appears to be the exact lyotropic discotic analogue. Williams *et al.* [14, 15] studied the structure of 4-methoxybenzylidene-4′-butylaniline (MBBA) in a glass tube treated with hexadecyltrimethylammonium bromide which was known to give a perpendicular surface alignment of the MBBA. (Our glass tubes were untreated). They used two different optical approaches to study this structure. The first of these concerned the pattern of flickering (seen using incident polarized light, with the analyser removed),

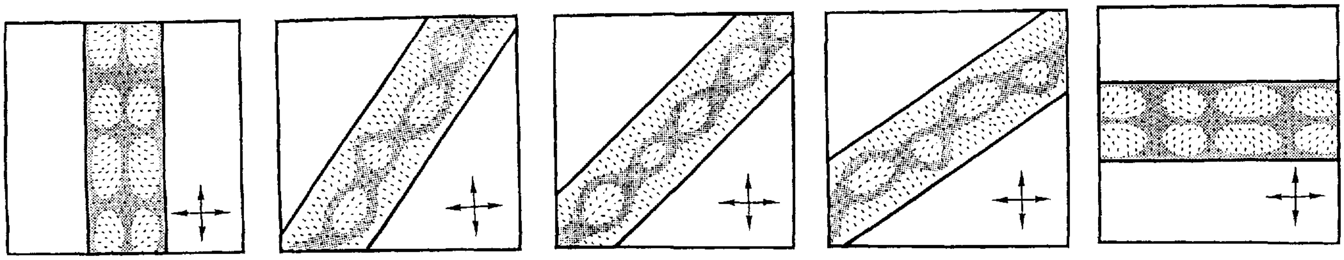

Figure 7. The explanation for the appearance of the cellular texture when observed between crossed polarizers, showing the progressive change in the extinction pattern as the sample is rotated. The shaded regions indicate the areas extinguished, i.e. places where the director lies along the analyser or polarizer direction.

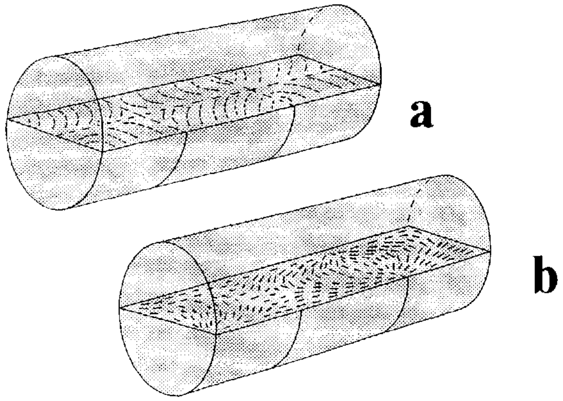

Figure 8. The three dimensional structure of the cellular texture; (*a*) shows the director field in an equatorial slice of the sample; (*b*) shows the corresponding pattern of alignment of the disc-like micellar aggregates, each short line representing the cross-section of a disc.

associated with the creation and destruction of cybotactic groups within the nematic phase. This flickering is highly anisotropic and follows the local director; hence the 'texture' of a time-exposure photograph shows the pattern of the director field.

Their second approach was particularly elegant. They examined the sample using an array of parallel rays of light. Each of these rays was effectively split into two, the ordinary and extraordinary, and the pattern of vectors of the displacement of the extraordinary from the ordinary images showed the alignment of the mesophase.

5. The rationale for the cellular texture

The cellular texture is a function of three factors:

- the shape of the containing vessel,
- the epitaxial alignment at the boundary of the sample,
- the elastic constants of the mesophase.

If one considers a transverse slice of the sample as shown in figure 9(*a*), epitaxial interactions cause the molecular director at the circumference of the sample to lie radially. Towards the centre of the sample, the phase becomes increasingly strained and the splay distortion energy at the centre approaches infinity. There are two ways in which this can be avoided. The first is for the pattern to break down near the axis and for the sample to create a central core. The second is for the alignment to bend as shown in figure 9(*b*), 'to escape into the third dimension' [15]. This trades off an acceptable small amount of bending energy against an unacceptable larger amount of splay energy. This curvature can occur in either

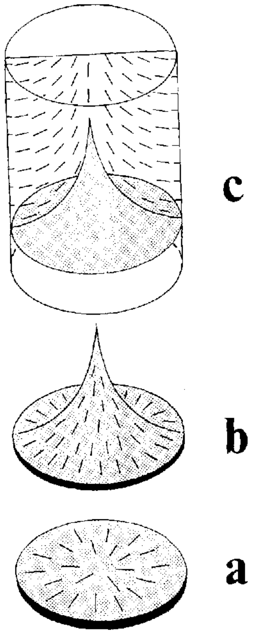

Figure 9. The rationale for the cellular texture, redrawn from [14]. The epitaxial alignment at the surface creates a radial director field. If the sample were homogeneous along its length, this would give rise to a structure where each transverse slice has the structure shown in (*a*). However in such a pattern, the splay energy becomes infinite at the centre and a distortion as shown in (*b*) is energetically favourable. (This has been called escape into the third dimension.) This can occur in either direction along the axis giving rise to the cellular texture as shown in (*c*).

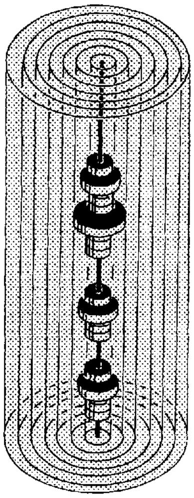

Figure 10. The explanation of the appearance of the lamellar sample shown in figure 2. Because of epitaxial interactions at the surface of the tube, lamellae attempt to lie in concentric cylindrical shells. As shown above in the outer regions of the sample, the curvature energy is relatively low, but towards the centre it becomes increasingly significant and the pattern tends to break abruptly. It appears that any breaks in the concentric pattern are filled with stacks of relatively undistorted lamellae lying in a transverse orientation.

direction perpendicular to the initial transverse slice. The apparent division of the phase into cells arises because of this choice. The boundaries of the 'cells' are the planes where one region curves to the right and the adjacent region curves to the left. Along the central $S = +1$ disclination, there is an alternation of point singularities.

Figure 2 shows the texture of the lamellar phase of the CsPFO/water system (which does not have the second of these options). The tendency for the pattern to break down abruptly near to the axis creates a core of perpendicularly aligned material. Irregular sharp-edged domains of uncurved lamellae tend to occur in the core zone as shown in the sketch (figure 10).

The precise shape of the curve followed by the director in the cellular texture is determined by the ratio of the splay and bend elastic constants (and is independent of the diameter of the tube). Williams *et al.* [15] obtained a good fit to their experimental observations using a $k_{11}:k_{33}$ ratio of 0·7. As far as we can judge, the shape of the curve for the CsPFO/water system is very comparable, implying a similar value for this ratio.

6. Conclusions

The cellular pattern formed by the nematic phase of the CsPFO/water system in cylindrical glass tubes arises from the epitaxial conditions at the sample surface and is adopted because it minimizes the splay deformation energy. It is the lyotropic discotic analogue of the texture previously described by Williams *et al.* [14, 15] for a thermotropic calamitic nematic system. This texture is a consequence of well-defined geometrical factors and we predict that it will be found in other comparable systems (for example thermotropic discotic nematics and lyotropic calamitic systems).

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