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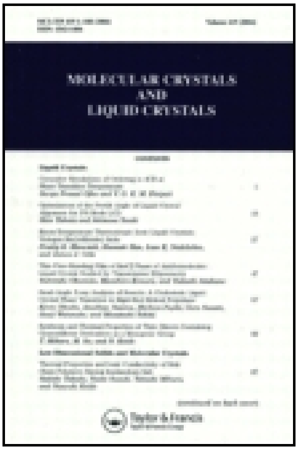

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Characterization of Lyotropic Nematics by Microscopy

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Characterization of Lyotropic Nematics by Microscopy

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(Received February 28, 1983)

A simple procedure is described for identification of the structure of the micelles (i.e., disks or cylinders) and the determination of the sign of the diamagnetic anisotropy of amphiphilic nematic mesophases. It is based upon the effects of shear, surface, and magnetic forces on the micrographic textures of thin films observed under the polarizing microscope.

INTRODUCTION

Lyotropic nematic mesophases consist of orientationally ordered solutions of either disk- or cylindrical-shaped micelles. They were discovered[1,2] in 1967, but serious research into their properties is relatively recent.[3–12] Nematic phases of disk-shaped micelles N_D occur as the precursor to the lamellar phase, whilst those consisting of cylindrical shaped micelles N_C are the precursor to the hexagonal phase.[10] The sign of the anisotropy of the diamagnetic susceptibility $[\Delta\chi = \chi_{\parallel} - \chi_{\perp}]$ is arguably one of their most distinctive properties, as it determines the response of the mesophase to an applied magnetic field. Mesophases with positive (N_D^+ and N_C^+) and negative [N_D^- and D_C^-] diamagnetic anisotropies have been reported.[10] The object of this paper is to describe a simple experimental procedure which we have found to be particularly useful for the identification of these four kinds of mesophase. It depends upon the effects of shear, surface, and magnetic forces on the micrographic texture of a thin film of the mesophase viewed under the polarizing microscope. The emphasis is on the procedure rather than on the interpretation of the textures which are involved and which have previously been reported.[2,4,8,9,10,13,14]

EXPERIMENTAL

Microscope

Polarizer and analyzer were inclined at angles of 45° to the direction of a static magnetic field as illustrated in Figure 1a. The magnetic field of 0.48 T was provided by a small electromagnet (Oxford Instruments,

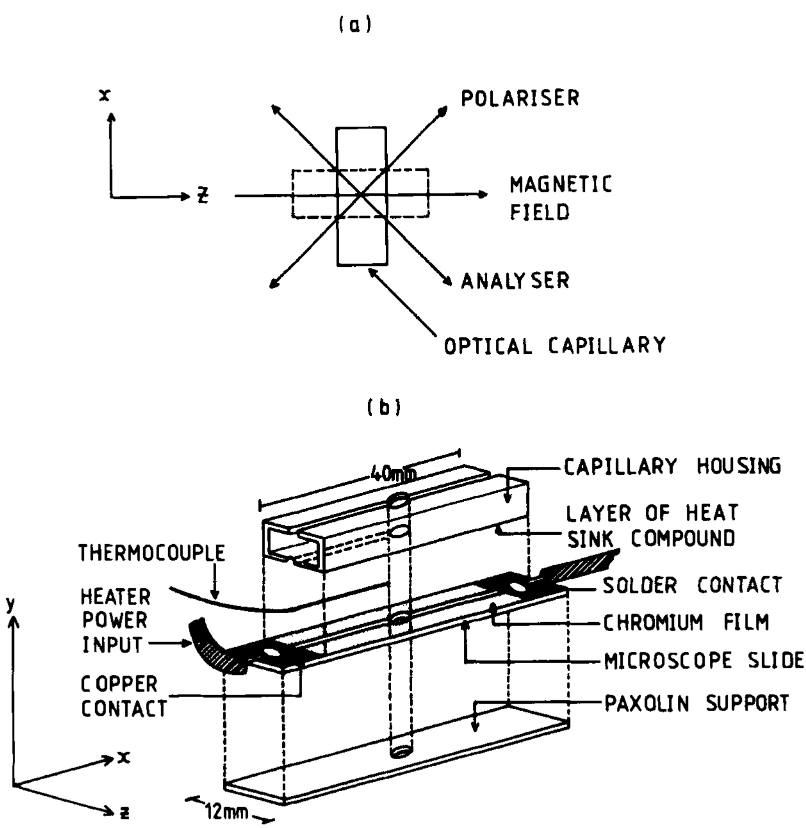

FIGURE 1 (*a*) System axes and (*b*) microscope hotstage.

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England) with pole diameter 2.5 cm and gap 1.5 cm. A home-built hot stage, as illustrated in Figure 1b, replaced the standard specimen stage. Resistive heating is provided by the thin film of chromium evaporated onto a microscope slide and the temperature controlled with a home-built controller.

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Materials

A variety of surfactant solutions was employed in the experiments described. Their compositions are summarized in Table I, together with the types of nematic phase they form at room temperature.

Method

Samples of the liquid crystals were introduced into rectangular optical capillaries [cleaned with Decon solution] with an optical path length of 200 μm (CAM LAB, Cambridge, England) by either capillary action or suction. The capillaries were sealed in a flame for some experiments, but left unsealed in others. Observations were made with a Vickers M17 polarizing microscope (York, England).

OBSERVATIONS

Flow alignment

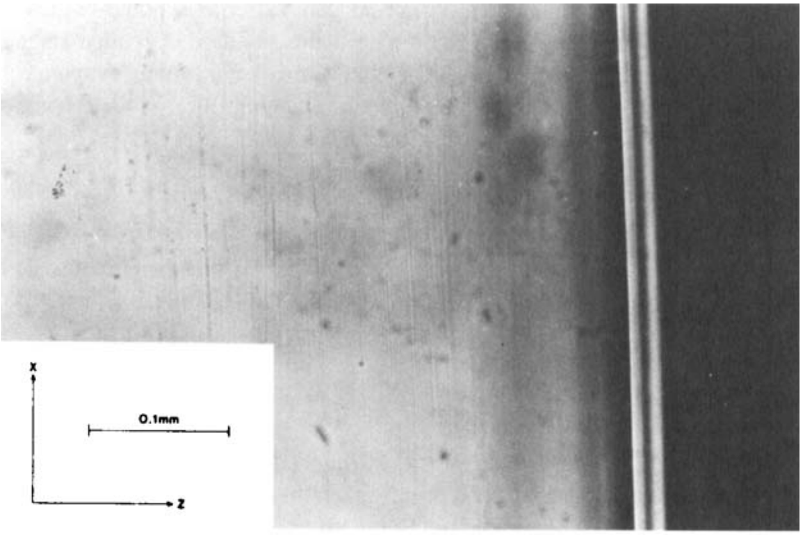
The sample is drawn by suction into the capillary at $T < T_{NI}$. Characteristically, different textures are observed for N_C and N_D mesophases as illustrated, respectively, in Figures 2a and 2b. Microscopic theory[15] predicts that for an ellipsoid under stationary shear flow, the director stabilizes

TABLE I

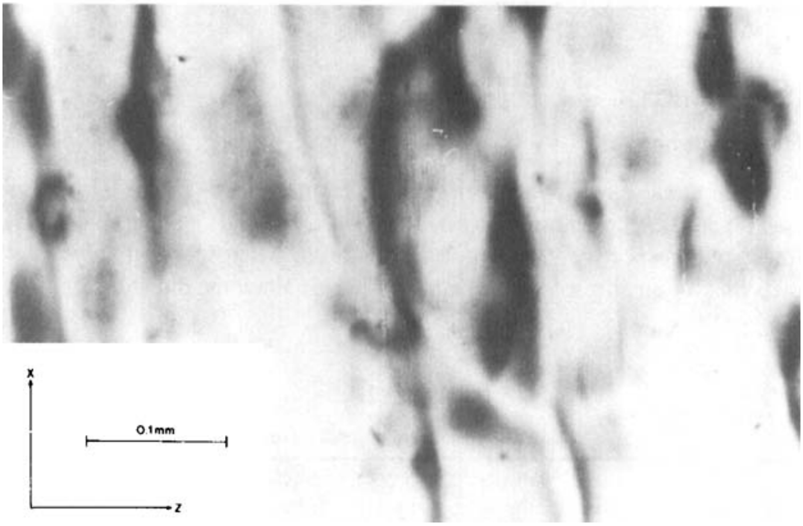
Compositions of nematogenic mixtures

Sample	Mesophase	MTABr % by wt.	MTATS % by wt.	Deconal % by wt.	NH_4Br % by wt.	^2H_2O % by wt.
I	N_D^+	14.75	16.34	3.28	8.20	57.38
II	N_D^-	28.38	—	4.05	6.76	60.81
III	N_C^+	36.00	—	—	—	64.00
IV	N_C^-	—	40.00	—	—	60.00

MTABr denotes myristyltrimethylammonium bromide (myristyl = $C_{14}H_{29}$)
MTATS denotes myristyltrimethylammonium toluene sulphonate (myristyl = $C_{14}H_{29}$)



(*a*)



(*b*)

FIGURE 2 Photomicrograph of (*a*) $N_C^{\pm}$ (sample IV) and (*b*) $N_D^{\pm}$ (sample I) nematics immediately following shear flow.

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at an angle θ, in the shear plane xy, relative to the direction of flow x given by

$$\cos 2\theta = \frac{1}{\lambda} = \frac{3S(I_{\parallel} - I_{\perp})}{2(I_{\parallel} + 2I_{\perp}) + S(I_{\parallel} - I_{\perp})} \tag{1}$$

where S is the order parameter and $I_{\parallel}$ and $I_{\perp}$ are the components of the moment of inertia in the principal axes system of the ellipsoid.

For long rod cylindrical particles ($I_{\perp} \to 0$), $\lambda^{-1} = 3S/(2) + S$) and the angle varies between $\pi/4$ (for $S = 0$) and zero (for $S = 1$). The planar texture observed for N_C materials (Figure 2a) is indicative of a homogeneous planar layer and consistent with Eq. 1 provided $S = 1$. But, for the nematogens under study here, $S < 0.8$, suggesting that surface forces assist in the alignment of the director.

For large flat disks ($I_{\parallel} \to 0$), $\lambda^{-1} = -3S/(4 - S)$ and the flow alignment angle is predicted to vary between $\pi/4$ (for $S = 0$) and $\pi/2$ (for $S = 1$). For the N_D nematogens under investigation $S < 0.5$ and the diameter of the micelles is 5–10 nm,[16] so that non-homeotropic layers are anticipated. The texture observed is shown in Figure 2b and is characteristic of all of the N_D phases we have studied. It is similar to the texture of an unaligned nematic film except that there is a distinct elongation of the pseudo-isotropic regions along the z direction which is perpendicular to the direction of flow (along x).

Surface alignment

The time evolution of the texture of an initially flow aligned sample depends upon the interaction of the nematic micelles with the surface of the glass capillary. The glass surface will be covered with at least a bilayer of adsorbed surfactant molecules so as to produce a hydrophilic surface. Neighboring cylindrical micelles will orient with their long axes parallel and disk micelles with their planes parallel to the surface. The net effect is to produce a homeotropic layer for N_D (pseudo-isotropic texture) and to leave unchanged the planar layer for N_C (birefringent texture unaffected).

Magnetic alignment

By observing the response of the nematic director to an applied magnetic field, the sign of $\Delta\chi$ can be determined. First, the magnetic field is suddenly applied along the z direction to either homeotropic layers of N_D

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phases or homogeneous planar layers of N_C phases with, in each case, the director initially along the x axis; these configurations are produced by flow alignment and annealing. For both N_D^- and N_C^- mesophases, i.e., $\Delta\chi < 0$, the effect of the magnetic field is simply to reinforce the existing alignment of the director, whilst, for N_D^+ and N_C^+ mesophases, Fréedericksz transitions with associated dynamic effects are observed.[17] Secondly, following the initial alignment of the director, the optical capillary is rotated so that its long axis lies parallel to the z direction [alternative orientation in Figure 1a]. In this configuration, the N_D^- and N_C^+ phases are essentially unchanged when the magnetic field is turned on, whilst the N_D^+ and N_C^- phases undergo Fréedericksz transitions. This sequence of observations gives an unambiguous assignment of the sign of $\Delta\chi$.

The textures observed in conjunction with the Fréedericksz transitions are of intrinsic interest.[8,9] The effect of the field upon the N_D^+ phase is to produce a homotropic-to-planar Fréedericksz transition which in thermotropic nematics is associated with back flow phenomena which are manifest in striated textures.[17] In our experiments with sample I and with other N_D^+ mesophases, the effects of back flow as manifest by the observed textures [see Figure 3a] are relatively weak. The reason for this can be understood by examination of Eq. 3.8.3 of Ref. 17. The magnitude of the hydrodynamic term, which leads to back flow is for a homeotropic-to-planar transition determined by the coefficient.

$$\lambda'_{hp} = (\lambda_2 - \lambda_1)/2\lambda_1 \tag{2}$$

and for a planar-to-homotropic transition by the coefficient

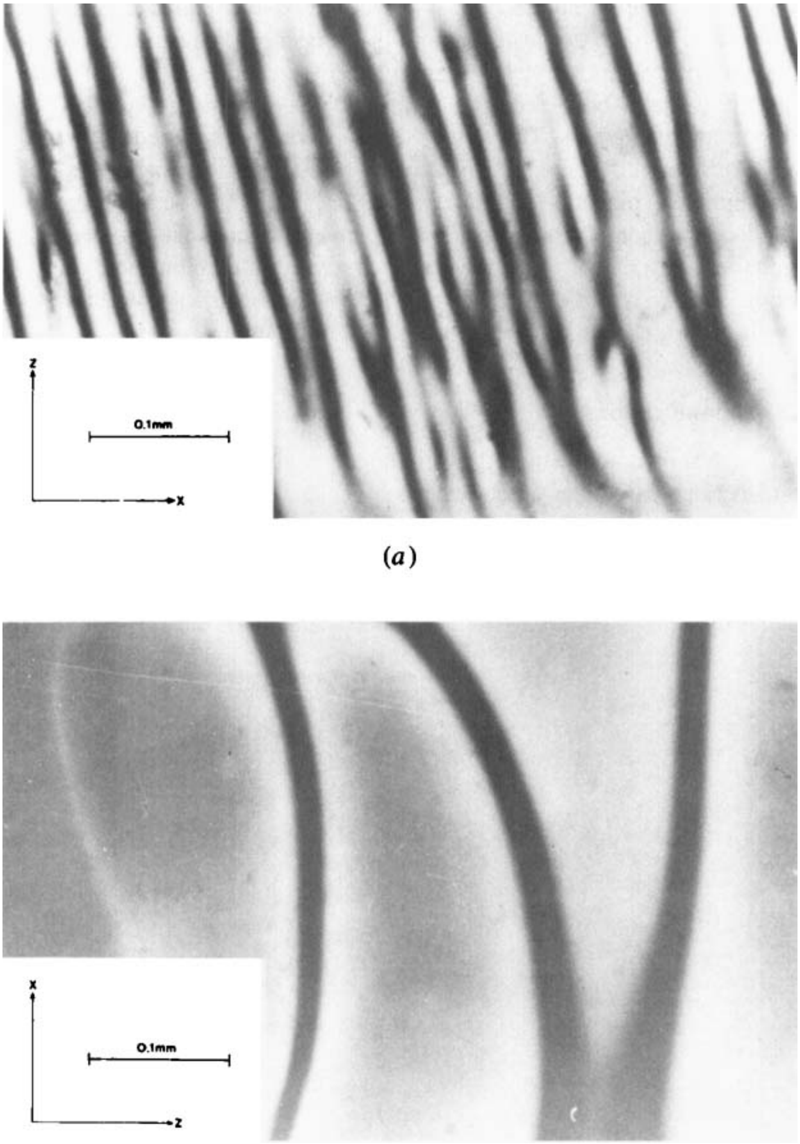
$$\lambda'_{ph} = (\lambda_2 + \lambda_1)/2\lambda_1 \,. \tag{3}$$

λ_1 and λ_2 are viscosity coefficients related by the flow alignment angle θ according to

$$\cos 2\theta = -(\lambda_1/\lambda_2) \tag{4}$$

For a mesophase of long rods, which under flow forms a well aligned planar layer, $\theta \rightarrow 0$ and $\lambda_1 \geqq -\lambda_2$. For such a mesophase Eq. 3 predicts weak back flow for a planar-to-homotropic transition, whilst Eq. 2 predicts strong back flow for a homotropic-to-planar transition. For a mesophase of disks, the opposite situation pertains, since for good flow alignment $\theta \rightarrow \pi/2$ and $\lambda_1 \leq \lambda_2$. Thus, our observations of a very weak back flow effect for sample I (N_D^+) is theoretically predicted.

For sample III (N_C^+) and IV (N_C^-) application of the magnetic field, respectively, perpendicular and parallel to the director gave rise to Fréedericksz transitions accompanied by the striated patterns of back flow as



(b)

FIGURE 3 Photomicrographs of transient textures observed for (*a*) N_C^+ (sample III) and (*b*) N_D^+ (sample I) phases on applying a magnetic field (0.47 T) along the *z* direction.

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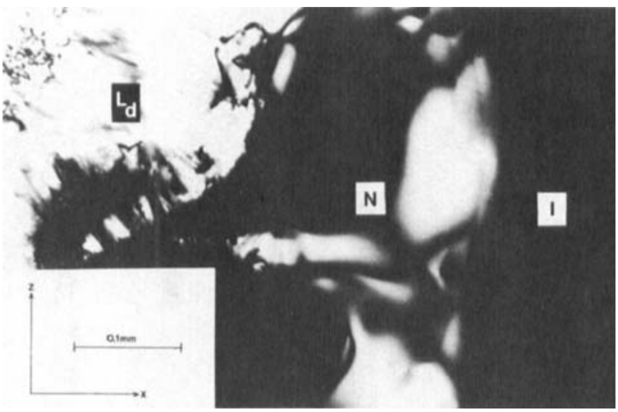
illustrated in Figure 3b. The transition for the N_C^- phase must be a mixture of both twist and planar-to-homotropic transitions, presumably a consequence of the geometry of the experiment. Well defined back flow effects have previously been reported[8,9] for N_C^+ phases undergoing planar-to-homotropic transitions. The observation of back flow for the N_C^+ phase for what is apparently a simple twist transition geometry is unexpected. There is no simple explanation for this observation, but it must be a consequence of either the geometry and/or surface alignment. In contrast to experiments with thermotropic nematics, there is no preferred (minimum energy) orientation of the director at the surface of the optical capillary and this could result in instabilities in the normal twist deformation.

Water penetration

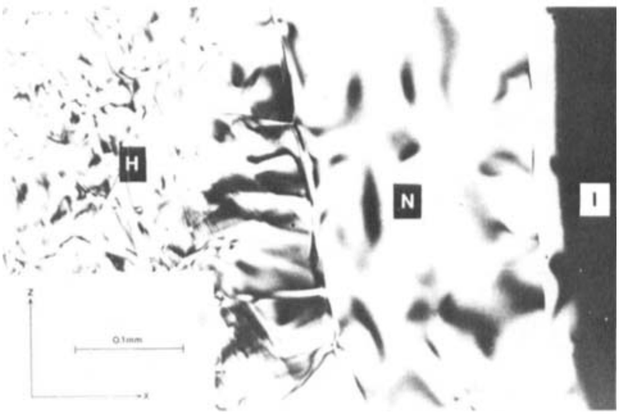
We have shown above how flow alignment combined with magnetic field effects can be used to characterize the structure and diamagnetic anisotropy of amphiphilic nematic mesophases. An alternative and often useful procedure, applicable to two component systems, is to observe the change in texture across the field of view when a concentration gradient is established either by allowing water to penetrate into a crystal of the surfactant or by



(*a*)

FIGURE 4 Photomicrographs of textures observed with concentration decreasing from left to right. (*a*) N_D^+ phase coexisting between lamellar and isotropic phases as observed for mesogen I, (*b*) as in (a), but in presence of external magnetic field, and (*c*) N_C^+ phase coexisting between hexagonal and isotropic phases of mesogen III. The effect of the magnetic field on the textures (*a*) → (*b*) enables the black areas between L_d and N in (a) to be distinguished as nematic and lamellar as shown in (b). The phases are denoted as follows: I, isotropic; N, nematic; N_p, nematic-planar layer; L_h, lamellar-homeotropic layer; L_d, lamellar-disordered layer; H, hexagonal.

(*b*)



(*c*)

FIGURE 4 (Continued)

allowing water to evaporate from the nematic phase itself. N_D phases are always found to be conjugate to lamellar phases (Figure 4a) and N_C phases conjugate to hexagonal phases (Figure 4c). The response of the texture to an external field (Figure 4b) provides the sign of the diamagnetic anisotropy; it also delineates the position of the lamellar-nematic phase boundary which is often indistinct.

Optical properties

All of the N_D phases studied to date are uniaxially positive and the N_C phases uniaxially negative. This is simply a consequence of the average

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orientation of the amphiphile being parallel to the symmetry axis of the micelle for disks and perpendicular for cylinders. Thus, measurement of the sign of the optical anisotropy provides an indication of the micellar structure.

CONCLUSION

We believe that the methods described provide a simple procedure for the unambiguous characterization of lyotropic nematics. It is, however, important to emphasize that the observed responses may not always be definitive as they depend upon the physical properties of the material which may be unfavorable. Nevertheless, with a little care and practice, and by systematically working through the procedure delineated unambiguous assignments should always be possible.

Acknowledgment

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