

would help reveal the nature of the coupling between concentration and smectic-order fluctuations in the binary mixtures.

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⁹DSC-2 is a differential scanning calorimeter produced by Perkin-Elmer Corporation.

¹⁰The arrow divides the interval between T_{sn} and T_{ni} in half, assigning half of the area to short-range smectic-*A* fluctuations and the other half to short-range isotropic fluctuations. Such a division is suggested by the broad minimum centered at the arrow.

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Rotational Viscosity of a Smectic-C Liquid-Crystalline Phase

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We report measurements of the rotational viscosity coefficient in the smectic-*C* and nematic phases of heptyloxyazoxybenzene. The measurements are interpreted in terms of a model of the smectic-*C* phase in which the molecules reorient about the normal to the smectic layers. Extrapolated to the nematic-smectic transition temperatures, the viscosity in the smectic-*C* phase is lower by a factor of 0.4 than that in the nematic phase. A reverse pretransition effect is observed in the nematic phase.

The presently accepted model of an ideal smectic-*C* liquid crystal is a structure in which the molecules are arranged in layers, and are oriented with their long axes parallel in a direction inclined at a definite angle, α , relative to the normal to the layers.¹ There is no long-range positional order within layers; thus a layer can be thought of as an oriented, two-dimensional liquid. This model implies an internal rotational degree of freedom for the molecular orientation: The molecules can reorient about an axis perpendicular to the smectic layers. In this note we report measurements of the dynamics of this motion, and show that it can be characterized by a simple rotational viscosity coefficient.

Rotational viscosity in nematic liquid crystals was measured by Tsvetkov² as early as 1939, and there has recently been renewed interest in the subject, following the formulation of the hydrodynamics of liquid crystals.^{3,4} However, it is believed that the results reported here are the

first measurement of rotational viscosity in a smectic phase.

In principle, the experimental method consists of measuring the mechanical dissipation in a liquid-crystal sample as it is slowly oscillated in a magnetic field. The setup consists of a torsional pendulum, somewhat resembling a moving-coil galvanometer. A small rectangular frame, about 50 mm long and 4 mm wide, is suspended with its long axis vertical between two thin gold ribbons, so that it can freely oscillate about that axis. The gold ribbons also serve as leads to a $1\frac{1}{2}$ -turn coil glued on the frame. The liquid-crystal sample is contained in a sealed glass tube, which fits inside the frame and with it constitutes the bob of the pendulum. The whole is placed inside a thermostatted Dewar, which in turn is in the gap of a large electromagnet. In order to avoid eddy-current damping, all the moving parts are made of insulating material, with the sole exceptions of the gold suspension

ribbons and the small-diameter resistance wire that makes up the moving coil. The coil on the bob serves both for excitation of the mechanical oscillations (by the application of well-defined current pulses when the bob passes through its equilibrium position) and for the determination of the bob motion (by the measurement of the induced voltage). Operation is under control of a dedicated PDP-8 minicomputer, which is programmed to keep track of bob position and to deliver the excitation pulses with the timing and magnitude required to maintain the oscillations at a preset amplitude. For a constant oscillation amplitude, the magnitude of the pulses is a direct measure of the damping of the system. The dissipation coefficient and frequency of the oscillations can be printed out on command, and are measured as functions of temperature and of oscillation amplitude.

Details of the experimental setup are planned for a later publication. Here we give only a few pertinent parameters: The sample reported on consisted of 0.0345 g of di-*n*-heptyloxyoxybenzene (DHAB). It was degassed by repeated freeze-thaw cycles and sealed under vacuum in a 2-mm-i.d. glass tube. The moment of inertia of the bob was 0.0267 g cm² and the oscillation period 0.92 sec. The magnetic field strength was 13.2 kOe. Temperature regulation was within 0.1°C.

An overview of the experimental results is given in Fig. 1. In the lower graph is plotted the dissipation coefficient, D , as a function of temperature. D is defined as is customary for an LC circuit:

$$D = \frac{1}{Q} = \frac{R}{\omega L}$$

$$= \frac{\text{energy dissipated in one period}}{2\pi \times \text{maximum stored energy}}$$

In the upper part of Fig. 1 is plotted the ratio of measured frequency to the frequency at 130°C. At the latter temperature the sample is in the isotropic phase, and the curves thus show the relative change in frequency due to the magnetic anisotropy of the liquid-crystalline sample.

The temperature ranges in which the different phases are stable are indicated at the top of Fig. 1. Note that the smectic-C phase will supercool easily, and that measurements were made in this supercooled state as well. In all phases measurements were made at a number of different oscillation amplitudes. In the smectic-

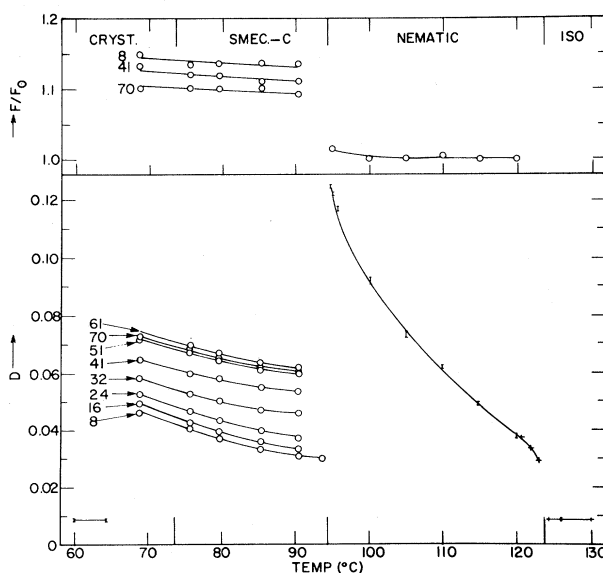


FIG. 1. Measured dissipation coefficient, D , and relative frequency, F/F_0 , as functions of temperature. The set of curves for the smectic-C phase is for different oscillation amplitudes as indicated by the numbers in degrees. The range of stability for the different phases is indicated at the top of the figure; the measurements near 69°C are in the supercooled smectic phase.

C phase both the dissipation and the frequency are amplitude dependent: The labels on the curves indicate the amplitude of the oscillations in degrees. In the other phases (crystalline, nematic, and isotropic liquid), the results were amplitude independent; the error bars on the curves indicate the maximum spread of the data for the same range of amplitudes.

In order to compare the observed dissipation behavior with that predicted from the smectic-C models, a computer program was written to calculate the dissipation and frequency as functions of the amplitude of oscillation. In setting up this calculation, we apply the following considerations:

(i) In the experiment the smectic phase was obtained by cooling from the nematic phase with the magnetic field applied. There is good evidence that the molecular alignment parallel to the magnetic field is conserved during the transition to the smectic phase.^{5,6} However, the smectic layers are inclined relative to this direction, and one obtains a polycrystalline material, in which the smectic layers have a specific inclination relative to the field direction, but are randomly distributed about this direction.

(ii) It has been shown^{5,6} that the smectic layer structure is "solid"; that is, the smectic layers, once formed, conserve their orientation when the magnetic field is rotated away from its original direction (at least for the field strengths used here).

(iii) In the present context, the "long molecular axis" must be interpreted as the major axis of the magnetic susceptibility tensor, because, in the experiment, the applied torques are magnetic in character. For short, we shall refer to this axis as the "director." In the calculation the susceptibility is assumed to be cylindrically symmetric about this axis. This is of course not required by the symmetry of the situation, and in fact a theory of the smectic-C phase has been advanced⁷ which predicts orientational order about this axis. The calculation can easily be adapted to the general case—the generalization of Eq. (1), below, is straightforward. However, the measurements reported here were done in a relatively strong magnetic field, and the deviations of the director, away from the magnetic field, remain small. Under these conditions, the results for the viscosity are nearly independent of the details of the susceptibility anisotropy.⁸

We can thus summarize the model for the smectic-C phase as follows: In a given crystallite (or domain) the director is restricted to a cone (which we shall refer to as a "domain cone") with apex angle of 2α ; the axes of the various domain cones are randomly distributed on an "alignment cone," which has its axis along the original magnetic field direction, and also has 2α as its apex angle.⁹

In setting up the equation of motion of the director, we equate the magnetic torque on the director with the viscous torque. The first can be obtained as the derivative, with respect to the director orientation, of the magnetic energy, E , per unit mass:

$$E = -\frac{1}{2} \Delta\chi H^2 \cos^2\theta, \tag{1}$$

where $\Delta\chi$ is the anisotropy of the magnetic susceptibility, per unit mass, H the magnetic field strength, and θ the angle between the director and the magnetic field direction.

The viscous torque per unit mass, Γ , is given by

$$\Gamma = (\gamma/\rho) d\xi/dt, \tag{2}$$

where γ is the rotational viscosity coefficient, ρ the density, and $d\xi/dt$ the angular velocity of the director on the domain cone. The equation of

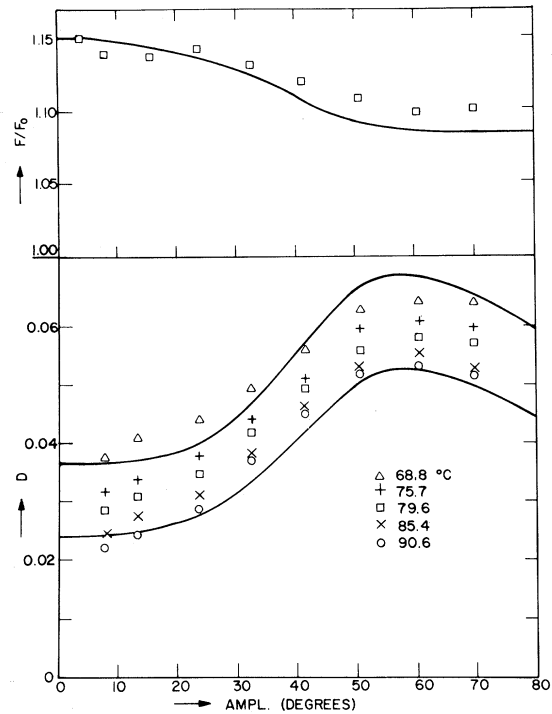


FIG. 2. The points are the data of Fig. 1 replotted as a function of oscillation amplitude. The curves are computed for the smectic-C model, as detailed in the text. Only one set of measurements for F/F_0 is drawn—the points for other temperatures are only slightly shifted vertically.

motion of the director is integrated numerically over an oscillation cycle of the pendulum, and the result summed over an isotropic distribution of domain orientations, to give the torque on the liquid crystal as function of time. Fourier analysis of this result decomposes the torque into a component which is in phase with the pendulum oscillation and one that is orthogonal to it. The first gives the change in frequency of the pendulum, and the second the dissipation due to the liquid crystal.

A comparison of calculation and observation is given in Fig. 2. It is a plot of the dissipation, D , and relative frequency, F/F_0 , as functions of oscillation amplitude at different temperatures in the smectic phase. The points give the experimental results, taken from Fig. 1 (after subtraction of the background dissipation measured in the isotropic and crystalline phases), while the solid curves give the result of the computer calculation. It should be noted that a set of two curves (for D and F/F_0) is completely determined by only three adjustable parameters: (i) the an-

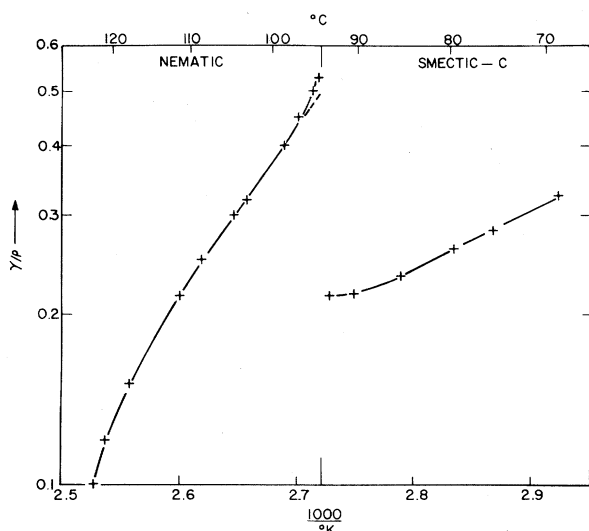


FIG. 3. Arrhenius plot of the rotational viscosity. The quantity plotted, γ/ρ , is the kinematic viscosity in cgs units, or stokes; γ is in poises and ρ is the density of the liquid crystal.

isotropy of the magnetic susceptibility ($\Delta\chi$), (ii) the inclination angle, α , between the director and the smectic planes, and (iii) the viscosity coefficient, γ . There is little interaction between the three parameters: $\Delta\chi$ is essentially determined by the deviation of F/F_0 from 1; α by the amplitude for which D is a maximum; and γ by the magnitude of D . The curves in Fig. 2 were calculated with $\Delta\chi = 9.5 \times 10^{-8}$ cgs and $\alpha = 37^\circ$; neither of these parameters depends significantly on temperature. The upper and lower curves for D are for viscosities of $\gamma/\rho = 0.320$ and 0.215 stokes, respectively. The calculated values of the relative frequency vary little with viscosity and the calculated curve for $\gamma/\rho = 0.260$ stokes is the only one given. Viscosities at the different temperatures were obtained by least-squares fits to the experimental points, and the results are given in the Arrhenius plot of Fig. 3. This figure also gives the results for the nematic phase. The most striking feature of these results is the drop in viscosity by a factor of 0.4 at the nematic-to-smectic transition. There is also a pronounced decrease in the temperature dependence of the viscosity: The activation energy characterizing this dependence drops from 54.9 J mole^{-1} for the lower temperatures of the nematic phase to 20.4 J mole^{-1} for the smectic phase. Qualitatively, the higher rotational free-

dom of the molecules in the smectic phase can be understood from their layered arrangement; within a layer cooperative rotation is largely unhindered and the main interference arises between the top of one layer and the bottom of the next, which move in opposite directions. In the nematic phase, on the other hand, a staggered position of adjacent molecules results in a blocking of their rotation.

The curves in Fig. 3 show clear pretransition effects near the smectic-nematic transition. The one in the nematic phase is notable, in that it shows an increased rate of rise in viscosity as the transition is approached, even though the measured viscosity in the smectic phase is lower than that in the nematic phase. The increase in viscosity can be ascribed to the formation of smecticlike cybotactic groups (transient clusters), which can be thought of as rotating as a whole as long as they are of small size. In the smectic-C phase, on the other hand, the smectic layers form a solid structure, and bodily rotation is blocked and does not contribute to the measured viscosity. The transition between the two cases would occur when the rotational relaxation time of the cybotactic group becomes comparable to the measuring time (in the present case the oscillation period of about 1 sec).

¹For a review see P. G. de Gennes, *The Physics of Liquid Crystals* (Clarendon Press, Oxford, England, 1974), Chap. 7.

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⁸A corollary is that the present measurements do not allow the determination of the two anisotropy parameters characterizing the general susceptibility tensor. Such a determination would be of much interest as an experimental check of the theory of Ref. 7, and may be possible by a careful study at low magnetic field strengths. This has not been attempted at this time.

⁹A sketch of this situation is given in Fig. 19 of Ref. 6.