Temperature Behavior of the Order-Parameter Invariants in the Uniaxial and Biaxial Nematic Phases of a Lyotropic Liquid Crystal

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Conoscopic observations have been made on a mixture of potassium laurate, 1-decanol, and D_2O in the discotic-uniaxial, biaxial, and cylindric-uniaxial nematic phases. The differences between the principal refractive indices have been measured, leading to a complete determination of the tensor order parameter in all the three phases. In the biaxial phase, the symmetric invariants of the order parameter are found to have a linear dependence on temperature, in good agreement with the prediction of the mean-field model.

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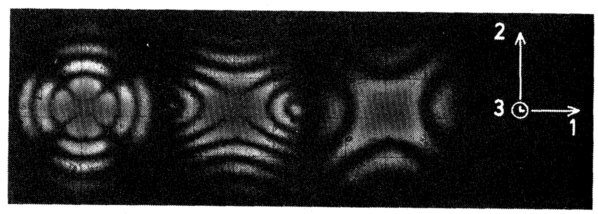
Mixtures of amphiphilic molecules having a hydrophilic head and a hydrophobic tail form, in aqueous solutions, anisotropic micellar aggregates,[1] which may orient mutually under proper temperature-concentration conditions, giving lyotropic nematic phases.[2] As expected from symmetry considerations,[3] three types of such nematics have been found.[4] Two of them are uniaxial, corresponding to different average alignments of the amphiphiles. In the discotic nematic phase, the amphiphilic molecules are statistically parallel to the optical axis, while they are normal to it in the cylindric one.[5] The biaxial nematic, on which few experimental studies have been made to date,[4,6] is an intermediate phase between the two uniaxial nematics. These nematic phases are characterized by an order parameter which is a second-rank, symmetric, traceless tensor with two different eigenvalues in the uniaxial phases and three in the biaxial one, or equivalently, by the symmetric invariants of this order parameter. Like any other second-rank tensor related to macroscopic properties, the optical dielectric tensor may be chosen as the order parameter.[7] It can be experimentally determined in each of the nematic phases from the measurement of the differences between the refractive indices, with use of conoscopy.[8] In this paper we report such a measurement which leads to what we believe to be the first determination of the two independent invariants of the order parameter in a biaxial nematic phase. We then show that their temperature variations in the biaxial range are satisfactorily accounted for by the mean-field approximation.

The studied sample, chosen from the phase diagram studied by Yu and Saupe,[4] is a mixture of potassium laurate (synthesized and carefully recrystallized in the laboratory), 1-decanol (> 99% purity from Fluka), and D_2O, in proportions 26.0/6.24/67.76 wt.%, respectively. A small amount of a ferrofluid (< 10^{-4} by weight) is added in order to help the alignment in the magnetic field.[9,10] As the temperature is incresed, the successive phases are isotropic (10.5°C), discotic-uniaxial (18°C), biaxial (20°C), cylindric-uniaxial. The compound is enclosed in a cell of 1 or 2.5 mm thickness (from Hellma), hermetically sealed to prevent concentration drifts. This condition has been properly achieved in our experiments since no drastic changes in the transition temperatures occur during the course of the experiments. The cell is placed inside a servo-controlled thermostat (of 0.02°C accuracy) which is itself held in a (horizontal) magnetic field. The field defines the 1 axis of the laboratory frame, the normal to the glass plates being the (vertical) 3 axis [Fig. 1(d)].

The orientation of the sample in the three nematic phases is achieved by a surface treatment with a silane compound[11] and repeated rotations of the cell in the magnetic field around the 3 axis.



(a) (b) (c) (d)

FIG. 1. Conoscopic patterns of a 2.5-mm-thick sample: (a) Discotic phase in the homeotropic orientation (director along the 3 axis). (b) Biaxial phase close to the discotic transition. (c) Cylindric phase in the planar orientation (director along the 1 axis). (d) Laboratory-frame axes; the 1 axis is parallel to the magnetic field and the 3 axis is perpendicular to the plates of the sample.

One obtains in this way the discotic-uniaxial phase homeotropically aligned along the 3 axis ($n_3 > n_2 = n_1$) as seen on the typical conoscopic pattern of Fig. 1(a); the biaxial nematic phase with the axes of the laboratory frame as eigendirections [$n_3 > n_2 > n_1$, Fig. 1(b)]; and the cylindric-uniaxial phase aligned along the direction of the magnetic field [$n_3 = n_2 > n_1$, Fig. 1(c)]. n_i stands for the index of refraction measured with the polarization along the i axis. The conoscopy is achieved with a He-Ne laser beam converging in the sample with a half-angle aperture of 50 deg. The interference pattern is thus very extensive, allowing for accurate measurements of birefringence (to about 10^{-5}). The positions of the interference fringes (Fig. 1) are measured at equilibrium along the 1 and 2 axes, and used in a least-squares fit which yields both the index differences $n_2 - n_1$—already measured by Saupe, Boonbrahm, and Yu[6]—and $n_3 - n_2$, which is determined here for the first time. These values are plotted in Fig. 2(a) versus temperature. As expected, one of the index differences vanishes in the uniaxial phases, while both are positive in the biaxial nematic phase. The experimental plots show that the uniaxial-biaxial phase transitions are second order within our temperature resolution (0.02 °C), and that the isotropic to discotic nematic phase change is only very weakly first order. Incidentally let us note that this is exactly the predictive criterion of Shih and Alben for the existence of a biaxial nematic phase.[3]

From the index differences, one readily derives the anisotropic part of the dielectric susceptibility tensor, at optical frequency, the diagonal elements of which are given by

$$\begin{aligned} \epsilon_{a1} &= -\frac{4\langle n\rangle}{3}\left((n_2 - n_1) + \frac{(n_3 - n_2)}{2}\right), \\ \epsilon_{a2} &= \frac{2\langle n\rangle}{3}\left((n_2 - n_1) - (n_3 - n_2)\right), \\ \epsilon_{a3} &= \frac{4\langle n\rangle}{3}\left(\frac{(n_2 - n_1)}{2} + (n_3 - n_2)\right), \end{aligned} \tag{1}$$

where $\langle n\rangle$ stands for the average index of refraction ~ 1.375. The symmetric invariants of this tensor, taken as the order parameter, may be written as[3]

$$\sigma_1 = \epsilon_{a1} + \epsilon_{a2} + \epsilon_{a3} = 0, \qquad \sigma_2 = \tfrac{2}{3}(\epsilon_{a1}^2 + \epsilon_{a2}^2 + \epsilon_{a3}^2), \quad \sigma_3 = 4\epsilon_{a1}\epsilon_{a2}\epsilon_{a3}. \tag{2}$$

σ_2 and σ_3 are independent quantities in the biaxial phase. In both uniaxial phases, they are related since the diagonal elements (1) are proportional to the usual "orientational order parameter" S.[7] The relation which connects the invariants in the uniaxial phases is therefore $\sigma_3 = \pm\sigma_2^{3/2}$, the sign being that of S: positive in the discotic phase and negative in the cylindric one. In the biaxial nematic phase, this relation reduces to the inequalities $-\sigma_2^{3/2} \leq \sigma_3 \leq \sigma_2^{3/2}$. Figures 2(b) and 3 show the variations of σ_2 and σ_3 versus temperature. The striking feature is that both have a linear dependence in the biaxial phase, instead of the more complex variations found in the index representation [Fig. 2(a)].

Let us analyze these results in terms of mean-field theory. The Landau–de Gennes expansion of the free energy in the isotropic and nematic phases[3,6,7] is written as a function of the invari-

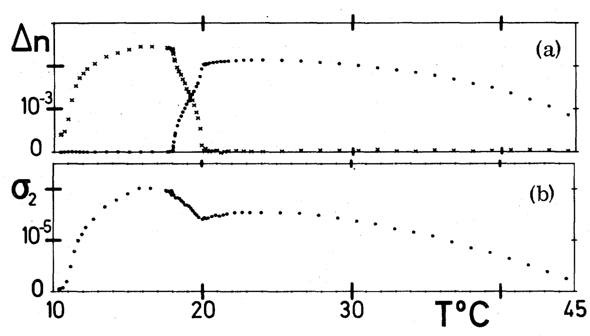


FIG. 2. (a) Index differences vs temperature in the discotic-biaxial-cylindric phases. $n_2 - n_1$ is represented by dots, and $n_3 - n_2$ by crosses. (b) Symmetric invariant σ_2 vs temperature in the three nematic phases.

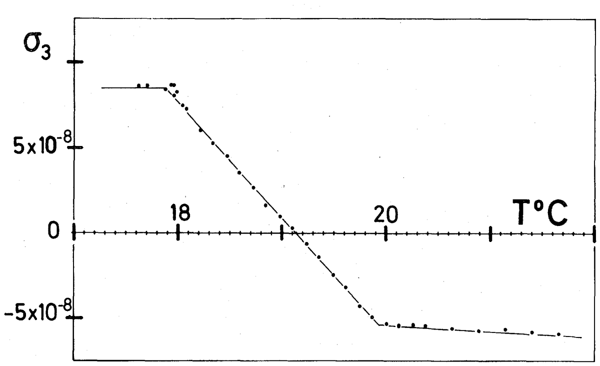


FIG. 3. Symmetric invariant σ_3 in the biaxial nematic phase. The points are mixed from two different runs of opposite temperature variations. This demonstrates reproducibility and the absence of hysteresis at the uniaxial-biaxial transitions.

ants of the order parameter:

$$G = a\sigma_2 + b\sigma_3 + \tfrac{1}{2}c\sigma_2^2 + d\sigma_2\sigma_3 + \tfrac{1}{2}e\sigma_3^2, \tag{3}$$

the coefficients being functions of temperature and concentrations, and satisfying the stability conditions $c > 0$, $e > 0$, $ce > d^2$. The absolute minimum of G is obtained at

$$\tilde{\sigma}_2 = \frac{bd - ae}{ce - d^2}; \quad \tilde{\sigma}_3 = \frac{ad - bc}{ce - d^2}. \tag{4}$$

These values of the invariants are elected if they are physically accessible, i.e., if the constraints $\sigma_2 \geq 0$ and $\sigma_3^2 \leq \sigma_2^3$ are fulfilled. The phase is then biaxial. In the uniaxial or isotropic phase, the invariants are given by the relative minimum of G, obeying the condition $\sigma_3^2 = \sigma_2^3$. The intermediate case $\tilde{\sigma}_3^2 = \tilde{\sigma}_2^3$ which can be matched continuously corresponds to a second-order uniaxial-biaxial phase transition.[12]

In the weak-coupling limit ($d \simeq 0$), $\tilde{\sigma}_3$ is proportional to the coefficient b which therefore governs the discotic-biaxial-cylindric sequence in a manner similar to the coefficient a at the isotropic to nematic phase transition.[7,13] All these features are clearly consistent with the experiments [Figs. 2(b) and 3] and justify the mean-field hypothesis. The weak-coupling assumption ($d \simeq 0$), however, is not necessary and may be released since whatever the value of d, both $\tilde{\sigma}_2$ and $\tilde{\sigma}_3$ are linear functions of a and b and therefore, of temperature. The major modification which occurs when $d \neq 0$ is that the relations $b = 0$ and $\tilde{\sigma}_3 = 0$ no longer coincide, resulting in some shift of the discotic-biaxial-cylindric sequence which will be discussed elsewhere.[10]

In summary, we determine the symmetric invariants of the order parameter along the three different lyotropic nematic phases. We find that, in the biaxial phase, their variations with respect to the temperature are linear until uniaxial phases appear at second-order transitions. These results agree quite well with the mean-field theory, in the *simplest* hypothesis that only the linear coefficients in the free energy are temperature dependent.

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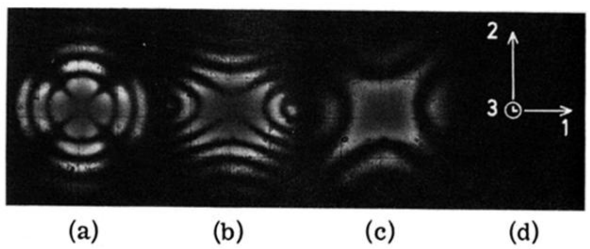

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