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Uniaxial and biaxial lyotropic nematic liquid crystals

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Experimental evidence for the existence of optically biaxial lyotropic nematics is presented. The first experimental measurements of the optical uniaxial birefringence Δn versus the temperature in a discotic nematic are reported; they show a discontinuity of Δn at the discotic-calamitic phase transition.

Some ternary lyotropic system as sodium decyl sulfate-decanol-water (SdS-Dec-H_2O) can show different mesophases and nematic phases.[1] The micellar aggregates that form such nematic phases can take different shapes.

Following the different structural anisotropy of the aggregates two different nematic phases can be seen,[2] i.e., discotic micellae originate a discotic nematic N_D and cylindrical micellae form the ordinary calamitic phase N_C.[3]

Such structural anisotropy brings different optical properties: the calamitic nematic that has the optical axis normal to the direction of the axis of the amphiphilic molecules (parallel only to the long axis of the aggregate), shows a negative optical sign while the discotic nematic with the optical axis, parallel to the molecular axis (parallel only to the short axis of the aggregate) shows a positive optical sign.[4]

Because of the cylindrical symmetry of the system, usually both phases are uniaxial (as well as in thermotropic liquid crystals[5]). However, very recently the existence of a lyotropic nematic biaxial phase as been observed.

A. Saupe noted such a phase in the lyotropic ternary system formed by potassium laurate-decanol-water during the discotic-calamitic phase transition. It should be considered that Saupe's results were obtained in a lyotropic system different from ours; furthermore, his systems were initially not oriented.

In this paper we present the first optical observation on the thermal behavior of the birefringence, and on the optical sign of oriented samples of a lyotropic liquid-crystal system formed by SdS-Dec-H_2O.

By following the ternary phase diagram presented by Charvolin *et al.*[1]various samples were prepared at constant water content C: $C_{H_2O} = 57$ wt.% according to that diagram: by varying the SdS concentration (from 35.5 to 38 wt.%) and decanol (7.5 to 5 wt.%) a calamitic or discotic nematic was obtained.

In order to have a good homogenization of the components [SdS was of commercial origin (Merck, 99% pure) as was the alcohol (Fluka, 99% pure)] they were heated up to 40 °C to prevent hydrolysis of SdS, and submitted to at least 1 h of ultrasonic sonication. The mixtures were kept in a closed cuvette at a constant temperature of 23 °C; in such conditions they do not change their properties for at least one month.

Our samples were oriented either homeotropically or planarly by appropriate treatments of the surface of the supporting glasses with silane polymeric solutions (ODS-E in the first case and MAP-E in the second one, both supplied by Chisso Corp.)

The samples were sealed with araldite glue to avoid variation of concentration due to the water evaporation, and they were thermoregulated in a electric oven within 1 °C for several hours. Orthoscopic and conoscopic observations were made by a polarizing microscope (Zeiss).

A first analysis of the textures, orthoscopically observed, permits us to build up the temperature-concentration diagram of Fig. 1. There exists two nematic phases that show similar but distinguishable textures.

Figure 1 also shows that in a small concentration range a discotic-calamitic phase transition is possible by increasing the temperature.

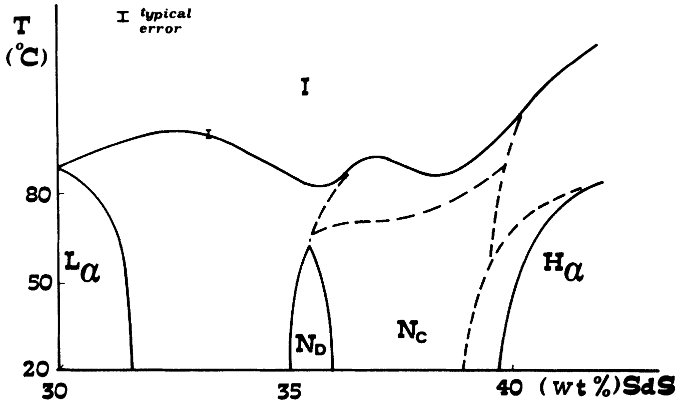

FIG. 1 Phase diagram, as deduced from microscopic observations in function of the SdS concentration. The water concentration is constant (57% in weight). L_α is the lamellar phase, H_α the hexagonal one. The discotic nematic is N_D and the calamitic N_C, I is isotropic phase. The other regions are areas of different phases coexistence.

In conoscopic vision, for both nematic phases, the typical interference picture of uniaxial material is noted: a cross showing an homeotropic orientation of the sample heated in both phases. The uniaxial cross opens and creates, within a narrow band of temperature (10 °C at 36.1 wt. % of SdS, 5 °C at 35.9 wt. %), two hyperbolas. This is characteristic of a biaxial phase. By using a phase compensator (first-order red) it is observed that the nematic at higher temperature (N_C) is optically negative and that at lower temperature (N_D) is positive with a birefringence of $\Delta n \sim 10^{-3}$ in both cases. Because of the small value of Δn it is possible to measure it directly using an Abbe refractometer.

Also in this case the samples were oriented as the prisms had been previously coated with the polymers. Thus $n_0, n_e, \Delta n$, and the averaged refractive index $\bar{n}$ in the experimental apparatus were measured.

In Fig. 2 we report the average index $\bar{n}$ behavior versus the temperature: $\bar{n}$ varies regularly versus the temperature. $\bar{n}$ is reported because the definitions of the uniaxial magnitudes n_0, n_e, and Δn in the biaxial range are no longer valid, and we should define three refractive indices and two birefringence values. Optically at the Abbe refractometer, in this region, various bands, broadened and confused, had been found; the possible error on $\bar{n}$ in this region is greater, but with our accuracy no discontinuity is visible. The results of Fig. 3 were obtained via conoscopic analysis and the modulus of the uniaxial birefringence from Abbe refractometer. It can be seen that the uniaxial birefringence shows a discontinuity when passing from the positive to the negative nematic. The band delimited by drawn lines corresponds to the region where a biaxial-like phase is present: we still measure a birefringence, but do not report it in the same graphics because of the

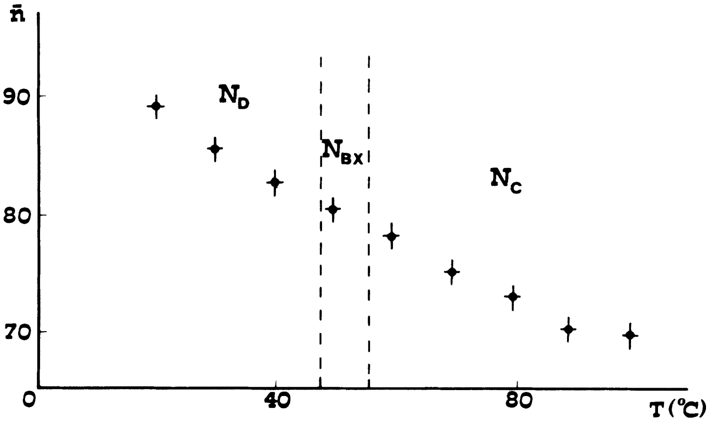

FIG. 2. The average refractive index for a concentration of 35.8 wt. % of sodiumdecysulfate versus the temperature.

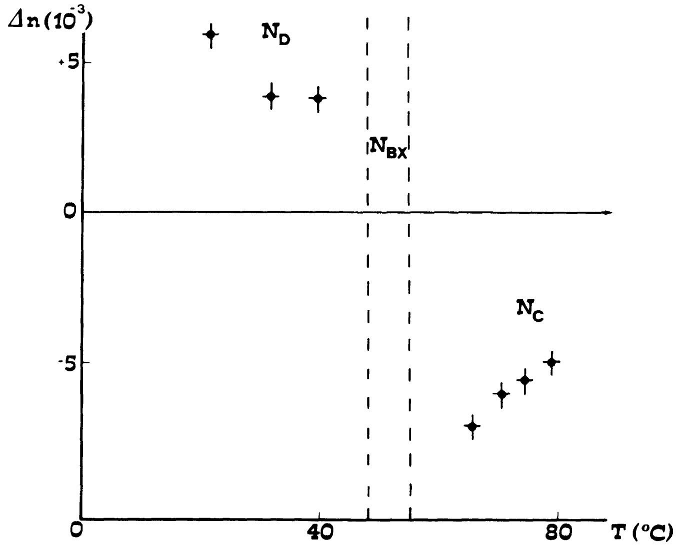

FIG. 3. The behavior of the uniaxial birefringence versus the temperature for the sample of Fig. 2.

previous discussion on the uniaxial and biaxial birefringences. A synthesis of the optical appearance of the studied nematics is drawn in Fig. 4, where the phase diagram of Fig. 1 is enhanced in concentration so as to show the biaxial phase location.

The existence of a biaxial phase bounded between two uniaxial phases with opposite optical sign has been discussed by Alben.[7,8]

Following generally a Landau model, he supposed that the phase transition between two uniaxial phases having opposite sign should have been of the first order. In addition, he made the supposition that between the two phases of an intermediate biaxial phase having a second-order phase transition with the neighboring phases.

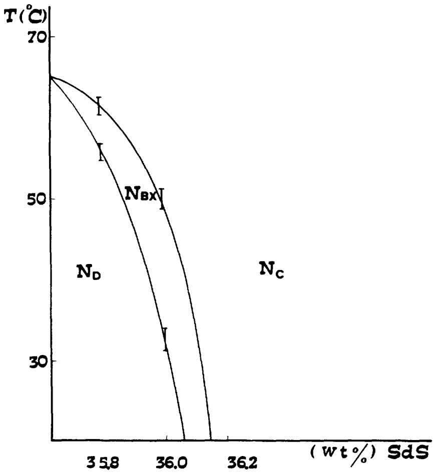

FIG. 4. Enlarged phase diagram of Fig. 1, a biaxial nematic N_B is also visible between the discotic and the calamitic nematic.

Thus, following such a model, the second-order tensorial properties that characterize the uniaxial[9] phases should present some discontinuities of the order parameter as well as of the optical anisotropy, when we pass from a uniaxial phase of one sign to that of the other kind.

A. Saupe[6] observed also a nematic biaxial phase between two uniaxial phases. We confirm such a phenomenon and we have the first experimental evidence for the transition behavior of the birefringence.

We present a qualitative molecular model, in order to explain, on the basis of our results, how a discotic—calamitic phase transition takes place. The principal point as seen in our arrangement is that the optical axis remains homeotropic.

We propose that the disks fluctuate with the increase of the temperature, and they tend to aggregate along the optical axis (this may be due to steric effects). In this way the aggregate could become fully anisotropic (and then optically biaxial).

When the aggregate is long enough, the shape becomes nearly calamitic, with the orientation still homeotropic, and the system is again uniaxial; otherwise the conoscopic image should move where the aggregates rotate. However, we do not see such an effect.

A remarkable improvement for the model should come from measurement by x-ray diffraction or nuclear magnetic resonance. The application of x-ray diffraction to these samples is in progress, as also are optical observations of the biaxiality.

We end with a few summary remarks: We confirm with direct optical measurements the existence of a biaxial lyotropic nematic in between two uniaxial nematics. Passing from a positive discotic phase to a negative calamitic one the uniaxial birefringence would have a discontinuity. The phase transition between the uniaxial and biaxial phases should be second order, following a Landau model.

First evidence, such as the refractive-index behavior, are consistent with this picture and our aim is to confirm it.

We thank Professor A. Saupe for providing us copies of unpublished manuscripts and Dr. J. Charvolin for stimulating and clarifying discussion.

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