Liquid Crystals

First-order transition between nematic phases in lyotropic liquid crystals

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First-order transition between nematic phases in lyotropic liquid crystals

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Experimental evidence for the existence of a first order transition between N_c–N_d uniaxial lyonematic phases as a function of the variable M_d (number of decanol molecules per amphiphilic molecule) is reported. The relevance of this evidence to molecular models for micellar aggregates is discussed. The evidence is for a change in micellar symmetry at this transition.

Since the discovery of biaxial [1] nematic lyomesophases N_b the conditions for the occurrence of direct first order transitions between the two uniaxial phases N_c and N_d have not been cleared up. In the original paper [1] on the biaxial phase in the potassium laurate (KL) system it was mentioned that in the system with sodium decylsulphate (SDS) a N_b phase was formed in a certain concentration range while observations in other ranges indicated a direct first order N_c–N_d transition. An earlier study in the SDS system [2] shows co-existence of N_c and N_d areas at the N_d–N_c transition on heating. However, this co-existence by texture observation is not a guarantee that the biaxial phase is absent since the possibilities of concentration and temperature gradients, as well as very narrow temperature and concentration intervals for the N_b phase, cannot easily be ruled out. Uniaxial–biaxial transitions are recognizable by irregular transient patterns in texture observation, but its lack of appearance does not assure the occurrence of a direct first order transition. The N_b phase in the SDS system was reported by some authors [3] and not found by others [4]. In detailed studies of second order transitions between biaxial and uniaxial phases [5] it was mentioned that experimentally, transitions have been observed that seem to lead directly from N_d to N_c via a first order transition. But it was not claimed that a direct first order transition was established.

This point is rather important regarding microscopic models for the micellar aggregates that constitute lyomesophases, since molecular theories that predict second order transitions were worked out for inherently biaxial objects [6]. The alternative to mixtures [7] of rods and disks leads to phase diagrams of apparently the same topology, but that might correspond in reality to spinodal [8] decomposition related to a first order phase transition. This theoretical background lead to the proposal [9] of a unique biaxial micellar form in all three nematic phases, with uniaxial phases corresponding to fluctuations about different axes of the same object. As well as this proposal is the idea that the biaxial range may shrink near a multicritical point to the isotropic I phase, but the transitions are always second order.

However, experimental evidence for the proposal of a unique micellar form has been questioned [10], and the conventional idea of different micellar symmetries

in the uniaxial N_c (cylindrical micelles) and N_d (discotic micelles) phases has strong experimental basis and theoretical support, since the curvature of the hydrocarbon/water interface is a critical parameter defining lyotropic structures [11]. Bicontinuous cubic structures occurring between hexagonal (curved interface) and lamellar (planar interface) phases have also the curvature of the lipid monolayer as a critical parameter [12]. It became important therefore to search for defined experimental evidence for the existence of a first-order transition, related most probably to a change in symmetry of the micellar object.

A recent investigation [13] of the nematic domain in the system sodium dodecyl (lauril) sulphate (SLS)/water/decanol brought evidence for the existence of N_c-N_d phases in equilibrium and for the existence of a sharp transition as a function of the parameter M_d (relative molar ratio, giving the number of decanol molecules per amphiphilic molecule). A threshold value $M_d = 0.38 \pm 0.01$ exists, with N_c phases for lower values and N_d phases for higher values. At the threshold N_c-N_d phases in equilibrium were observed.

The evidence could not be considered conclusive regarding the existence of a first order transition, however, because phase diagrams were obtained by texture observations with polarized optical microscopy (OM), which do not discriminate between N_c and N_b phases. So one could not completely exclude the existence of an intermediate biaxial phase within a small concentration gradient.

To clear up this point the present investigation was undertaken using OM and a facility for temperature variation in both orthoscopic and conoscopic geometry. A sample with composition 24.74 per cent SLS/5.16 per cent decanol/70.10 per cent H_2O (M_d value very near the threshold) was observed in a flat microslide of 0.2 mm inner thickness. At room temperature (22.0 ± 0.5)°C the sample showed N_c and N_d regions well aligned by the surface and with a defined boundary, which stayed stable for days; an example is shown in the photomicrograph of the figure. No gradient of temperature existed in the sample and there was no obvious concentration gradient. In conoscopic geometry the N_d homeotropic region was optically uniaxial positive with a very well defined uniaxial cross and no evidence of biaxiality was seen when crossing the boundary to the planar N_c region. It should be remarked that it is not possible to discriminate between N_c and N_b phases by the usual OM observations, but that a continuous transition from N_d to N_b should be sensed in conoscopy by the appearance of biaxiality just at the boundary (N_b phases usually have one axis perpendicular to the surface [5]). The boundary has been carefully crossed several times at different scanning speeds and in several places without sign of biaxiality. Furthermore, under rotation of the stage, the planar N_c texture changed colour and presented a position of complete extinction (not to be expected for a N_b phase with the two axes in the plane). It can therefore be concluded that there is a real discontinuity at the boundary and a first order transition between the two phases in equilibrium.

It is not possible to rule out from these observations the possibility of a N_d-N_b first order transition, since the discrimination between N_b and N_c phases is difficult. However, uniaxial–biaxial first order transitions have neither been experimentally observed before nor predicted theoretically, even in theories [14] that consider more complex order parameters. It is therefore possible to conclude that this represents a first-order N_d-N_c transition, as predicted from Landau theory [8].

Upon heating, the N_d homeotropic region showed a reversible transition to a N_c phase at 27°C; the eventual occurrence of a biaxial phase at this transition with
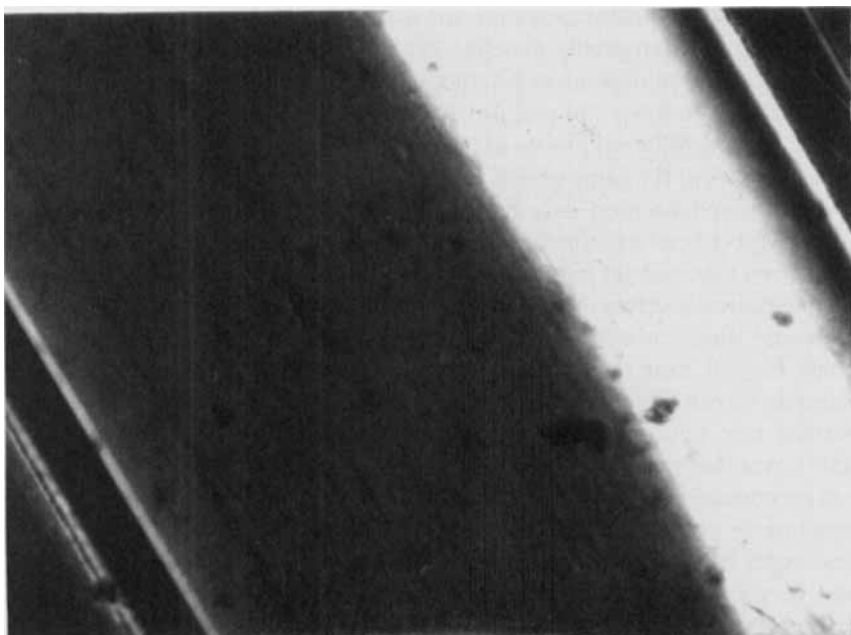
Figure 1. Photomicrograph showing the coexistence of N_d and N_c phases in equilibrium at room temperature. N_d has homeotropic black texture and is optically uniaxial positive. N_c has clear planar texture. Capillary width is 2·5 mm.

temperature could not be ruled out. The previous N_c–N_d boundary remained as a defect in the planar N_c texture at higher temperatures; the previous N_d region did not become homogeneously planar, but showed texture because of the different director directions in the plane of the surface. Conoscopic observation did not show any sign of biaxiality over the whole sample field. The sample remained in good condition for more than a month.

There is therefore evidence that, at least as a function of concentration (variable M_d), the N_c–N_d transition can be first order in this system. The N_c and N_d phases in equilibrium must therefore correspond to slightly different values of the cross-over point [13] $M_d = 0\cdot38 \pm 0\cdot01$.

This means that the conventional picture of cylindrical micellar symmetry in N_c phases and discotic micellar symmetry in N_d phases may be kept (even if micellar cross sections might be noncircular and small fractions of one form might be present in the phase where the other form dominates). The effect of decanol addition in changing the micellar form has been cleared up by theoretical studies [15] showing that the cosurfactant molecules are preferentially partitioned into the lower curvature micellar regions. Such anisotropy of decanol distribution has been observed also experimentally [16]. All evidence is therefore in favour of changes in micellar form, that may occur in a continuous or discontinuous way.

It should be stressed that the theoretical molecular models based on bricks do not really explain the phase transitions observed in lyonematics. Such theories predict [17] that an object with a given deviation from axial symmetry could change from an uniaxial to a biaxial phase with temperature, but not so easily to an uniaxial phase

with opposed sign. The phase diagram proposed by Alben for biaxial objects [6] allows for $I-N_c-N_b-N_d$ transitions only for a very particular cross over region, for particles that are just marginally platelike in their excluded volume interaction, but including an orientation dependent interaction energy which favours rod-like order. One could still try to keep the picture of a very particular biaxial form near the threshold M_d, giving different phases as a function of temperature due to fluctuations about different axes of the same object. It is however difficult to reconcile this picture with the first order transition as a function of M_d. It should be stressed also that biaxial phases have been obtained in thermotropic systems [18], but no inversion of axiality has been reported yet in thermotropic phases made up of a single constituent.

For lyonematics, it seems therefore to be really necessary to take into account the deformable and transient nature of the micelles, a point already stressed by Gelbart [19]. It may be that near the threshold M_d, temperature induced changes in chain length, already shown [20] to be a possible explanation for re-entrant behaviour, play an important role (although this process could not so easily invert the micellar anisometry). Another possible model has been proposed [10] but it does not yet have enough experimental and theoretical support.

In conclusion, predictions from Landau theory [8] allow possibilities of either a direct first order transition or second order transitions with an intermediate biaxial phase, but they give no information on the microscopic level. Experimentally, there is clear evidence for a first order transition at least as a function of concentration and second order transitions as a function of temperature. There are not yet molecular theories that account for all observed experimental evidence in lyonematics. The characteristics of self-assembly in lyotropic systems is in fact fundamental, and the most common phase transitions in lyotropics (isotropic–hexagonal and hexagonal–lamellar) have no equivalence among thermotropics.

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