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## Liquid Crystals

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### Study of the reciprocal space image of the biaxial nematic phase in the plane of the amphiphilic bilayer

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## Study of the reciprocal space image of the biaxial nematic phase in the plane of the amphiphilic bilayer

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High resolution synchrotron X-ray measurements have been performed on the uniaxial and biaxial phases of the lyotropic mixture potassium laurate, decanol and water. An elegant magnetic orientational procedure allows us to obtain the cut of the reciprocal space image of the biaxial phase at the plane perpendicular to the amphiphilic bilayer. The analysis of densitometric profiles of the diffracted bands indicate an anisotropic micellar correlation in the plane of the amphiphilic bilayer. It is suggested that an anisotropic distribution of decanol and potassium laurate in this plane could be responsible for this effect.

### 1. Introduction

Mixtures of two types of amphiphilic molecules and a solvent can exhibit three types of nematic phase [1,2] depending upon the temperature and relative concentrations. Two of these are uniaxial and a third one is biaxial ( $N_B$ ). The uniaxial phases have been further classified [3] as calamitic ( $N_C$ ) and discotic ( $N_D$ ), according to whether the director  $\mathbf{n}$  orients parallel or perpendicular to the magnetic field ( $H$ ) respectively.

In previous work [4,5], high resolution X-ray measurements have been performed to study the three nematic phases of lyotropic mixtures. The diffraction patterns obtained were shown to be consistent with the model of similar micelles in the three nematic phases. In this picture, the micelles do not suddenly change their shape on undergoing uniaxial to biaxial phase transitions. The macroscopic symmetry of the three nematic phases are thus the macroscopic consequence of different orientational fluctuations of the micelles. These orientational fluctuations being full rotations around the director in the uniaxial nematic phases, and only small amplitude oscillations in the biaxial nematic phase. This scheme is also compatible with the fact that the uniaxial to biaxial transitions are second order [6] with correlation length always larger than the micellar size [7].

It is important to note that while many authors use the picture of discs and rod-like micelles for lyotropic nematics, there is not any direct experimental evidence of these

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shapes for the micelles. The picture of discs and rods was proposed for the first time by Reeves and co-workers [8] on the basis of NMR measurements and considerations of the anisotropy of diamagnetic susceptibility of the phases. The first X-ray diffraction patterns [9] obtained with the uniaxial phases were then interpreted assuming a static configuration, neglecting the possible orientational fluctuations of the micelles. At that time [2], the  $N_B$  phase had not been observed.

In this paper, we present new measurements of X-ray diffraction patterns of the  $N_B$  phase obtained with a high resolution synchrotron source. A new cut of the reciprocal space, not previously obtained is presented and the analysis of the densitometric profiles of the diffraction bands is made on the basis of the intrinsic biaxial micelles model.

## 2. Experimental

The lyotropic sample investigated in this experiment was a mixture of potassium laurate (26.50 wt%), 1-decanol (6.68 wt%) and  $D_2O$  (66.82 wt%). A small quantity of ferrofluid (about  $10^{10}$  grains  $cm^{-3}$ ) was added in order to increase the nematic coupling to the external magnetic field [10], without modifying the other physical properties of the nematic phase [11]. The samples were sealed in Lindemann glass capillaries of 1.5 mm diameter and were placed in a temperature controlled device with an accuracy of 0.2°C. The capillary axis is vertical (transmission geometry) and perpendicular to the X-ray beam. X-ray diffraction patterns were obtained by a photographic method. X-ray monochromatic radiation (Ge (111) crystal,  $\lambda = 1.66 \text{ \AA}$ ) produced by the synchrotron at Orsay (Laboratoire pour l'Utilisation du Rayonnement Electromagnétique-LURE) was used.

A critical point in structural studies by X-ray diffraction experiments is to keep the sample well-oriented during the experiments. The laboratory frame is defined as follows. The  $z$  axis coincides with the (vertical) capillary axis and the X-ray beam is along the  $y$  axis. The samples are homogeneously oriented by a combination of two magnetic fields:  $H_x = 1 \text{ kG}$  along the  $x$  axis (static) and  $H_z \sim 150 \text{ G}$  along the  $z$  axis, each applied every 10 s for about 3 s. The field  $H_x$  is obtained from two permanent magnets fixed in the experimental device. The field  $H_z$  is also obtained from permanent magnets which rotate around an axis parallel to the  $y$  axis. When  $H_z$  is applied, the total field ( $H = H_x + H_z$ ) also lies in the  $xz$  plane, in a direction of about  $\pm 10^\circ$  to the  $x$  axis. This experimental procedure is applied before and during the X-ray exposure. In this condition, a  $N_D$  phase orients with  $\mathbf{n}$  parallel to the  $y$  axis and the  $N_B$  phase with the symmetry axes (directors) along the  $xyz$  axes. The exposure times are about 10 h. The experimental resolutions,  $\Delta q$  [12], of the set up are  $9 \times 10^{-4}$  and  $1.5 \times 10^{-3} \text{ \AA}^{-1}$  along the  $z$  axis and the  $x$  axis, respectively.

In order to test the existence of the three nematic phases, optical birefringence ( $\delta n$ ) measurements have been performed with a Leitz orthoplan-pol microscope with a calcite compensator. The sample was sealed in flat glass microslides (100  $\mu\text{m}$  thick) and placed in a temperature controlled device with an accuracy of 0.2°C. Well-oriented  $N_D$  and  $N_B$  phases were obtained combining the surface alignment with a magnetic field. A magnetic field ( $\sim 300 \text{ G}$ ) is placed in the horizontal direction. With this orientational procedure, the  $N_D$  phase is oriented with the director  $\mathbf{n}$  in the vertical direction. The birefringence measured ( $\delta n$ ) is the difference between the refractive indices in the orthogonal direction of the horizontal plane.

### 3. Results and discussion

Figure 1 shows the values of  $\delta n$  as a function of the temperature. The  $N_B$  phase is observed in the temperature range of  $14.6^\circ\text{C} < T < 20.6^\circ\text{C}$ .

To check the orientational procedure in the X-ray diffraction experiment we studied the reciprocal space image of the  $N_D$  phase at  $T = 14^\circ\text{C}$ . Figure 2(a), sketched in figure 2(c), shows the diffraction pattern of the  $N_D$  phase with  $\mathbf{n}$  oriented parallel to the  $z$  axis. The  $a$  and  $b$  bands of the pseudo-lamellar structure along the  $z$  axis are present as is the  $c$  band along the  $x$  axis. When the orientational procedure is applied,  $\mathbf{n}$  orients along the  $y$  axis (i.e. parallel to the X-ray beam). Figure 2(b) shows the reciprocal space image of the  $N_D$  phase in this condition. Only the  $c$  band is visible, isotropically positioned around the direction of  $\mathbf{n}$ . The inexistence of the  $a$  and  $b$  bands in this cut of the reciprocal space assures the good quality of the alignment.

Figure 3 shows the reciprocal space image of the  $N_B$  phase ( $T = 18.6^\circ\text{C}$ ). The absence of the  $a$  and  $b$  bands indicate that the X-ray beam is oriented perpendicularly to the plane of the amphiphilic bilayers of the micelles. As discussed in [4], the reciprocal space image of the  $N_B$  phase is a hollow barrel with an elliptical section. To our knowledge, figure 3 is the first experimentally obtained cut of the  $N_B$  reciprocal image in a plane perpendicular to the axis of the barrel.

Figure 4 shows the densitometric profiles of the bands along the  $z$  (see figure 4(a)—named  $c_z$ ), and  $x$  (see fig. 4(b)—named  $c_x$ ) axes, respectively. The scattering wave number [12]  $s$  and the spacing distances  $s^{-1}$  of the bands  $c_z$  and  $c_x$  are  $1.27 \times 10^{-2} \text{ \AA}^{-1}$  and  $78 \text{ \AA}$  and  $1.03 \times 10^{-2} \text{ \AA}^{-1}$  and  $97.1 \text{ \AA}$ , respectively. The spacing distance produced by the pseudo-lamellar ordering of the amphiphilic double layers of the micelles ( $a$  band) is  $48.8 \text{ \AA}$ . The  $c$  bands are wide and dissymmetrical. The width at half-height allows us to evaluate the mean correlation distance [13] between the micelles along the  $x$  and  $z$  axes (i.e. under our experimental conditions, in the plane of the amphiphilic bilayer):  $\xi_x \approx 70 \text{ \AA}$  and  $\xi_z \approx 130 \text{ \AA}$ , respectively. The shape anisotropy of the available

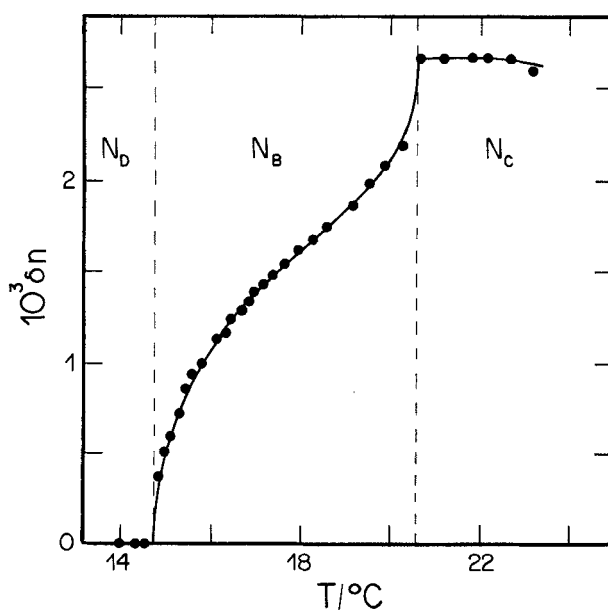


Figure 1. Optical birefringence  $\delta n$  as a function of the temperature.

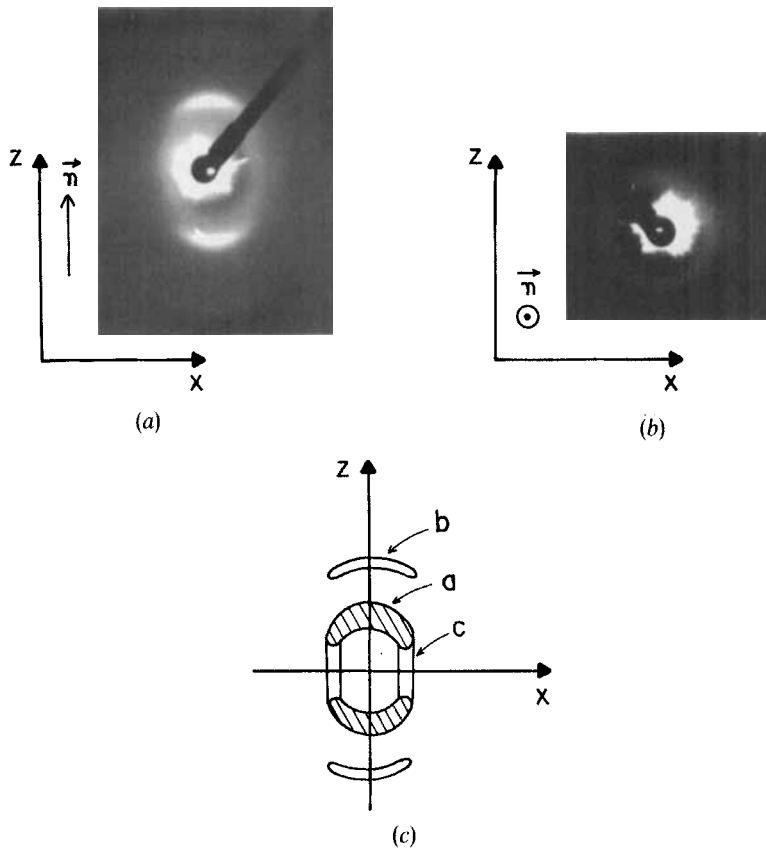


Figure 2. X-ray diffraction pattern of a discotic nematic phase  $N_D$  at  $T = 14^\circ\text{C}$ . The  $b$  band is very weak. (a) The director  $\mathbf{n}$  is oriented parallel to the  $z$  axis. (b) the director  $\mathbf{n}$  is oriented parallel to the  $y$  axis. (c) Sketch of the X-ray diffraction pattern of figure 2(a).

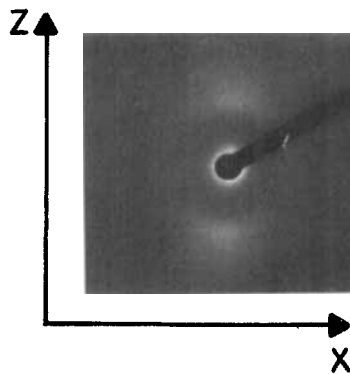


Figure 3. X-ray diffraction pattern of a biaxial nematic phase ( $N_B$ ) at  $T = 18.6^\circ\text{C}$ . The X-ray beam is perpendicular to the amphiphilic bilayer plane.

volume per micelle is about  $(1/1.6/2)$  at this particular temperature of the nematic biaxial phase. To evaluate the average micellar dimensions we assume that the water equally covers the surface of the micelles [3, 5]. The potassium laurate double layer,  $c'$  [5, 14], is about  $26 \text{ \AA}$  thick. With these considerations, we obtain the micellar dimensions in the plane of the amphiphilic bilayer:  $B' = 56 \text{ \AA}$  and  $A' = 75.1 \text{ \AA}$ . These evaluated average dimensions gives a shape anisotropy  $(1/2 \cdot 2/2 \cdot 9)$ .  $A'$  differs from  $B'$  by about 30%. The shape anisotropy obtained here is smaller than that presented in [5]. This small shape anisotropy is not enough to give nematic order, considering Onsager's theory. Thus, it is necessary to consider other interactions, other than the excluded volume, to explain the existence of the nematic order in lyotropics. We suggest that collective interactions between micelles could be responsible for an increase in the effective anisotropy to give a biaxial macroscopic symmetry.

An important point that arises from the analysis of figure 4 is the difference of the diffracted maximum intensity and the width at half-height of the bands  $c_x$  and  $c_z$ ; the intensity of  $c_z$  is about six times bigger than the  $c_x$  intensity and the width of  $c_x$  is about 1.7 times bigger than the  $c_z$  width. These experimental results lead to puzzling questions, from the microscopic point of view, as to the organization of the micelles to give a biaxial nematic phase. To discuss this aspect it is necessary to analyse in more detail the scattered intensity  $I_s$ .  $I_s$  can be written essentially as [13] the product of the interference function of the correlation volume multiplied by the square of the micellar form factor. In the case of large correlation volumes, essentially the interference function defines the position and width of the band. In the case of small correlation volumes (not much larger than the micellar dimensions), both functions (interference and form factor) must be considered. The evaluated mean correlation distances  $\xi_x$  and

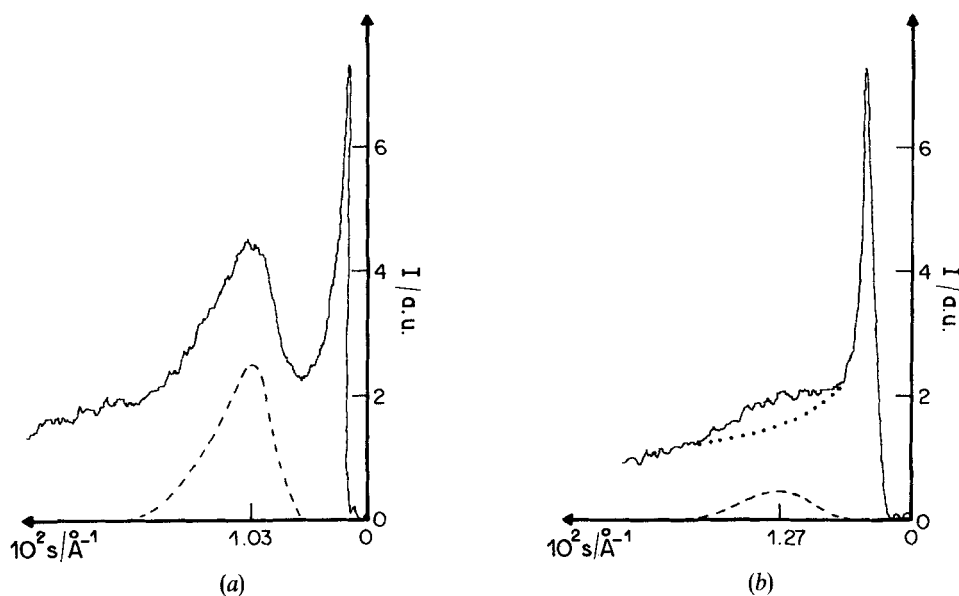


Figure 4. Densitometric profiles (solid lines) of the diffraction bands of figure 3. The sharp peaks at small values of  $s$  are due to small angle X-ray scattering cut by the beam stopper. The dashed lines are the diffraction bands, from small angle scattering, the background and diffuse scattering being removed. The intensity is in arbitrary units. (a) Along the  $z$  axis. (b) Along the  $x$  axis. (Dotted line denotes the base line.)

$\xi_y$  compare (though naturally larger) to the average micellar dimensions  $B'$  and  $A'$ , respectively. Under these conditions both functions must be taken into account. A possible source of anisotropy of these functions in the plane of the amphiphilic bilayer is the distribution of decanol and potassium laurate on the micellar surface. Neutron scattering studies [15] show that the alcohol concentrates at the flat core of the micelle rather than at the high-curvature rim. In the intrinsic biaxial micelles model [4, 5] we also expect different curvatures of the micellar borders in the plane of the amphiphilic bilayer (i.e. the micellar side  $A'C'$  should be flatter than the  $B'C'$  side). In this picture, the decanol molecules would concentrate at the flattest border ( $A'C'$ ). This anisotropic distribution of alcohol in the  $xz$  plane could be responsible for modifications of the form factor of the micelles in this plane. Thus the interference function could be modified by this effect since the concentration of  $H_3O^+$  (from decanol) and  $K^+$  (from potassium laurate) in the electric double layer [16] of the micelles along the  $x$  and  $z$  axes would be different. In consequence, since the  $H_3O^+$  ion provides a stronger attraction than  $K^+$  in the electric double layer, the micelles are tight together with an intermediate strength along their long side ( $A'C'$ ) as compared to the interactions along the two other sides ( $A'B'$  and  $B'C'$ ). This mechanism would explain why the micelles are more correlated along the  $B'$  direction than the  $A'$  direction but less than the  $C'$  direction. These different correlations in the three directions are the only one effect able to explain the strong observed hierarchy in the diffracted intensities of the bands:  $c_x \ll c_z \ll a$  (i.e.  $1 < 6 \ll 100$ ). This anisotropic binding of the micelles, which arises from an anisotropic distribution of  $H_3O^+$ , would thus be a good explanation for the existence of the biaxial nematic phase.

#### 4. Conclusions

The analysis of the cut of the reciprocal space image of the biaxial nematic phase (lyotropic mixture of potassium laurate, decanol and water) in the plane of the amphiphilic bilayer indicates that:

- (i) The shape anisotropy of the micelles in this plane is small (about 30 per cent);
- (ii) The maximum diffracted intensities are strongly different along the  $x$  and  $z$  axes. We suggest that the intensity ratios are due to different correlations in the  $xz$  plane and are indicative of an anisotropic distribution of alcohol in this plane;
- (iii) The anisotropic distribution of alcohol introduces an anisotropic distribution of the electric interactions between the micelles and therefore allows for the existence of the biaxial and uniaxial nematic phases even though the micelles have a very small shape anisotropy.

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#### References

- [1] CHISTYAKOV, I. G., 1975, *Advances in Liquid Crystals*, edited by G. H. Brown (Academic Press), pp. 143–167.
- [2] YU, L. J. and SAUPE, A., 1980, *Phys. Rev. Lett.*, **45**, 1000.
- [3] HENDRIKX, Y., CHARVOLIN, J., RAWISO, M., LIEBERT, L., and HOLMES, M. C., 1983, *J. Phys. Chem.*, **87**, 399.

- [4] FIGUEIREDO NETO, A. M., GALERNE, Y., LEVELUT, A. M., and LIEBERT, L., 1985, *J. Phys. Lett., Paris* **46**, 499.
- [5] GALERNE, Y., FIGUEIREDO NETO, A. M., and LIEBERT, L., 1987, *J. chem. Phys.*, **87**, 1851.
- [6] GALERNE, Y., and MARCEROU, J. P., 1983, *Phys. Rev. Lett.*, **51**, 2109; 1985, *J. Phys., Paris*, **46**, 81.
- [7] LARCERDA SANTOS, M. B., GALERNE, Y., and DURAND, G., 1984, *Phys. Rev. Lett.*, **53**, 787; GALERNE, Y., 1988, *Molec. Crystals. liq. Crystals*, **165**, 131.
- [8] FUJIWARA, F., REEVES, L. W., SUZUKI, M., and VANIN, J. A., 1979, *Solution Chemistry of Surfactants*, Vol. 1, edited by K. L. Mittal (Plenum), pp. 63–77.
- [9] CHARVOLIN, J., LEVELUT, A. M., and SAMULSKI, E. T., 1979, *J. Phys. Lett., Paris*, **40**, 587.
- [10] BROCHARD, F., and DE GENNES, P. G., 1970, *J. Phys., Paris*, **31**, 691.
- [11] FIGUEIREDO NETO, A. M., LEVELUT, A. M., LIEBERT, L., and GALERNE, Y., 1985 *Molec. Crystals. Liq. Crystals*, **129**, 191.
- [12]  $\Delta q = 2\Delta s$ , where  $s = (2 \sin \theta)/\lambda$  and  $2\theta$  is the scattering angle.
- [13] The mean correlation distance  $\zeta$  from Scherrer's definition is equal to the usual correlation length multiplied by  $\pi$ ; see GUINIER, A., 1956, *Theorie et Technique de la Radio-cristallographie* (Dunod), p. 462.
- [14] LUZZATI, V. MUSTECCHI, H., SKOULIOS, A., and HUSSON, F. R., 1960, *Acta crystallogr.*, **13**, 660.
- [15] HENDRIKX, Y., CHARVOLIN, J., and RAWISO, M., 1984, *J. Colloid Interface Sci.*, **100**, 597.
- [16] VERWEY, E. J. W., and OVERBEEK, J. T. G., 1948, *Theory of the Stability of Lyotropic Colloids* (Elsevier), pp. 1–63.