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Temperature-concentration behaviour of the order parameter in the nematic phases of a lyotropic liquid crystal

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Résumé. — Les variations en fonction de la température des invariants du paramètre d'ordre sont mesurées dans les phases nématiques uniaxes et biaxes de différents mélanges de laurate de potassium, 1-decanol, D_2O . Elles montrent que les transitions de phase nématique uniaxe-biaxe sont du second ordre et de champ moyen, y compris dans le cas de la concentration réentrante qui donne la séquence nématique discotique-biaxe-discotique en température croissante.

Abstract. — The temperature variations of the order parameter invariants are measured in the uniaxial and biaxial nematic phases of different mixtures of potassium laurate, 1-decanol, D_2O . They show that the uniaxial to biaxial nematic phase transitions are second-order and mean-field, including in the case of the reentrant concentration, which gives the sequence discotic-biaxial-discotic of nematic phases when increasing temperature.

Mixtures in aqueous solutions, of amphiphilic molecules having a hydrophilic head and a hydrophobic tail may form anisotropic micellar aggregates [1] which under particular conditions, may exhibit an orientational long-range ordering characteristic of the nematic phases. According to symmetry arguments, three types of lyotropic nematic phases are possible, and indeed, have been observed : two are uniaxial [2] and another one is biaxial [3]. The two uniaxial nematic phases are known as discotic (N_L), and cylindrical (N_C), depending on their magnetic anisotropy [4]. These uniaxial phases have been studied in detail using different physical means, such as optical observations of the textures under polarizing microscope, X-ray and neutron scattering, NMR-measurements, etc. (see for example Ref. [5] and references therein). On the contrary, the first observation of the biaxial nematic phase (N_{BX}) is recent [3], and little information is available on it to-date [6]. In the temperature-concentration diagram (Fig. 1 of Ref. [3]), the biaxial phase appears to be an intermediate phase all along the border between the two uniaxial phases [7], as predicted by statistical models [8-10]. This phase diagram shows also that for a particular choice of temperature and concentration, reentrant

configurations exist ; i.e. on heating the sample, the following sequence can be observed : $N_L \rightarrow N_{BX} \rightarrow N_C \rightarrow N_{BX} \rightarrow N_L$.

In this paper we present optical measurements of the tensorial order parameter in the three nematic phases encountered when varying temperature in samples of different concentrations, chosen around the reentrant zone. This is a simple and convenient method to investigate the biaxial domain and its transitions to the uniaxial phases, and also to study the uniaxial phases and their transitions to the isotropic phase.

1. Theoretical

1.1 ORDER PARAMETER. — The order parameter of the uniaxial and biaxial nematic phases is a second rank tensor to which the anisotropic part of the macroscopical quantities, obeying linear physics, is proportional. Because of this required property of linearity the magnetic susceptibility is usually preferred as an order parameter to the dielectric or optical susceptibility [11]. However, although the anisotropic part of the optical susceptibility is not a good order parameter in the thermotropic liquid crystals, experimentally it seems not to be bad for the lyotropics [6]. This observation can be justified by the very low birefringence value ($\sim 2 \times 10^{-3}$, i.e. about 100 times smaller than in thermotropics), which indicates that the mutual interactions between the induced electric

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dipoles, due to the anisotropic part of the microscopical susceptibility, are negligible in the lyotropics, and therefore that the dielectric susceptibility is as good as the magnetic susceptibility for the measurement of the order parameter.

The anisotropic part of the optical susceptibility $\bar{\epsilon}_a$ is expressed as a function of the optical index differences. In the eigen axes frame, referred to by the subscripts 1, 2, 3, it reduces to the diagonal elements :

$$\begin{aligned}\epsilon_{a_1} &= -\frac{4\langle n \rangle}{3} \left((n_2 - n_1) + \frac{(n_3 - n_2)}{2} \right) \\ \epsilon_{a_2} &= \frac{2\langle n \rangle}{3} ((n_2 - n_1) - (n_3 - n_2)) \\ \epsilon_{a_3} &= \frac{4\langle n \rangle}{3} \left(\frac{(n_2 - n_1)}{2} + (n_3 - n_2) \right)\end{aligned}\quad (1)$$

where $\langle n \rangle$ is the average index of refraction ~ 1.375 . In the uniaxial nematic phases, these diagonal elements are proportional to the usual « orientational order parameter » $S = 1/2 \langle 3 \cos^2 \theta - 1 \rangle$, θ being the angle between a randomly chosen molecular axis and the symmetry axis of the nematic phase (director). In the N_L phase, constituted of « disk-like » micelles, the molecules are preferably parallel to the director, while they are mostly perpendicular to it in the N_C phase, due to the « cylindrical shape » of the micelles. As a consequence, the limit for a fully ordered phase is $S = 1$ in the N_L phase, and $S = -1/2$ in the N_C phase.

For our study, which considers only uniformly oriented samples, no reference frame is needed. It is then very convenient to reduce the tensorial order-parameter to its symmetric invariants [12]. They are :

$$\begin{aligned}\sigma_1 &= \epsilon_{a_1} + \epsilon_{a_2} + \epsilon_{a_3} = 0 \\ \sigma_2 &= \frac{2}{3} (\epsilon_{a_1}^2 + \epsilon_{a_2}^2 + \epsilon_{a_3}^2) \\ \sigma_3 &= 4 \epsilon_{a_1} \epsilon_{a_2} \epsilon_{a_3}\end{aligned}\quad (2)$$

$\sigma_1 = 0$, $\bar{\epsilon}_a$ being a traceless tensor. In the uniaxial nematic phases, because the diagonal elements (1) are proportional to S , σ_2 and σ_3 are related by : $\sigma_3 = \pm \sigma_2^{3/2}$ (the sign being that of S , positive in N_L and negative in N_C [13]). In the biaxial phase, σ_2 and σ_3 are independent. The relation then transforms to the inequalities $-\sigma_2^{3/2} < \sigma_3 < \sigma_2^{3/2}$ which expresses that the N_{BX} phase is intermediate between the uniaxial N_C and N_L phases.

1.2 FREE ENERGY EXPANSION IN THE MEAN-FIELD THEORY. — In the mean-field theory, where the effects of fluctuations are neglected, the free energy is expanded in terms of the order parameter. The gradient terms being suppressed, all references to the laboratory frame are useless. The order parameter can therefore be reduced to the invariants, and the free energy is

expanded as :

$$G = a\sigma_2 + b\sigma_3 + \frac{1}{2}c\sigma_2^2 + d\sigma_2\sigma_3 + \frac{1}{2}e\sigma_3^2, \quad (3)$$

the coefficients being regular functions of temperature and concentrations. In a first order approximation, a and b are supposed to vary linearly with temperature while the other coefficients are constant. The minimum of G is given by :

$$\sigma_2 = \frac{bd - ae}{ce - d^2}, \quad \sigma_3 = \frac{ad - bc}{ce - d^2}. \quad (4)$$

The values of the invariants are effective if they are physically accessible, i.e. if the condition $\sigma_3^2 < \sigma_2^3$ is fulfilled; the phase is then biaxial. If this inequality is not fulfilled, the physical values of the invariants are given by the relative minimum of G satisfying the constraint $\sigma_3 = \pm \sigma_2^{3/2}$, and the phase is either uniaxial-nematic or isotropic. In this case, it is preferable to express σ_2 and σ_3 as functions of S . To a multiplicative constant and to the lowest orders in S , equation (3) becomes then the usual free-energy expansion [11] :

$$G_1 = aS^2 + bS^3 + \frac{c}{2}S^4. \quad (5)$$

This equation shows that the coefficient a controls the isotropic to uniaxial-nematic phase-transition, the nature of the nematic phase being determined by the sign of b . Similarly, the variations of b , through σ_3 in equation (3), determine the existence of the biaxial-nematic phase. This is clear in the weak-coupling limit ($d \simeq 0$), where σ_3 is directly proportional to b . So, driven by the variations of b , σ_3 varies freely in the N_{BX} phase until the uniaxial constraint ($\sigma_3^2 = \sigma_2^3$) is met in a continuous way, making a second-order uniaxial to biaxial nematic phase transition [12].

The uniaxial-nematic to isotropic phase-transition is, in general, first-order because of the S^3 term in G_1 [11]. It becomes weakly first-order as predicted by Shih and Alben [8] if a N_{BX} phase exists in the vicinity. This point can be understood in the following manner. The jump ΔS of the order-parameter at the uniaxial-nematic to isotropic transition is given by equation (5) : $\Delta S = -\frac{3b}{4c}$. Because the coefficient b goes to zero in the biaxial phase (or close to the N_{BX} phase in the case $d \neq 0$), the ratio b/c may be assumed to still remain small at the nematic-isotropic transition. So, the weak value of ΔS can be understood as a consequence of the existence of the N_{BX} phase [14].

2. Experimental.

2.1 SAMPLES, EXPERIMENTAL SET-UP AND METHOD. — The measurements reported in the paper are performed on mixtures of potassium laurate (KL) (synthesized and recrystallized in the laboratory), 1-decanol and

D₂O, of concentrations approximately chosen from the phase diagram studied by Yu and Saupe [3, 7]. Three samples of increasing KL-concentration are presented here :

- a) KL 25.5/Decanol 6.38/D₂O 68.12 wt %
- b) KL 26.0/Decanol 6.24/D₂O 67.76 wt % (same as in Ref. [6]),
- c) KL 26.03/Decanol 6.24/D₂O 67.73 wt %.

The samples are prepared following the usual method [3]. They are enclosed in a Hellma cell of 1 or 2.5 mm thickness, and hermetically sealed to prevent concentration drifts. In this way, the main physical properties are retained for weeks. The temperature of the sample is controlled by means of a thermostat (of 0.02 °C accuracy) composed of two independent systems : a water-circulating first-stage (Haake *G/D*₃) and an electronically servo-regulated second-stage. The orientation of the sample is realized by combining a silane-treatment on the surfaces of the cell [15] with the bulk coupling of the nematic director to a magnetic field **H** (~ 16 kG). For this reason, all the experimental set-up is built between the poles of an electromagnet. In this manner, the sample can be oriented correctly enough for measuring the refractive indices by conoscopy, its director being aligned parallel to **H** in the N_C phase, and homeotropic (i.e. perpendicular to the surfaces of the cell) in the N_L phase. In this latter case, the orientation is achieved by repeated rotations of the sample around the normal to the cell in the presence of **H**. These two axes, the (horizontal) magnetic field and the (vertical) rotational axis, define the laboratory frame. They are respectively, the 1 axis and 3 axis along which the director aligns in both uniaxial-nematic phases (Fig. 1). The measurement of the optical indices is done using a conoscopic method which is realized with a He-Ne laser beam converging in the sample by means of a wide-aperture microscope-objective (half-angle of the aperture ~ 50 deg.). In this manner, a very extensive interference pattern is obtained, allowing for accurate measurements of optical index differences (to about 10⁻⁵).

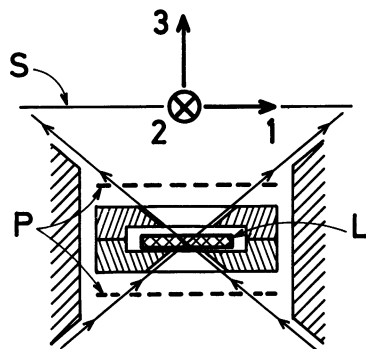


Fig. 1. — Schematic set up. The sample L is placed inside a thermostat, between the poles of an electromagnet. It is illuminated by a strongly converging laser beam. The light, polarized before and after the sample (with the polarizers P), interferes on the screen S parallel to the 1-2 plane.

A series of photographs of these interferences is shown in figure 2 (except Fig. 2f which gives the directions of the polarizers and of the axes of the laboratory frame). Figure 2a is the typical conoscopic pattern of the discotic-uniaxial phase homeotropically aligned along the 3 axis; figures 2b, c, d are photos of the biaxial nematic phase with the eigen directions along the axes of the laboratory frame; and figure 2e shows the pattern obtained in the N_C phase oriented along the 1 axis. Note that no qualitative change occurs between figure 2d and figure 2e, and that a simple observation of the conoscopic pattern is hardly able to determine the temperature of the N_{BX} to N_C phase transition. The positions of the interference fringes are measured at equilibrium along the 1 and 2 axes, for the two orientations of the polarizers, perpendicular and parallel, which correspond respectively to measurements of integer and half integer interference orders. These values, together with the sample thickness and the average index $\langle n \rangle \sim 1.37$, are introduced in a least squares fit. Both the index differences $n_2 - n_1$ and $n_3 - n_2$ are thus found. This method does not give the sign of $n_2 - n_1$ and $n_3 - n_2$ which is found independently by looking at the modification of the conoscopic pattern when a slide of known-birefringence material is superposed on the sample.

2.2 RESULTS.

2.2.1 *Index differences versus temperature.* — Typical measurements of the index differences $n_2 - n_1$ and $n_3 - n_2$ are shown in figure 3 as functions of temperature, the letters a, b, c, indicating the concentrations

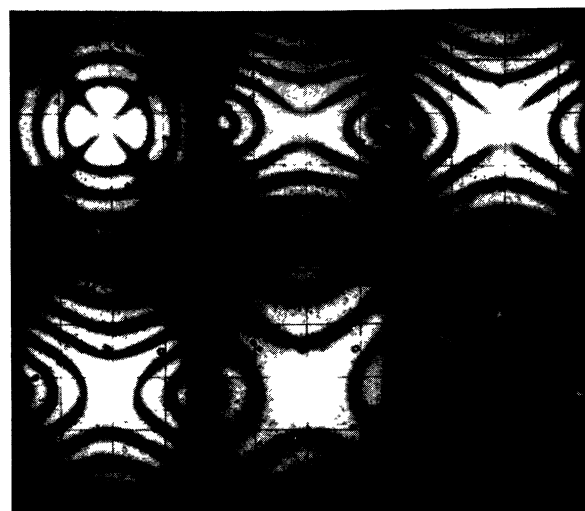


Fig. 2. — Conoscopic patterns of the 2.5 mm-thick sample b : a) N_L phase in the homeotropic orientation (director along the 3 axis). b), c) and d) N_{BX} phase when increasing temperature from the N_L to the N_C transition. e) N_C phase in the planar orientation (director along the 1 axis). f) Laboratory-frame axes and polarizers P; the 1 axis is parallel to the magnetic field and the 3 axis is perpendicular to the plates of the sample.

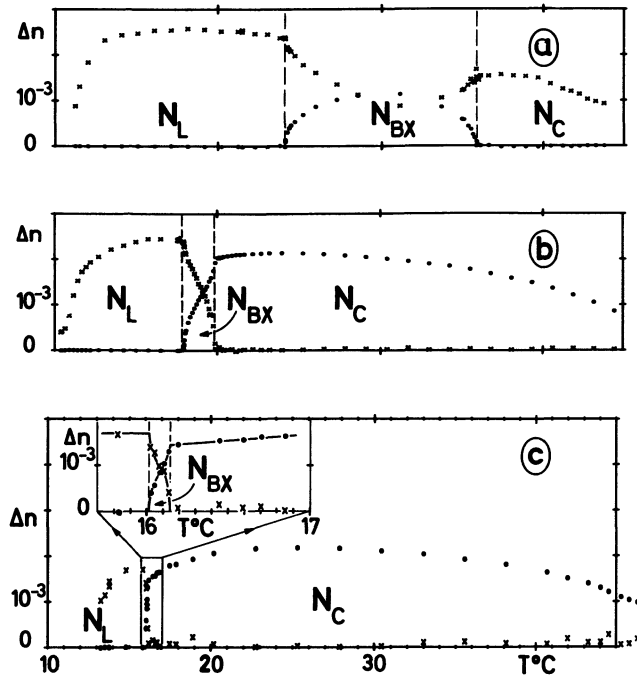


Fig. 3. — Index differences ($n_2 - n_1$: ● ; $n_3 - n_2$: ×) measured as functions of temperature in the samples *a*, *b*, and *c* respectively. Because they are thinner (1 mm) the samples *a* and *c* give less accurate measurements than sample *b* (2.5 mm). Sample *c* has a narrow N_{BX} temperature range. The insert displays an expansion by a factor 10 of the temperature scales. The full line in the insert is just a guide for the eye.

of the different samples. The uniaxial phases, and their transitions to the biaxial phase, appear clearly in these plots. They correspond to one vanishing index difference : $n_2 - n_1 = 0$ in N_L , $n_3 - n_2 = 0$ in N_C . In samples *b* and *c* (Figs. 3b and 3c), the succession $N_L - N_{BX} - N_C$ is thus encountered when increasing temperature. In sample *a* which contains less KL than the two other samples, the reentrant sequence $N_L - N_{BX} - N_L$ is observed. In samples of lower KL-concentration, only the N_L phase is found [3, 7].

From these results, one can readily notice some general features.

In every cases, when both the N_L and N_C phases exist, the N_{BX} phase appears as an intermediate phase which prevents a direct N_L - N_C transition (Figs. 3b, 3c). As is discussed in § 2.2.2, this point is consistent with the mean-field analysis.

From the index differences, $n_3 - n_2$ in N_L and $n_2 - n_1$ in N_C , one can deduce an estimate of the temperature variations of the order parameter S in the uniaxial phases. Because the maximum index difference in N_L is smaller than twice the maximum index difference in N_C , it is suggested that the N_L phase has, in general, a lower order parameter than the N_C phase. This point is, to a certain extent, confirmed by X-ray measurements [16].

No hysteresis to within our 0.02 °C temperature resolution is observed at the uniaxial to biaxial phase transitions, nor is any jump of the index differences measured. This confirms that the uniaxial to biaxial phase transitions are second-order [17] as predicted by the mean-field theories.

On the contrary, the isotropic to N_L phase transition is weakly first-order as is shown by the small jump of the birefringence data (at $T = 11$ °C, Fig. 3b), though partly rounded off in the coexistence region. The N_C to isotropic phase change is also measured to be weakly first-order, for the same reasons, but with less accuracy because of the planar orientation of the N_C phase. The order parameter jump in both nematic-isotropic transitions can be estimated to ~ 0.2 if one supposes that the maximum of S , around the biaxial phase is about 0.8 [16]. The same estimate performed on a sample not having a biaxial phase (sample of lower KL-concentration than sample *a*) gives $\Delta S \sim 0.4$ at the N_L -isotropic transitions which indicates a usual first-order nematic-isotropic transition. This is a confirmation of the predictive criterion of Shih and Alben [8] that the existence of an N_{BX} phase is connected to a weakly first-order nematic to isotropic phase transition.

2.2.2 Invariants of the order parameter. — As previously discussed (§ 1.1) it is convenient to represent the experimental data using the invariants of the order parameter. Figure 4 displays the invariants σ_2 and σ_3 as functions of temperature in the biaxial domain of sample *b*. It shows that σ_2 and σ_3 behave linearly with temperature, within the experimental uncertainties, according to mean-field theory. Figure 5 represents a similar result in the narrow temperature range of the N_{BX} phase of sample *c*. Note that this measurement is rather a demonstration of a practical method for determining the uniaxial to biaxial phase transitions by just drawing the linear intercepts in $\sigma_3(T)$.

In fact, the linear variations of $\sigma_2(T)$ and $\sigma_3(T)$ in the N_{BX} phase are only valid as a first-order approximation. It concerns narrow biaxial temperature-ranges only (~ 1 °C if compared to our accuracy of measurement). Around the reentrant zone where a wide biaxial domain (~ 10 °C) exists, the linear approximation has to be rejected. Moreover, reentrance being typically a return to the initial N_L phase, linear behaviours for $\sigma_2(T)$ and $\sigma_3(T)$ are clearly impossible. Figure 6 shows such a non-linear behaviour of $\sigma_3(T)$, as measured in sample *a*. The linear approximations remain, however, possible over reduced (but finite) temperature ranges (~ 1 °C), even near the uniaxial-biaxial transitions. This indicates that the uniaxial-biaxial transitions are mean-field also in this case. If they were critical, the invariants would vary like $|T - T_c|^{2\beta}$ near the transitions (T_c : transition temperature, $\beta \sim 1/3$ [18]), which would be marked by infinite derivatives $d\sigma/dT$ on the biaxial side of the uniaxial-biaxial transitions. Such a critical behaviour

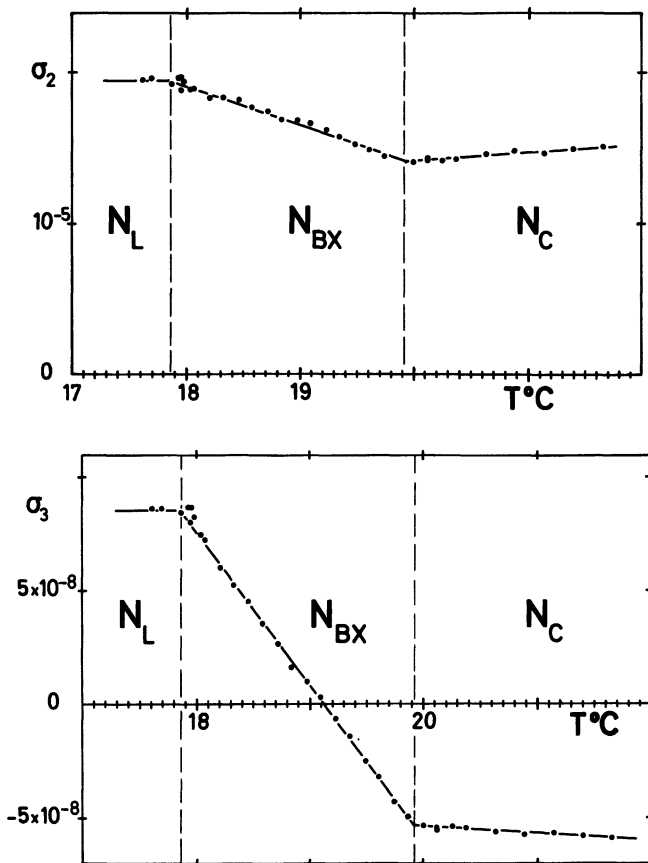


Fig. 4. — Symmetric invariants versus temperature in the N_{BX} phase of sample b : $\sigma_2(T)$ and $\sigma_3(T)$, respectively up and down.

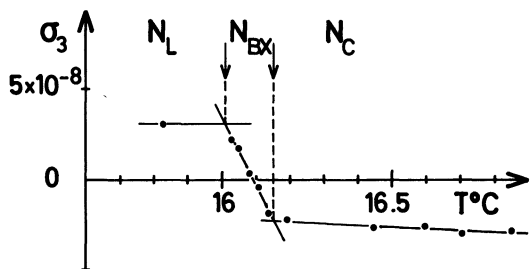


Fig. 5. — $\sigma_3(T)$ in the N_{BX} phase of sample c . Such a plot yields a practical way for determining the uniaxial to biaxial nematic transitions.

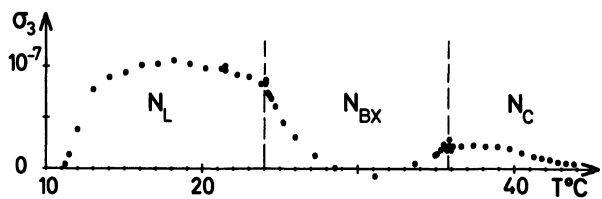


Fig. 6. — $\sigma_3(T)$ in the reentrant sequence $N_L-N_{BX}-N_L$ of sample a . The linear approximation is no longer possible on the whole N_{BX} range, but remains valid on smaller scales ($\sim 1^\circ\text{C}$), especially near the uniaxial-biaxial transitions, which are therefore mean-field.

is not observed within the accuracy of our T and σ -measurements [19].

The results of the order parameter measurements can advantageously be collected in a (σ_2, σ_3) -plot (Figs. 7a and b according to the sample). The arrows indicate the variations of the point (σ_2, σ_3) as the temperature is increased. In the uniaxial phases, it follows the branches which correspond to the constraint $\sigma_3 = \pm \sigma_2^{3/2}$ (sign + for N_L , - for N_C). Its position (σ_2, σ_3) is given by the minimum of the free energy G in the physically accessible σ -space. If we make the simple assumption that $G(\sigma_2, \sigma_3)$ is a one-minimum function continuously varying with temperature, it results in continuous variations for (σ_2, σ_3) with temperature, which implies the impossibility of going directly from the N_L to the N_C phase without crossing the N_{BX} phase. Such a behaviour, which has been predicted by statistical models [8-10], is consistent with all the phase diagrams [3, 7] in which the N_L and N_C phases are both present.

3. Conclusion.

The measurements of the invariants of the order parameter as functions of temperature in samples

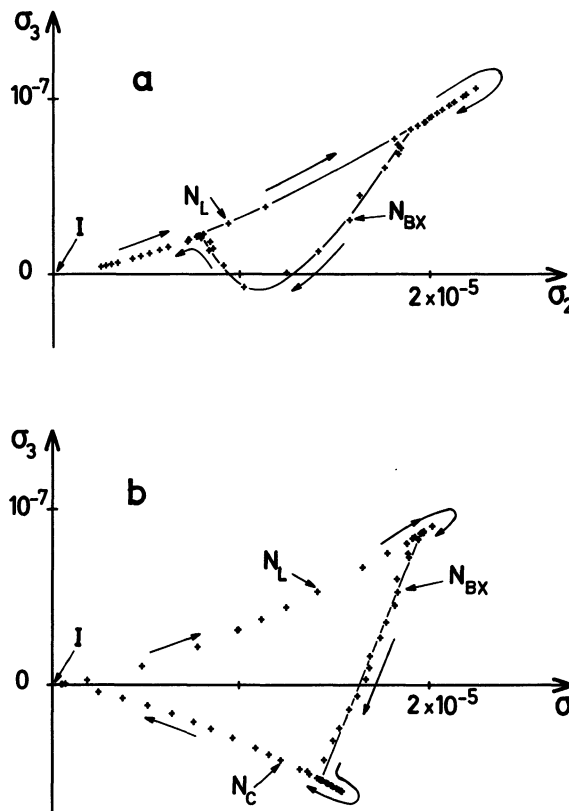


Fig. 7. — (σ_2, σ_3) -plots for the samples a and b , respectively. The arrows indicate the variation of (σ_2, σ_3) for increasing temperature from and back to the isotropic phase (I). The straight line in figure b is a consequence of both the linear variations of σ_2 and σ_3 with temperature.

of different concentrations, show that the uniaxial to biaxial nematic phase transitions are second-order and mean-field, to within our accuracy of measurement. This conclusion of a mean-field behaviour of the uniaxial-biaxial transitions is also valid at the reentrant concentration, though the invariants σ_2 and σ_3 then have non-linear variations with temperature. On the contrary, the uniaxial to isotropic phase transitions, which are known to be mean-field,

are found to be weakly first-order when a biaxial phase exists in the vicinity, following the prediction of Shih and Alben.

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References

- [1] LAWSON, K. D. and FLAUTT, T. J., *J. Am. Chem. Soc.* **89** (1967) 5489.
- [2] RADLEY, K., REEVES, L. W. and TRACEY, A. S., *J. Phys. Chem.* **80** (1976) 174.
- [3] YU, L. J. and SAUPE, A., *Phys. Rev. Lett.* **45** (1980) 1000. SAUPE, A., BOONBRAHM, P., YU, L. J., *J. Chimie Phys.* **80** (1983) 7.
- [4] CHARVOLIN, J., LEVELUT, A. M., SAMULSKI, E. T., *J. Physique Lett.* **40** (1979) L-587.
- [5] HENDRIKX, Y., CHARVOLIN, J., RAWISO, M., LIÉBERT, L., HOLMÉS, M. C., *J. Phys. Chem.* **87** (1983) 3991.
- [6] GALERNE, Y., MARCEROU, J. P., *Phys. Rev. Lett.* **51** (1983) 2109.
- [7] FIGUEIREDO NETO, A. M., LIÉBERT, L., GALERNE, Y., to be published.
- [8] SHIH, C. S., ALBEN, R., *J. Chem. Phys.* **57** (1972) 3055. ALBEN, R., *Phys. Rev. Lett.* **30** (1973) 778. ALBEN, R., *J. Chem. Phys.* **59** (1973) 4299.
- [9] RABIN, Y., McMULLEN, W. E., GELBART, W. M., *Mol. Cryst. Liq. Cryst.* **89** (1982) 67.
- [10] CHEN, Z. Y. and DEUTCH, J., *J. Chem. Phys.* **80** (1984) 2151. CAFLISH, R., CHEN, Z.-Y., BERKER, A., DEUTCH, J., *Phys. Rev. A* **30** (1984) 2562.
- [11] DE GENNES, P. G., *The Physics of Liquid Crystals* (Clarendon Press, Oxford) 1974.
- [12] FREISER, M. J., *Phys. Rev. Lett.* **24** (1970) 1041.
- [13] One can equivalently notice that the uniaxial condition may be written $\epsilon_{a_1} = \epsilon_{a_2} < 0$ in the N_L phase, and $\epsilon_{a_2} = \epsilon_{a_3} > 0$ in the N_C phase which implies $\sigma_3 = \sigma_2^{3/2}$, and $\sigma_3 = -\sigma_2^{3/2}$, respectively.
- [14] Note inversely that lyotropics can have weakly first-order uniaxial-nematic to isotropic phase transitions without any evidence of a neighbouring N_{BX} phase; see : ROSENBLATT, C., KUMAR, S., LITSTER, J. D., *Phys. Rev. A* **29** (1984) 1010.
- [15] BARTOLINO, R., CHIARANZA, T., MEUTI, M., COMPAGNONI, R., *Phys. Rev. A* **26** (1982) 1116.
- [16] FIGUEIREDO NETO, A. M., GALERNE, Y., LEVELUT, A. M., LIÉBERT, L., to be published.
- [17] The possibility of a first order transition smoothed by a coexistence region between the N_L and N_C phases must also be discarded though such a demixtion would optically very much resemble a biaxial phase. Two arguments may be proposed. First, the biaxial samples remain clear for months, indicating that the demixtion, if it exists, did not reach the 1 μm -scale after this period. Second, the measured temperature variations of the index differences, which display infinite derivatives at each uniaxial-biaxial phase transition, are not consistent with the smoothing effects that a demixtion would produce. For these reasons, the uniaxial to biaxial nematic-phases transitions observed in our lyotropic systems, are second-order phase transitions, and the N_{BX} phase is really a phase and not a demixtion.
- [18] BOONBRAHM, P. AND SAUPE, A., *J. Chem. Phys.* **81** (1984) 2076.
- [19] Note that the uniaxial-nematic to isotropic phase transitions are known to be mean-field, though first order, in lyotropics as in thermotropics; see KUMAR, S., YU, L. J., LITSTER, J. D., *Phys. Rev. Lett.* **50** (1983) 1672.