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Does nematic order depend on diamagnetism ? (*)

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Résumé. — Dans un système binaire formé de molécules « bâtonnets » d'anisotropie diamagnétique de signe opposé, la phase nématique se comporte de façon homogène sous l'action d'un champ magnétique. Nous montrons en particulier l'existence d'une concentration « seuil » pour laquelle l'annulation de l'anisotropie mesurée découle directement de celle de l'anisotropie moléculaire. En l'absence de champ extérieur nous révélons qu'en ce point magnétiquement isotrope l'ordre nématique est perturbé de façon inattendue.

Abstract. — The nematic phase of a binary mixture involving rod-like molecules with opposite diamagnetic anisotropy behaves homogeneously when submitted to a magnetic field. In particular we show the existence of a threshold concentration for which the vanishing of the measured anisotropy is directly connected to the vanishing of the average molecular anisotropy. At this magnetically isotropic point it is observed that the nematic order is surprisingly perturbed.

1. Introduction.

Most of the thermotropic rod-like liquid crystals exhibit in nematic or smectic A phases a positive diamagnetic anisotropy defined for these uniaxial media as :

$$\Delta\chi = \chi_{\parallel} - \chi_{\perp}$$

$\chi_{\parallel}$ and $\chi_{\perp}$ being the diamagnetic susceptibility parallel and perpendicular to the director.

Yet there is no fundamental hindrance to a sign-inversion of the diamagnetic anisotropy. In order to achieve this it is necessary either to increase the importance of the aliphatic tails compared to the aromatic core while keeping the mesogenic and rod-like properties, or to reduce the absolute value of the magnetic susceptibility perpendicular to the director. The latter way has been explored by replacing the aromatic cores by saturated rings : a new class of thermotropic nematogens appeared with rather elongated molecules ($\Delta n > 0$) and negative magnetic anisotropy [1, 2].

Whatever the nematogen is, the expected response to an applied external magnetic field depends solely on the sign of the magnetic anisotropy. A homogeneous nematic phase with $\Delta\chi > 0$ orients its director parallel to the magnetic field (Fig. 1a) : a single domain is obtained in the bulk. In contrast, a negative magnetic anisotropy leads to a non uniform director and

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Fig. 1. — Orientation of the director in a nematic liquid crystal aligned by a magnetic field for molecules with positive diamagnetic anisotropy (a) and with negative diamagnetic anisotropy (b) (no spinning).

no preferred orientation in the plane perpendicular to the magnetic field is achieved (Fig. 1b) except during a spinning experiment [3]. This latter behaviour applies to the lyotropic nematics involving disc-like micelles [4] or rod-like micelles [5], to the thermotropic nematics with disc-like molecules [6] and to the carbonaceous mesophase [7].

Let us specify now the magnetic and thermodynamic properties at the isotropic nematic transition for binary mixtures of molecules with opposite diamagnetic anisotropy.

2. Experimental results and discussion.

We choose two compounds with good thermal stability and similar clearing points :

— the *trans*, *trans*-4-butyl-4' cyanocyclohexylcyclohexane (CCH4) $\Delta\chi < 0$

— the octyloxycyanobiphenyl (80CB) $\Delta\chi > 0$

These compounds were purchased from Merck and used without further purification.

In spite of the resemblance of the chemical formulae the phase diagram CCH4-80CB (Fig. 2) shows a non ideal behaviour. In particular a minimum for the I-N phase boundary is located at $x = 0.5$. Therefore we plot the magnetic values *versus* the reduced temperature T/T_{IN} .

The diamagnetic susceptibility was measured by the Faraday method [8] along the magnetic field direction. It corresponds in the nematic state to $\chi_{\parallel}$ if $\Delta\chi > 0$ and to $\chi_{\perp}$ if $\Delta\chi$ is negative. In the latter case the occurrence of multidomains does not influence the magnetic values. The average susceptibility $\bar{\chi}$ defined as

$$\bar{\chi} = \frac{\chi_{\parallel} + 2\chi_{\perp}}{3}$$

was measured experimentally in the isotropic phase.

Fig. 2. — Binary isobaric diagram ($P = 1$ atm) between CCH₄ (on left) and 80CB (on right).

Thus this double determination allows us to calculate the magnetic anisotropy $\Delta\chi$ directly if its sign is known :

$$\begin{aligned}\Delta\chi > 0 \quad \Delta\chi &= \chi_{\parallel} - \chi_{\perp} = \frac{3}{2}(\chi_{\parallel} - \bar{\chi}) \\ \Delta\chi < 0 \quad \Delta\chi &= \chi_{\parallel} - \chi_{\perp} = 3(\bar{\chi} - \chi_{\perp}).\end{aligned}$$

The diamagnetic susceptibilities measured along the magnetic field are reported in figure 3 for the two pure compounds and for several CCH₄-80CB mixtures. The discontinuity at the isotropic-nematic transition defined as :

$$d(\chi)_{\text{IN}} = |\bar{\chi} - \chi_{T/T_{\text{IN}}=0.999}|$$

decreases (Fig. 3a, b, c, d) when increasing the 80CB molar fraction from zero and vanishes for $x_{80\text{CB}} \sim 0.20$ (Fig. 4). Of course at the opposite side of the diagram, decreasing $x_{80\text{CB}}$ from 1 makes the susceptibility discontinuity decrease (Fig. 3i, h, g, f, e). A zero value is found at the junction with the former part of the curve in the figure 4 ($x_{80\text{CB}} \sim 0.2$) without any gap. This point is the unique location for which the macroscopic diamagnetic anisotropy vanishes. Such a continuous evolution from one side to the other is important for it shows that the nematic phase of binary mixtures CCH₄-80CB behaves homogeneously concerning the apparent orientation effects when submitted to a magnetic field (i.e. there is no orientational segregation of macroscopic domains with opposite diamagnetic anisotropy).

Furthermore the molecular anisotropy $\Delta\chi_0$ of the two pure compounds has been evaluated using W. H. Flygare's tables [9] :

$$\begin{aligned}\Delta\chi_0(\text{CCH}_4) &= -0.40 \times 10^{-7} \text{ cm}^3 \text{ g}^{-1} \\ \Delta\chi_0(80\text{CB}) &= +1.52 \times 10^{-7} \text{ cm}^3 \text{ g}^{-1}.\end{aligned}$$

Despite errors due mostly to the choice of a molecular conformation, these computed values

Fig. 3. — Thermal evolution of the diamagnetic susceptibility for CCH₄, 80CB and various mixtures.

Fig. 4. — Plot of the diamagnetic susceptibility discontinuity at the isotropic-nematic transition *versus* concentration of 80CB, a) CCH₄, b) CCH₄-0.06 80CB, c) CCH₄-0.11 80CB, d) CCH₄-0.15 80CB, e) CCH₄-0.20 80CB, f) CCH₄-0.25 80CB, g) CCH₄-0.39 80CB, h) CCH₄-0.59 80CB, i) 80CB.

are close to data of A. Buka *et al.* [8b] for homologous compounds. Using the additivity law for the molecular diamagnetic anisotropy, the averaged $\Delta\chi_0$ vanishes for a mixture $x_{80CB} = 0.21$. This value agrees well with the observed experimental results (Fig. 5). Thus the vanishing of the macroscopic $\Delta\chi$ is directly connected to the vanishing of $\Delta\chi_0$ by compensation. A similar conclusion is implied in the more complex NMR studies [10-12] of multicomponent systems with an inversion of the magnetic anisotropy.

Accepting the hypothesis of uniaxial rod-like molecules, the mean-field theories for the isotropic nematic transition connect $\Delta\chi(T)$ to $\Delta\chi_0$ and to the orientational order parameter $\eta(T)$:

$$\Delta\chi(T) = \Delta\chi_0 \cdot \eta(T) .$$

Fig. 5. — Concentration dependence of the diamagnetic anisotropy for the CCH4-80CB system.

If $\Delta\chi_0 = 0$, we verify that the experimental value $\Delta\chi$ vanishes too, in agreement with the negligible molecular biaxiality of such systems [8b]. In addition, the macroscopic parameter $\Delta\chi$ no longer represents the order parameter at the switching point but the nematic order (i.e. $\eta(T)$) should not be modified.

Of course ΔS_{IN} still remains observable and is connected to the orientational order parameter. Therefore the sudden decrease of the transition entropy close to the threshold molar fraction $x_{80CB} = 0.20$ is unexpected (Fig. 6). These accurate DSC measurements show that ΔS_{IN} varies asymmetrically as does $\Delta\chi$ (Fig. 5) around the point of zero magnetic anisotropy.

Unlike some entropy anomalies previously described in other systems [13, 14], this reduction cannot be attributed to another thermodynamical event occurring elsewhere in the phase diagram. In particular the non-ideal behaviour of the CCH4-80CB mixtures gives a minimum for T_{IN} at a molar fraction far from the threshold value (Fig. 2). Thus the nematic order is reduced specifically near $x_{80CB} = 0.20$ because the microscopic anisotropy $\Delta\chi_0$ tends to zero there. We simply suggest that the fluctuations of a local magnetic field do perturb the orientational order (at very short range) in the absence of an external field.

Fig. 6. — Variation of the IN transition entropy *versus* concentration of 80CB.

To our knowledge the influence of diamagnetic anisotropic dispersion forces (somewhat comparable to the anisotropy of the attractive Van der Waals forces) have never been made clear in molecular models of the isotropic-nematic transition. We can estimate that these diamagnetic interactions contribute at least 5 % of the orientational order ($\Delta S_{IN} \sim \eta^2$).

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