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Ultrasonic shear and capillary viscosity study of 4-cyano-4'-n-heptylbiphenyl in the nematic and the isotropic state

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Résumé. — Nous avons mesuré les propriétés visqueuses en phase nématique et isotrope du 4-cyano-4'-n-biphenyl (7-CB) par viscosimétrie capillaire et ultra-sonore à des fréquences comprises entre 50 et 70 MHz. En phase nématique nos résultats, comparés à ceux obtenus sous cisaillement de basse fréquence, posent d'importantes questions sur le comportement du coefficient α_3 de Leslie [1, 2].

Abstract. — Using capillary viscometry and ultrasonic shear at frequencies between 50 and 70 MHz, we have measured viscous properties of 4-cyano-4'-n-biphenyl (7-CB) in the nematic and the isotropic state. The data in the nematic state, when compared with results from low frequency shear experiments, raise important questions on the behaviour of the Leslie coefficient α_3 [1, 2].

Viscous properties of liquid crystals may be studied with capillary viscometry, low frequency shear or ultrasound. In the present study we used conventional capillary viscometry in zero magnetic field and ultrasonic shear impedometry at frequencies between 50 and 70 MHz [3].

Our data on the ultrasonic shear of the present compound, 4-cyano-4'-n-heptylbiphenyl or 7-CB, are new and our data on capillary viscosity are in good agreement with data obtained by other workers before [8]. Ultrasonic shear on the related compound 5-CB has been studied by Kiry *et al.* [6, 7], whereas low frequency oscillatory shear studies have been carried out by Clark *et al.* [1], and by Skarp *et al.* [2].

The capillary viscometry was carried out for two capillary sizes, of radius 0.33 mm and 0.25 mm, with mean flow speeds not less than 40 mm/s and 25 mm/s respectively. By this we ensure that the saturation angle of director alignment was obtained. The ultrasonic shear impedometer is of the type first proposed by Mason *et al.* [5] and described extensively by Martinoty *et al.* [3].

In figure 1 we show a sketch of the impedometer with the ultrasonic path indicated.

Fig. 1. — Sketch of ultrasonic impedometer and ultrasound path. a : Fused silica bloc. b : Transducers. c : Sample.

Sample alignment parallel to the impedometer surface was obtained by unidirectional rubbing with tissues of either the clean surface, or of a thin layer of PVA (poly vinyl alcohol) which had been deposited first on the impedometer surface, both methods giving identical results. Perpendicular orientation was obtained by deposition of a layer of lecithin on the impedometer surface.

We checked the performance of the apparatus with dibutyl phtalate for which extensive literature data are available. Agreement within 1 % was obtained. For some of the check experiments a layer of PVA or lecithin was deposited on the surface first. The results were identical to those obtained on a clean surface, and therefore it is safe to assume that these layers do not influence the acoustic impedance of the sample in any way other than by orientation of the liquid crystal.

Checks on frequency dependence showed no frequency dependence within the experimental error of 2 %. No further reference to frequency will be made.

The acoustic impedance of the sample is found from the reflection coefficient of the ultrasound against the top surface of the fused silica impedometer bloc, and hence a viscosity is found. Dependent on the orientation of the director $\mathbf{n}$ with respect to the ultrasound displacement $\mathbf{u}$ and the ultrasound wavevector $\mathbf{k}$ three different viscosity coefficients are obtained, as shown in figure 2

$$\begin{aligned} \text{orientation A : } \mathbf{n} &\perp \mathbf{u} \text{ and } \mathbf{k}, \\ \text{orientation B : } \mathbf{n} &\parallel \mathbf{u} \text{ and } \perp \mathbf{k}, \\ \text{orientation C : } \mathbf{n} &\perp \mathbf{u} \text{ and } \parallel \mathbf{k}. \end{aligned} \quad (1)$$

Fig. 2. — Sample orientations, A, B and C, $\mathbf{n}$ is the director, $\mathbf{u}$ the ultrasound displacement and $\mathbf{k}$ the ultrasound propagation vector.

According to the Rapini equality

$$\eta_B = \eta_C \equiv \eta_{B,C} \quad (2)$$

which we found confirmed in our experiments.

For the capillary viscosity we use the symbol η_s and for the ultrasound viscosity in the isotropic state the symbol η_{us} .

The data for 7-CB are shown in figure 3.

For the nematic state the following relationships between the observed viscosities and the Leslie coefficients can be written down [4, 6].

$$\begin{aligned} \eta_s &= \frac{1}{4} \alpha_1 (1 - \gamma_1^2 / \gamma_2^2) + \frac{1}{2} (\alpha_2 + \alpha_4 + \alpha_5) \quad (\text{at saturation angle}) \\ \eta_A &= \frac{1}{2} \alpha_4 \\ \eta_B &= \frac{1}{2} (\alpha_4 + \alpha_6 - \alpha_3 \gamma_2 / \gamma_1) \\ \eta_C &= \frac{1}{2} (\alpha_4 + \alpha_5 - \alpha_2 \gamma_2 / \gamma_1) \\ \gamma_1 &= \alpha_3 - \alpha_2 \\ \gamma_2 &= \alpha_3 + \alpha_2 = \alpha_6 - \alpha_5. \end{aligned} \quad (3)$$

Therefore for $\alpha_3 = 0$

$$\eta_s = \eta_{B,C}. \quad (4)$$

Fig. 3. — Data on 7-CB. ○ capillary viscometer data ; × orientation A ; + orientation B, C ; △ ultrasound data in isotropic state. Inset : $\Delta\eta$ vs. $T_c - T$. Drawn lines best fit to equation (7).

For $\alpha_3 \neq 0$, defining $\Delta\eta = \eta_s - \eta_{B,C}$

$$\Delta\eta = \alpha_2 \alpha_3 [\alpha_1 / \gamma_2^2 + 1 / \gamma_1]. \quad (5)$$

Although the experiment accuracy on $\Delta\eta$ is only 25 % it follows clearly from figure 3 that $\Delta\eta$ is everywhere significantly different from zero, the lowest value being (2.6 ± 0.6) mPaS.

From equation (5) we have

$$\begin{aligned} \alpha_2, \alpha_3 &\neq 0, 0 \\ \alpha_1 &\neq -\gamma_2^2 / \gamma_1, \end{aligned} \quad (6)$$

over the whole nematic range.

The fact that $\alpha_2 \neq 0$ is unremarkable, being in line with other nematics. However, we find that also $\alpha_3 \neq 0$ over the whole nematic range. Our data do not allow to find a numerical value for α_3 as α_1 and α_2 are unknown. Some idea of its magnitude can be obtained though by inserting « typical » values for α_1 and α_2 in equation (5). For convenience we take $\alpha_1 = 10$ mPaS ; $\alpha_2 = -80$ mPaS. At $T_c - T = 2$ K this yields

$$\begin{aligned} \alpha_3 &= -1.8 \text{ mPaS} \\ \gamma_1 / \gamma_2 &= -0.96. \end{aligned}$$

This behaviour of α_3 agrees with the data obtained by Skarp *et al.* [2], but is at variance with the behaviour which Clark *et al.* [1] deduce from observations of instability onset in low frequency oscillatory shear experiments. From these experiments it follows that α_3 is negative for $T > 31$ °C, in agreement with our observations. However at $T = 31$ °C, the inversion temperature, α_3 becomes 0, whereas at even lower temperatures, continuing in the undercooled state for $T < T_{KN}$, α_3 is observed to be positive. We have marked the inversion temperature in our figure 3, and it is evident, that there is no feature at all in $\Delta\eta$ at this temperature, which excludes such behaviour for α_3 by equation (5).

This discrepancy raises interesting questions with respect to the interpretation of the data. Expression (3a) for the capillary viscosity at saturation angle assumes that α_3 is negative, and is invalid otherwise. For positive α_3 the alignment angle might stabilize at some different value due to subtleties not included in the simple theory used to derive (3a). Alternatively disclinations might form, invalidating (3a).

On the other hand, the existence of an inversion temperature for α_3 at 31 °C makes it necessary that α_3 decreases when the temperature is reduced from higher values to 31 °C, and it would be expected that $\Delta\eta$ would reflect this behaviour. We do see no sign of this. Undercooling cannot play a role, as the sample temperature for each measuring point is established independently. Therefore, without speculating on the behaviour of $\Delta\eta$ at positive α_3 , our data provide no evidence for α_3 going to 0 as $T \downarrow 31$ °C for the frequencies used.

It was pointed out to us, that 8-CB has a well established inversion point for α_3 and we hope to study this material soon.

Values for α_4 are found immediately from η_A . In table I we show our data for 7-CB and the literature data for 5-CB.

Table I. — *Data in nematic state, α_4 at $T_{NI} - T = 2$ K, 1 PaS = 10 Poise.*

Sample	W_s/k_B	W_A/k_B	W_{BC}/k_B	α_4	α_{40}
	K	K	K	PaS	PaS
	$\times 10^3$	$\times 10^3$	$\times 10^3$	$\times 10^{-3}$	$\times 10^{-8}$
5-CB	3.3	4.3	3.3	53	4.5
7-CB	3.9	3.9	2.9	20	15

The temperature dependence of the viscosities, both in the isotropic and the nematic state is of the form

$$\eta(T) = \eta_0 e^{W/k_B T}, \quad (7)$$

where W is an activation energy.

Removing the temperature dependence using equation (7) we find the underlying trend, with higher values for η_0 in 7-CB than 5-CB, as is reasonable to expect.

The activation energies for η_s , η_A and $\eta_{B,C}$ are unremarkable. We include the information in table I.

Because of the experimental accuracy it is not meaningful to state the activation energy of $\Delta\eta$.

In the isotropic state the ultrasound viscosity η_{us} is complex. We consider here only the real part, which is given by

$$\eta'_{us}(\omega) = \eta_s - \frac{2\mu^2}{\nu} \frac{1}{1 + \Gamma^2/\omega^2} \quad (8)$$

where μ and ν are bulk viscosities and Γ a relaxation time.

As we find no frequency dependence the second term in the denominator is apparently small and therefore :

$$\eta_s - \eta'_{us} \cong 2\mu^2/\nu. \quad (9)$$

In table II we show the data for the isotropic state of 7-CB together with the literature data for 5-CB at $T - T_c = 2$ K. The smaller values for 7-CB are caused by the higher value for the transition temperature. Again the underlying trend after removal of the temperature dependence is higher for 7-CB, analogous to the behaviour in the nematic state.

More details of the present data, and comparable data on 5-CB and 6-CB will be published in a full paper.

Table II. — *Data in isotropic state, η_s , η'_{us} and $\eta_s - \eta'_{us}$ at $T - T_{NI} = 2$ K, 1 PaS = 10 Poise.*

Sample	W_s/k_B	W_{us}/k_B	η_s	η_{us}	$\eta_s - \eta'_{us}$	η_{s0}	η'_{us0}	$\eta_{s0} - \eta'_{us0}$
	K	K	PaS	PaS	PaS	PaS	PaS	PaS
	$\times 10^3$	$\times 10^3$	$\times 10^{-3}$	$\times 10^{-3}$	$\times 10^{-3}$	$\times 10^{-8}$	$\times 10^{-8}$	$\times 10^{-8}$
5-CB	4.3	4.2	22	16	6	2.6	1.9	0.7
7-CB	4.0	3.8	22	17	5	10	7.6	2.4

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