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To cite this version:

HAL Id: jpa-00209578
https://hal.archives-ouvertes.fr/jpa-00209578
Submitted on 1 Jan 1983
Flow-measurements of the viscosity coefficients of two nematic liquid crystalline azoxybenzenes

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(Reçu le 2 août 1982, accepté le 14 octobre 1982)

Résumé. — On a construit un appareil pour mesurer les viscosités de cisaillement $\eta_1$, $\eta_2$, $\eta_3$ et $\eta_{12}$ de Miesowicz. Celles-ci sont déterminées lors de l'écoulement d'un liquide nématisque dans un capillaire rectangulaire qui fait partie d'un appareil thermostaté. L'ensemble est situé entre les pôles d'un électro-aimant pour contrôler le directeur $\mathbf{n}$. De plus, on a déterminé l'angle d'alignement par écoulement en mesurant la variation de la birefringence dans l'échantillon entre la situation où $\mathbf{n}$ est fixé parallèle à l'écoulement et celle où il est aligné par l'écoulement. On donne des résultats pour des ensembles complets de coefficients de viscosité de $p$-methoxy-$p'$-butylazoxybenzène et de $p, p'$-dibutylazoxybenzène. Les résultats sont bien en accord avec des rapports visco-élastiques obtenus par des techniques de diffusion de la lumière. La relation d'Onsager-Parodi est bien vérifiée compte tenu de la précision expérimentale.

Abstract. — To determine the Miesowicz viscosity coefficients a shear-flow set-up has been built, which allows the measurement of $\eta_1$, $\eta_2$, $\eta_3$ and $\eta_{12}$. These coefficients are determined by pressing the liquid crystal through a rectangular capillary which forms part of a thermostated set-up placed between the poles of a magnet in order to control the director $\mathbf{n}$. In addition, the flow-alignment angle $\theta_0$ is determined from the change in optical path difference between the ordinary and extraordinary components of polarized light, comparing the situation with $\mathbf{n}$ aligned along the flow-direction and with flow-alignment, respectively. Results are given for the complete set of viscosity coefficients of $p$-methoxy-$p'$-butylazoxybenzene and $p, p'$-dibutylazoxybenzene. The results show good agreement with visco-elastic ratios found with light-scattering techniques. Within the experimental accuracy the Onsager-Parodi relation is well fulfilled.

1. Introduction. — Though a nematic liquid crystal flows as easily as a conventional organic liquid consisting of similar molecules, an analysis of the viscosities turns out to be rather complicated when the state of alignment (given by the director $\mathbf{n}$) is considered. In the first place, the flow depends on the angles between $\mathbf{n}$ and the flow direction and the velocity gradient. Secondly, translational motions couple to inner orientational motions, and the flow will cause the director to rotate. This behaviour can be described by the hydrodynamic theory of Ericksen and Leslie [1], which involves six viscosity coefficients, of which five are independent [2].

Experimentally the direction of $\mathbf{n}$ must be controlled and/or measured, and conventional viscometric equipment is of little use. This is probably the cause that in spite of the importance of the viscosities for the dynamics of many physical effects (including the switching times of display devices) experiments that can be quantitatively interpreted are relatively scarce. Only recently some authors [3, 4, 6] have started systematic measurements again. Nevertheless, to obtain for a given compound a complete set of coefficients (if possible at all) one has to rely on data from various sources which often do not seem to be compatible [5]. The only exceptions are recent results by Knepe et al. [6-8].

In this paper we describe in some detail the viscous
behaviour of two nematic liquid crystals: p-methoxy-p'-butylazoxybenzene (N4) and p,p'-dibutylazoxybenzene (DIBAB). Four coefficients ($\eta_1$, $\eta_2$, $\eta_3$, and $\eta_{12}$, to be defined below) are obtained from shear-flow experiments in a magnetic field. In addition the flow-alignment angle $\theta_0$ is determined in a separate experiment, while moreover the rotational viscosity $\gamma_1$ is obtained from the dynamics of the Frederiks transition for twist. This latter type of measurement will be described in detail elsewhere [9]. The two compounds are chosen such that a comparison can be made with results for visco-elastic ratios obtained by Van Eck et al. [10] using light-scattering techniques.

2. Theory. — 2.1 MIESOWICZ VISCOSITIES. — We consider a simple shear-flow between two flat plates forming a rectangular capillary. Immediately three relevant geometries are evident (see Fig. 1) that give a viscosity coefficient and a shear-torque coefficient. The latter describes the torque on the director due to the shear:

(a) $n//\nu$: viscosity $\eta_1$, shear-torque coefficient $K_1$.

(b) $n//\nu$: viscosity $\eta_2$, shear-torque coefficient $K_2$.

(c) $n \perp (\nu, \nu)$: viscosity $\eta_3$, no shear-torque coefficient.

We have followed here the notation of Helfrich [11, 12]. In the original paper by Miesowicz [13] the definitions of $\eta_1$ and $\eta_2$ are interchanged. Apart from the shears depicted in figure 1 that are anti-symmetric in $x$ and $z$, also a coefficient $\eta_{12}$ exists that is symmetric in these coordinates. It cannot be visualized in a pure shear, but appears in the general expression for the effective viscosity $\eta_{\text{eff}}$ [2] when $n$ makes an arbitrary angle with $\nu$ and $\nu$ (see Fig. 2):

$$\eta_{\text{eff}} = (\eta_1 + \eta_{12} \cos^2 \theta) \sin^2 \theta \cos^2 \phi + \eta_2 \cos^2 \theta + \eta_3 \sin^2 \theta \sin^2 \phi.$$  

As we see the maximum contribution of $\eta_{12}$ is found if $n$ is in the shear-plane at an angle of 45° with $\nu$.

The volume flow rate $I$ for a liquid with viscosity $\eta$ through a rectangular capillary with length $l$, thickness $d$ and width $b$ is [14]

$$I = \frac{b d^3}{12 \eta l} \left[ 1 - \frac{192}{\pi^2} \frac{d^2}{b} \right] \Delta \rho = c_1 \frac{\Delta \rho}{\eta}.$$  

where $c_1$ is a geometrical factor and $\Delta \rho$ is the pressure difference over the capillary. Higher order terms in $d/b$ have been disregarded. In the experiment the liquid crystal flows through the capillary due to a pressure difference created between two gas-filled volumes on each side of the capillary, respectively. In this system the two volumes $V_1$ and $V_2$ are at pressures $p_1$ and $p_2$, respectively. If the flow starts at $t = 0$ then the pressure difference at a time $t$ will be

$$\Delta \rho(t) = p_1(t) - p_2(t),$$

and the volumes will be

$$V_1(t) = V_1(0) + \Delta V(t),$$

$$V_2(t) = V_2(0) - \Delta V(t),$$

where $\Delta V > 0$ indicates that the flow direction is from $V_1$ towards $V_2$. Using

$$p(t) V(t) = p(0) V(0)$$

we can now express $\Delta \rho(t)$ as a function of $V_1(0)$, $V_2(0)$, $p_1(0)$, $p_2(0)$ and $\Delta V(t)$. Taking into account that $\Delta V(t) \ll V_1(0)$ and $|V_1(0) - V_2(0)| \ll V_1(0)$ we find

$$\Delta \rho(0) - \Delta \rho(t) = \left\{ (p_1(0) V_1(0) + p_2(0) V_2(0)) / (V_1(0) V_2(0)) \right\} \Delta V(t) = c_2 \Delta V(t).$$

The constant $c_2$ depends only on the initial conditions. Knowing that $\Delta V(t) = \int_0^t I dt$, we can use relations (2) and (6) to find

$$\Delta \rho(t) = \Delta \rho(0) \exp(-ct/\eta)$$

where $c = c_1 c_2$. This allows us to calculate the viscosity coefficient $\eta$ from the measurement of $\Delta \rho(t)$.

In order to be able to interpret a specific $\eta_{\text{eff}}$, the orientation of the director must be controlled, for example by an external magnetic field. For the magnetic inductions $\mathbf{B}$ used in practice, and for typical values of an elastic constant $K$ and of the diamagnetic anisotropy $\Delta \chi$, the magnetic coherence length $\xi = (K \mu_0 |\Delta \chi|)^{1/2}/B$ is of the order of a few μm. The
misalignment due to wall effects and thus the influence of elastic torques is confined to small layers of this thickness close to the walls. They can be disregarded in comparison to the total thickness $d$. With the magnetic field in the shear-plane then two types of torques on the director of the flowing liquid crystal are left:

(a) The torque density $N_m$ exerted by the magnetic induction $B$, given by

$$N_m = \frac{1}{2} \mu_0^{-1} \Delta \chi B^2 \sin 2 \psi,$$

where $\psi$ is the angle between $B$ and $n$.

(b) The torque density $N_s$ from the shear:

$$N_s = - (\kappa_1 \sin^2 \theta + \kappa_2 \cos^2 \theta) \frac{\partial \nu}{\partial x}.$$

In equilibrium $N_m + N_s = 0$. Taking the magnetic field parallel to the $x$-axis (see Fig. 2), we find that for a large magnetic field $\theta$ is close to $90^\circ$ and

$$\tan \theta = \frac{\Delta \chi B^2}{\mu_0 \kappa_1}. $$

In the case of a large magnetic field along the $z$-direction we have $\theta \approx 0$ and find similarly:

$$\tan \theta = - \frac{\mu_0 \kappa_2}{\Delta \chi B^2}. $$

The expression for the velocity gradient $\partial \nu/\partial x$ can be derived from

$$v(x) = \nu_0 \left(1 - \frac{4 x^2}{d^2}\right) \frac{\Delta p}{8 \mu_0 \eta_{\text{eff}}} \left(1 - \frac{x^2}{d^2}\right). $$

From the equations above and equation (1) one can estimate, for a certain magnetic field strength, the maximum pressure difference $\Delta p$ that can be used without disturbing the uniform alignment appreciably.

2.2 FLOW-ALIGNMENT. — The total torque from the shear-flow on the director $n$, when it is in the shear-plane, is given by equation (9). In principle this allows for an equilibrium situation at which $N_s = 0$. This occurs for the angle $\theta_0$, the flow-alignment angle, given by

$$\tan^2 \theta_0 = - \frac{\kappa_2}{\kappa_1}. $$

Often $|\kappa_2| >> \kappa_1$, resulting in values for $\theta_0$ close to zero. If $\kappa_2/\kappa_1 > 0$ no solution for $\theta_0$ exists and the flow is not stable [3, 15, 16]. From thermodynamic considerations one finds that for rod-like molecules $\kappa_1 > 0$ [17], so that these instabilities are due to a positive sign of $\kappa_2$.

Following Gäthwiller [3] $\theta_0$ can be determined from the change in optical path difference between the ordinary and extraordinary components of polarized light by comparing the situation with $n$ magnetically aligned along $v$ and without a magnetic field, respectively. For $n$ parallel to the $z$-axis (see Fig. 3), the optical path difference $\Gamma_0$ will be

$$\Gamma_0 = (n_e - n_0) d,$$

$n_0$ and $n_e$ being the ordinary and extraordinary refractive indices, respectively. When $n$ makes an angle $\theta(x)$ with the $z$-axis, the optical path difference $\Gamma$ will be

$$\Gamma = \int_{-d/2}^{d/2} \left[n(\theta) - n_0\right] d\theta$$

$$\frac{1}{n^2(\theta)} = \frac{\sin^2 \theta}{n_0^2} + \frac{\cos^2 \theta}{n_e^2}.$$  

Without a magnetic field one can have a stable situation where the total shear-torque $N_s$ is zero. For sufficiently large shear-rates $\theta(x)$ tends to the value $\theta_0$, except for thin transition layers at the boundaries and in the middle. In that situation $\theta(x)$ will be given by (see Fig. 3)

$$\theta(x) = \begin{cases} \theta_0, & x > 0, \\ -\theta_0, & x < 0. \end{cases}$$

For small values of $\theta_0$ ($\sin^2 \theta_0 \ll 1$) the change in the optical path difference is

$$\Delta \Gamma = - \frac{1}{2} \kappa_2 d \left(\frac{n_e^2}{n_0^2} - 1\right) \sin^2 \theta_0.$$  

3. Experimental. — 3.1 SHEAR-FLOW. — For the shear-flow measurement a commercially obtainable rectangular flow capillary (Hellma Kuvette 136-OS) with a cross section of $0.20 \times 9.0$ mm is used. At the beginning and at the end of this type of capillary the flow direction is not parallel or orthogonal to the magnetic field (see Fig. 4). Therefore cut-outs have been made at both ends of the capillary so that these regions can be disregarded. This leaves an effective length of 27.8 mm. The two parts of the flow-cell are glued together. This causes the thickness $d$ of the capillary to increase to a value slightly larger than the specified $0.200 \pm 0.005$ mm. Knowledge of the exact value of $d$ is required, because $d$ appears to
Fig. 4. — (a) Side-view of the top and of the lower part of the rectangular capillary; (b) Top-view of the lower part of the rectangular capillary.

Therefore $d$ is determined by using two methods: directly by optical interference, and indirectly by measuring the viscosity of reference oils (Bendix no. 27 and no. 152). Typical results from both methods are $d = 0.204 \pm 0.002 \text{ mm}$ and $d = 0.205 \pm 0.002 \text{ mm}$ respectively, which shows that no further corrections are needed.

For each of the four viscosity coefficients ($\eta_1$, $\eta_2$, $\eta_3$ and $\eta_{12}$) a module has been constructed. For each module a brass holder keeps the capillary at the right position in the magnetic field (see Fig. 5). These modules fit into a heated chamber between the poles of the magnet. The walls of this chamber are electrically heated to a temperature somewhat below the required temperature and the final temperature inside the chamber is regulated with a hot air stream. The air is circulated from the heated chamber to a heat exchanger, which is connected to a constant temperature bath. Temperatures from $15 \degree C$ up to $80 \degree C$ have been obtained with an accuracy of $0.2 \degree C$. The temperature is measured with a thermocouple that is fixed to the brass holder of the capillary. The magnet is a Bruker BE15 with a gap of 54 mm and pole caps of 60 mm diameter, that can provide a magnetic field of 1.1 tesla.

The capillary is connected to a pressure difference system via two glass tubes. To avoid hydrostatic pressure differences the levels of the liquid in the glass tubes are always kept in the same horizontal plane. The pressure difference system consists of two large volumes ($V \approx 2 \times 10^{-3} \text{ m}^3$), an electronic manometer, and a valve to change the direction of the pressure difference over the capillary (see Fig. 5). The electronic manometer (Datametrics, Barocel 590/1400) is used to determine the pressure difference over the capillary. It has a capacitive sensing element and can measure pressure differences from $-1000 \text{ Pa}$ to $1000 \text{ Pa}$. The total diaphragm displacement, with full range pressure applied, is only $0.16 \times 10^{-6} \text{ m}^3$. For the range used in practice ($50$-$200 \text{ Pa}$) the accuracy is $0.05 \%$. To avoid pressure differences due to temperature differences between the volumes $V_1$ and $V_2$, the whole set-up is placed in a box in which the temperature is kept constant. A second manometer gives the total pressure in $V_1$. At the beginning of each measurement a pressure difference of about $100 \text{ Pa}$ is created manually. The actual measurement then consist of successive readings of the pressure difference and the thermo-voltage, which are recorded on tape at fixed time intervals for automatic data-handling.

3.2 FLOW-ALIGNMENT. — The module for $\eta_2$ is designed with holes so that a laser beam can pass through the sample, which is fitted with crossed polarizers at an angle of $45\degree$ with the flow-direction. At the start of a measurement the maximum magnetic field is applied to align $n$ parallel to the flow-direction. Then the field is switched-off, the angle $\theta$ changes from zero to the flow-alignment angle $\theta_0$, and the related change in the intensity of the laser beam is recorded as a function of time. From the change in optical path difference, equation (17), we can calculate the flow-alignment angle. The best result is achieved with a relatively thick capillary, $500 \mu\text{m}$ in our case.

4. Results. — When measuring the Miesowicz coefficients the director $n$ is aligned by a magnetic field. Two effects might disrupt the uniform orientation of $n$:

(a) In the situation corresponding to $\eta_1$ or $\eta_2$, the shear-torque tries to misalign the director.
(b) Due to the boundary conditions a boundary layer may exist in which the director does not have the required direction.

The first effect is determined by the values of the magnetic field and the pressure difference (Eq. (10) and (11)). The magnet has a maximum field of 1.1 T and we use a pressure difference of 100 Pa or less. With these values we calculate that in the worst case this leads to an increase of 0.5% in the value of \( \eta_1 \), and will be of no significance in the case of \( \eta_2 \). The correction for \( \eta_1 \) given by Kneppe et al. [6] assuming \( \eta_2 = \eta_1 = 0 \) gives a similar result.

The second problem is the surface-alignment. Kneppe et al. [6] assumed that due to boundary conditions at the surface of the capillary there is a boundary layer with viscosity \( \eta_s \), while the bulk layer has the required viscosity \( \eta_1 \). With this division into two regions they calculated:

\[
\frac{1}{\eta_i} = \frac{1}{\eta_s} + \frac{\text{const.}}{B} \left( \frac{1}{\eta_1} - \frac{1}{\eta_s} \right), \quad i = 1, 2, 3, \tag{18}
\]

with \( \eta_{i1} \) being the measured viscosity. If one plots \( 1/\eta_{i1} \) against \( 1/B \) one can find \( \eta_s \) by extrapolating to \( 1/B = 0 \) (see Fig. 6). Another possibility to avoid alignment problems is to give the surface of the capillary the proper boundary conditions. For the case of \( \eta_1 \) a dope, 0.1% cetyltrimethylammonium-bromide (CTAB) [ref. 2b, Ch. 2] was added to the liquid crystal to get homeotropic boundary conditions. Results for the case of DIBAB with and without this dope are shown in figure 6 together with the results for \( \eta_2 \) and \( \eta_3 \).

The results of the measurements of the Miesowicz coefficients of N4 and DIBAB are given in figures 7 and 8. For \( \eta_2 \) and \( \eta_3 \) they can also be found in tables I

Table I. — Results for the viscosities of N4 (\( T_c = 73.8 \, ^\circ\text{C}, \gamma_1 \) from [9], \( \eta_1 \) calculated via eq. (21)).

<table>
<thead>
<tr>
<th>( T (^\circ\text{C}) )</th>
<th>( \eta_2 ) (Pa.s)</th>
<th>( \eta_3 ) (Pa.s)</th>
<th>( \eta_{45} ) (Pa.s)</th>
<th>( \theta_0 )</th>
<th>( \gamma_1 ) (Pa.s)</th>
<th>( \eta_1 ) (Pa.s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>0.024</td>
<td>0.047</td>
<td>—</td>
<td>4.2°</td>
<td>0.152</td>
<td>0.178</td>
</tr>
<tr>
<td>30</td>
<td>0.021</td>
<td>0.040</td>
<td>—</td>
<td>4.3°</td>
<td>0.122</td>
<td>0.144</td>
</tr>
<tr>
<td>34</td>
<td>0.017</td>
<td>0.034</td>
<td>0.051</td>
<td>4.5°</td>
<td>0.099</td>
<td>0.117</td>
</tr>
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<td>38</td>
<td>0.015</td>
<td>0.028</td>
<td>0.044</td>
<td>4.7°</td>
<td>0.081</td>
<td>0.097</td>
</tr>
<tr>
<td>42</td>
<td>0.013</td>
<td>0.025</td>
<td>0.039</td>
<td>5.1°</td>
<td>0.067</td>
<td>0.081</td>
</tr>
<tr>
<td>46</td>
<td>0.012</td>
<td>0.021</td>
<td>0.034</td>
<td>5.5°</td>
<td>0.056</td>
<td>0.069</td>
</tr>
<tr>
<td>50</td>
<td>0.011</td>
<td>0.018</td>
<td>0.030</td>
<td>6.1°</td>
<td>0.046</td>
<td>0.058</td>
</tr>
<tr>
<td>54</td>
<td>0.010</td>
<td>0.015</td>
<td>0.027</td>
<td>6.8°</td>
<td>0.038</td>
<td>0.049</td>
</tr>
<tr>
<td>58</td>
<td>0.009</td>
<td>0.013</td>
<td>0.023</td>
<td>7.7°</td>
<td>0.032</td>
<td>0.042</td>
</tr>
<tr>
<td>62</td>
<td>0.008</td>
<td>0.012</td>
<td>0.019</td>
<td>8.8°</td>
<td>0.026</td>
<td>0.035</td>
</tr>
<tr>
<td>66</td>
<td>0.007</td>
<td>0.011</td>
<td>0.015</td>
<td>10.4°</td>
<td>0.022</td>
<td>0.031</td>
</tr>
<tr>
<td>70</td>
<td>0.007</td>
<td>0.010</td>
<td>0.013</td>
<td>13.2°</td>
<td>0.017</td>
<td>0.026</td>
</tr>
</tbody>
</table>
and II where also the clearing temperatures \( T_c \) are indicated. \( \eta_{12} \) is calculated from \( \eta_{45} \) using

\[
\eta_{12} = 4 \eta_{45} - 2(\eta_1 + \eta_2). \tag{19}
\]

The results are given in figure 9 for N4 only.

With the flow-alignment set-up \( \theta_0 \) has been measured for N4 and DIBAB (see Fig. 10 and tables I and II). The errors due to the assumption \( \sin^2 \theta \ll 1 \) (eq. (17)) are smaller than the experimental errors. In addition \( p,p' \)-octylcyanobiphenyl (8CB) has been considered, for which Skarp et al. [15] found that for temperatures below \( (T_c - 1) \) °C no flow-alignment exists. Our measurements (see Fig. 11 and table III) are in agreement with these results.

5. Discussion. — We have so far considered five viscosity coefficients. As already mentioned, the hydrodynamic theory of nematic liquid crystals involves six viscosity coefficients. In order to obtain the full set we have to rely on the Onsager-Parodi relation [18], which can be written in the form

\[
\eta_1 - \kappa_1 = \eta_2 - \kappa_2. \tag{20}
\]

In principle one can check this equation experimentally if we use additional results for the rotational viscosity \( \gamma_1 = \kappa_1 + \kappa_2 \) from Van Dijk et al. [9]. In practice, however, equation (20) is always fulfilled within the experimental accuracy due to the relatively large errors in \( \eta_1 \). This is best illustrated when (20) is rewritten in quantities that are directly measurable:

\[
\eta_1 = \eta_2 + \gamma_1 \left( \frac{1 + \tan^2 \theta_0}{1 - \tan^2 \theta_0} \right). \tag{21}
\]

The results for \( \eta_1 \) calculated in this way and measured directly are compared in table IV. For N4 a comparison with direct measurements of \( \eta_1 \) and with the results from Knepp et al. [7] is given in figure 7. Application of equation (21) gives values for \( \eta_1 \) with errors of less than 5 %. The results for \( \eta_1 \) of N4 and DIBAB obtained in this way are given in tables I and II.

We can also compare our results with visco-

<table>
<thead>
<tr>
<th>( T (^\circ \text{C}) )</th>
<th>( \eta_2 ) (Pa.s)</th>
<th>( \eta_3 ) (Pa.s)</th>
<th>( \theta_0 )</th>
<th>( \gamma_1 ) (Pa.s)</th>
<th>( \eta_1 ) (Pa.s)</th>
</tr>
</thead>
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<td>0.059</td>
<td>0.076</td>
</tr>
<tr>
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<td>—</td>
<td>6.0</td>
<td>0.055</td>
<td>0.072</td>
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<tr>
<td>23</td>
<td>0.015</td>
<td>0.025</td>
<td>6.7</td>
<td>0.051</td>
<td>0.067</td>
</tr>
<tr>
<td>24</td>
<td>0.014</td>
<td>0.023</td>
<td>7.5</td>
<td>0.046</td>
<td>0.063</td>
</tr>
<tr>
<td>25</td>
<td>0.014</td>
<td>0.023</td>
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<td>0.042</td>
<td>0.058</td>
</tr>
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<td>0.022</td>
<td>9.5</td>
<td>0.038</td>
<td>0.055</td>
</tr>
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<td>27</td>
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<td>0.021</td>
<td>10.5</td>
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<td>0.021</td>
<td>12.0</td>
<td>0.029</td>
<td>0.045</td>
</tr>
<tr>
<td>29</td>
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<td>0.020</td>
<td>13.6</td>
<td>0.024</td>
<td>0.041</td>
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<tr>
<td>30</td>
<td>0.013</td>
<td>0.020</td>
<td>16.0</td>
<td>0.019</td>
<td>0.035</td>
</tr>
</tbody>
</table>

Table III. — Results for \( \theta_0 \) of 8CB \( (T_c = 40.1 \, ^\circ \text{C}). \)

<table>
<thead>
<tr>
<th>( T (^\circ \text{C}) )</th>
<th>( \theta_0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>39.1</td>
<td>6.2°</td>
</tr>
<tr>
<td>39.3</td>
<td>8.9°</td>
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<td>39.6</td>
<td>12.0°</td>
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<td>39.7</td>
<td>12.9°</td>
</tr>
<tr>
<td>39.8</td>
<td>13.8°</td>
</tr>
</tbody>
</table>
Table IV. — Validity of the Onsager-Parodi relation (Eq. (21)) for some compounds at 25 °C.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\eta_1 (10^{-3} \text{ Pa.s})$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>direct</td>
</tr>
<tr>
<td>N4</td>
<td>170 ± 17</td>
</tr>
<tr>
<td>DIBAB</td>
<td>55 ± 5</td>
</tr>
<tr>
<td>MBBA</td>
<td>136 ± 6 (°)</td>
</tr>
<tr>
<td>5CB</td>
<td>114 ± 5 (°)</td>
</tr>
</tbody>
</table>

(*) From Knepp et al. [6, 8] and Gähwiller [21].
(*) From Knepp et al. [7, 8] and Skarp et al. [4].

The results for these ratios are compared in figures 12-14. When calculating the ratios for N4 the elastic constants from De Jeu et al. [19] were used, and for DIBAB $K_1$ and $K_3$ from De Jeu et al. [20] and $K_2$ from Van Dijk et al. [9]. Comparing the results we note that the visco-elastic ratios from light-scattering are in several cases higher than the results from flow-measurements, especially for $\eta_{\text{twist}}/K_2$. From equations (22) and (23) one necessarily finds that $\eta_{\text{splay}}/\eta_{\text{twist}} \leq 1$, but from light-scattering it was found that $\eta_{\text{splay}}/\eta_{\text{twist}} > 1$. This means that the values for $\eta_{\text{splay}}/K_1$ from light-scattering are probably too high. In the case of N4 the results of $\eta_{\text{twist}}/K_2$ and $\eta_{\text{bend}}/K_3$ are in good agreement for both techniques.

Knepp et al. [7] have discussed the dependence of the viscosities of several nematics on the temperature (via an activation energy) and on the orientational order. In particular they observed that $\eta_1/\bar{\eta}_1$, where $\bar{\eta}_1 = \frac{1}{3}(\eta_1 + \eta_2 + \eta_3)$, shows a rather universal behaviour. Our results for DIBAB fit into this general trend.

We conclude from our results that it is quite possible to determine with a reasonable accuracy a complete set of nematic viscosities from flow-measurements. Some complications arise with the geometry for $\eta_1$ because of unfavourable boundary effects. An additional measurement of the rotational viscosity $\gamma_1$ makes it possible to get around these problems in a simple way. Finally we note that Leslie has described the nematic viscosities with a set of coefficients $a_1, ..., a_6$, different from the more experimental ones used in this paper. Via the known relations (Ref. [21]) these can, if desired, be calculated from the results given.

Acknowledgments. — This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (Foundation for Fundamental research on Matter-FOM) and was made possible with financial support from the Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek (Netherlands Organization for the Advancement of Pure Research-ZWO).
References


