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Determination of the rotational viscosity of nematic liquid crystals over an extended range

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A method for measuring rotational viscosities of nematic liquid crystals is described. Rotational viscosities from 10^{-3} to 10^6 Pa s can be determined if this method is combined with the usual rotating field method using the same device. Furthermore, non-newtonian behaviour can be detected by the new method.

1. Introduction

The switching element of a liquid crystal display is usually a nematic liquid crystal film between two glass plates. The response time of such a display is determined mainly by the rotational viscosity of the liquid crystal, which depends strongly on temperature. Because of the growing interest in outdoor applications, the temperature dependence of the rotational viscosity is one of the most important properties of a nematic material for liquid crystal displays. There are many methods of determining rotational viscosities at high temperature [1–7], but at low temperature all these methods become very time consuming. The fastest are the relaxation methods [2–4, 6, 7], but they require the determination of additional quantities which vary with temperature.

We have developed a new method of measuring rotational viscosities between 1 and 10^6 Pa s. The liquid crystal sample is placed in a magnetic field and suspended from a torsion wire. The suspension of the wire can be rotated through a certain angle. The time constant of the subsequent relaxation to the new equilibrium position allows the rotational viscosity γ_1 to be determined. This method complements the rotation method which allows the determination of γ_1 with values between 10^{-3} and 10 Pa s, and both methods can be used with the same experimental device. As the new method applies different angular velocities and torques during the measurement, the observation of non-newtonian behaviour, which seems to be an important effect in polymeric liquid crystals, is possible.

2. Theory

A theory for the rotational movement of a nematic liquid crystal sample in a magnetic field under the influence of mechanical and viscous torques is developed. The mechanical torque is exerted on the sample vessel by the torsion of a suspension wire. A viscous torque is generated in the nematic liquid crystal if the director rotates with respect to the liquid. In this development we use the following symbols: D is the torsion constant of the wire; V is the volume of the sample; B is the magnetic induction; I is the motion of inertia; Θ is the angle between the director and magnetic field (see figure 1, $\Theta > 0$); Φ is the torsion angle of the wire (see figure 1, $\Phi > 0$);

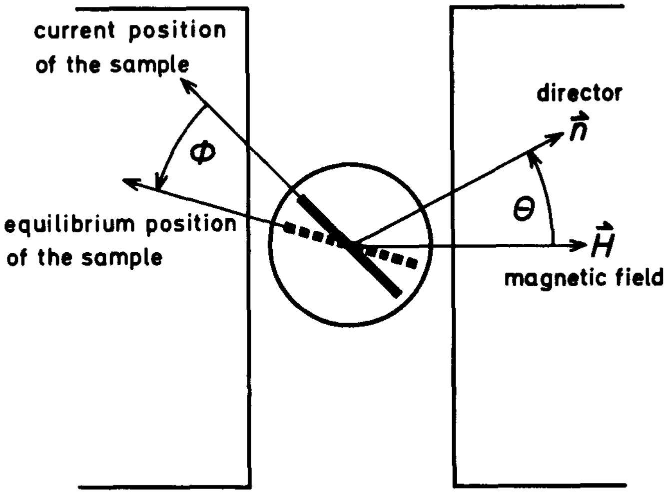

Figure 1. Definition of the angles Θ and Φ. The solid and the broken lines in the circle (a cross-section of the tube containing the liquid crystal) denote two mirror positions.

ω is the angular velocity of the director with respect to the liquid; χ_a is the anisotropy of the magnetic susceptibility; γ_1 is the rotational viscosity.

We make the following assumptions:

(1) The acceleration term ($I\, d^2\Phi/dt^2$) can be neglected.
(2) The flow of the liquid crystal with respect to the sample tube can be neglected.
(3) The director is uniformly aligned in the sample.
(4) The damping of the sample by the surrounding gas and the suspension wire can be neglected.
(5) The back-flow effect can be neglected.

The following torques are taken into account:

the mechanical torque of the suspension wire $D\Phi$,

the magnetic torque

$$-\frac{\chi_a B^2 V}{\mu_0}\sin\Theta\cos\Theta,$$

and the viscous torque

$$-\gamma_1 \omega V = -\gamma_1 \frac{d(\Theta + \Phi)}{dt} V.$$

The balance of the external torques leads to

$$D\Phi - \frac{\chi_a B^2 V}{\mu_0}\sin\Theta\cos\Theta = 0 \qquad (1)$$

and the balance of the torques on the director gives

$$-\gamma_1 V \frac{d(\Theta + \Phi)}{dt} - \frac{\chi_a B^2 V}{\mu_0}\sin\Theta\cos\Theta = 0. \qquad (2)$$

Elimination of the magnetic torques in equations (1) and (2) gives

$$D\Phi = -\gamma_1 V \frac{d(\Theta + \Phi)}{dt}. \qquad (3)$$

For $\Theta \ll \Phi$ (i.e. $D\mu_0/\chi_a B^2 V \ll 1$), $d\Theta/dt$ can be neglected and the resulting differential equation can be integrated to give

$$\Phi = \Phi_0 \exp(-t/\tau) \tag{4}$$

where $\tau = \gamma_1 V/D$. If the equilibrium position is changed the sample tube performs an exponential rotational movement to the new equilibrium position. As all the quantities in equation (4) are easily determined, this method allows the rotational viscosity to be calculated very simply. Since this method uses a relaxation process for the measurement of γ_1, it is called a relaxation method in contrast to the rotation method, which uses a permanently rotating magnetic field [1] or sample [5].

The main advantage of this relaxation method is that the driving moment during the relaxation process is the torsion moment of the suspension wire. Therefore, only the torsion constant of the wire has to be known in addition to the relaxation time τ. Other relaxation methods use elastic [3, 6, 7] or magnetic [2, 4] moments, in which case it is necessary to measure also the elastic constants or the anisotropy of the magnetic susceptibility.

If the condition $\Theta \ll \Phi$ is not fulfilled, the differential $d\Theta/dt$ in equation (3) has to be calculated from equation (1)

$$\begin{aligned} D\frac{d\Phi}{dt} &= \frac{\chi_a B^2 V}{\mu_0}\cos 2\Theta \frac{d\Theta}{dt} \\ &= \frac{\chi_a B^2 V}{\mu_0}\left[1 - \left(\frac{2\mu_0 D}{\chi_a B^2 V}\Phi\right)^2\right]^{1/2}\frac{d\Theta}{dt}. \end{aligned} \tag{5}$$

Insertion of this in equation (3) leads to

$$D\Phi = -\gamma_1 V\left[1 + \frac{1}{(a^2 - 4\Phi^2)^{1/2}}\right]\frac{d\Phi}{dt}. \tag{6}$$

Integration gives

$$\ln\Phi - \frac{1}{a}\operatorname{artanh}(1 - 4\Phi^2/a^2)^{1/2} = -\frac{t}{\tau} + C, \tag{7}$$

where $a = \chi_a B^2 V/\mu_0 D$. Equation (7) has no real solution for

$$4\Phi^2/a^2 > 1 \tag{8}$$

or

$$|\Phi| > \frac{\chi_a B^2 V}{2\mu_0 D}.$$

For higher values of Φ, the torsion moment of the wire exceeds the maximum magnetic moment, which is $\chi_a B^2 V/2\mu_0$.

For small values of Φ/a, equation (6) can be simplified to

$$\begin{aligned} D\Phi &= -\gamma_1 V\left[1 + \frac{1}{a(1 - 4\Phi^2/a^2)^{1/2}}\right]\frac{d\Phi}{dt} \\ &\approx -\gamma_1 V\left(1 + \frac{1}{a}\right)\frac{d\Phi}{dt}, \end{aligned} \tag{9}$$

and an exponential rotational movement to the equilibrium position results. The effective rotational viscosity $\gamma_{1,\mathrm{eff}}$ for an evaluation with equation (4) is therefore

$$\gamma_{1,\mathrm{eff}} = \gamma_1\left(1 + \frac{1}{a}\right). \tag{10}$$

Evaluation of γ_1 with equation (7) or (4) and equation (10) requires B and χ_a to be determined as well. For very viscous samples, χ_a can be determined, by a method developed for smectic samples [8], from measurement of the oscillation period of the sample in a magnetic field using the same set-up.

At this point some remarks on the assumptions (1)–(5) should be made.

(1) The ratio of the acceleration term to one of the terms in equation (1) amounts to $I/D\tau^2$. This ratio is less than 2×10^{-4} under our experimental conditions ($\tau > 200\,\mathrm{s}$).

(2) The ratio of the relaxation constant for the damping of flow of the liquid crystal to the relaxation constant τ amounts to $\varrho R^2/\tau\eta$, where η is a mean shear viscosity coefficient. This ratio is less than 5×10^{-5}.

(3) The ratio of the volume with surface alignment to that with field alignment amounts to $2\xi/R$ [5], where ξ is the magnetic coherence length. This ratio is less than 6×10^{-4}. Furthermore, it can be shown that the influence of flow alignment caused by the flow described under (2) is of the same order of magnitude as the influence of the flow itself.

(4) The ratio of the damping term to one of the terms in equation (1) is $(\ln d)\,(I/D)^{1/2}/\pi\tau$ where $d = 1{\cdot}045$ is the decrement for a free oscillation of a solid sample. This ratio is less than 2×10^{-4}.

(5) A detailed discussion of the influence of back-flow is given in [5].

3. Experimental

The experimental set-up has been described in detail elsewhere [5], and so we give only a short description, including some improvements that have been made. Figure 2 shows the set-up. The sample tube T1 (high-precision N.M.R. sample tube, 15 mm diameter) contains the liquid crystal C (2–8 cm^3) and is suspended from the glass rod R and the torsion wire W (spring steel wire, 70 μm diameter, 1 m long). It can be rotated by means of the stepping motor S (1000 steps per revolution). The sample is placed between the pole faces P of an electromagnet (25 cm pole face diameter, 50 mm pole gap, 0–1·6 T) and surrounded by a double-walled glass tube T2 which is kept at constant temperature, to within $\pm 0{\cdot}02$ K, by means of a thermostat. The laser L, the mirror M and 30 differential photodiodes D form the detection system for the rotational movement of the sample. The photodiodes and the stepping motor are connected to a personal computer for data acquisition. Additionally, this allows a greater variety of measuring modes to be used.

High rotational viscosities are measured as follows. The magnet or the stepping motor is rotated to a position in which no magnetic torque is exerted on the sample. The stepping motor is then rotated by one revolution in about 100 s. After the motor has stopped, the rotation of the sample is determined as a function of time ($\Phi = \Phi(t)$) and the rotational viscosity is calculated from equation (4). For very viscous samples, the rotation of the director with respect to the sample vessel can be neglected during the rotation of the stepping motor, and the angle Θ between the director and the magnetic field corresponds, therefore, to the vessel rotation directly after the end of the motor rotation. This angle should be small compared with Φ_0 for an evaluation

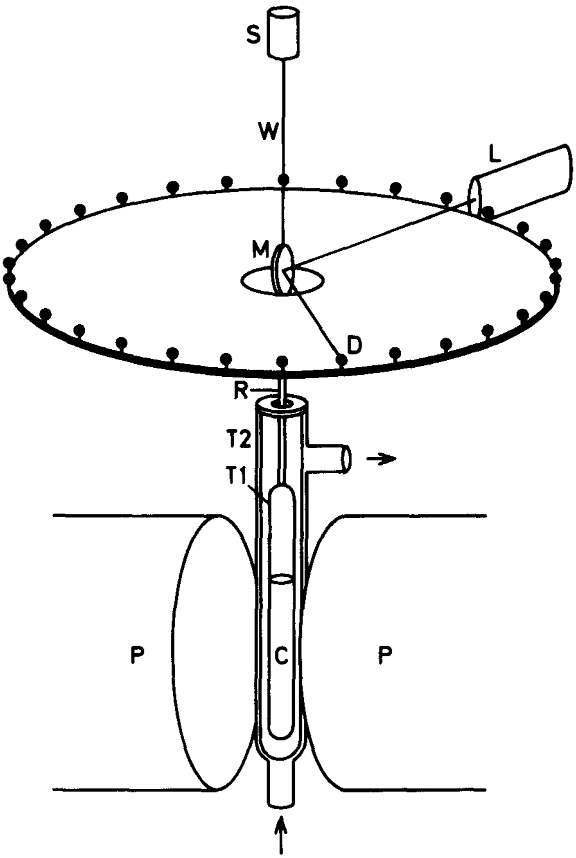

Figure 2. The experimental set-up.

according to equation (4). As the ratio Θ/Φ is nearly independent of temperature (see equation (1)), one determination at low temperature is sufficient.

The liquid crystal studied was ZLI 2248 (Merck AG) which is a commercial mixture for twisted nematic displays. The clearing point temperature is 85–97°C; no smectic phase or crystallization could be detected for $T > -65°C$.

4. Results and discussion

Experimental results and the predicted dependence (see equation (4)) of the angle Φ (see figure 1) on time are shown in figure 3; γ_1 is easily calculated from the slope for known sample volume and torsion constant of the wire. Deviations from the logarithmic dependence can result from the non-cylindrical shape or magnetic properties of the sample vessel, from the formation of disclinations in the sample and from failure of the assumptions leading to equation (4). The influences of the sample vessel and the disclinations were studied as follows. The equilibrium positions of the sample vessel filled with liquid crystal ZLI 2248 were determined for different directions of the magnetic field (1·5 T) at 60°C (nematic phase) and 90°C (isotropic phase); the maximum deviation from the zero-field equilibrium position was 2° (this corresponds to an error of about 1 per cent in the angle Φ). The deviation increases with the strength of the magnetic field. However, the maximum torque which can be exerted by the torsion

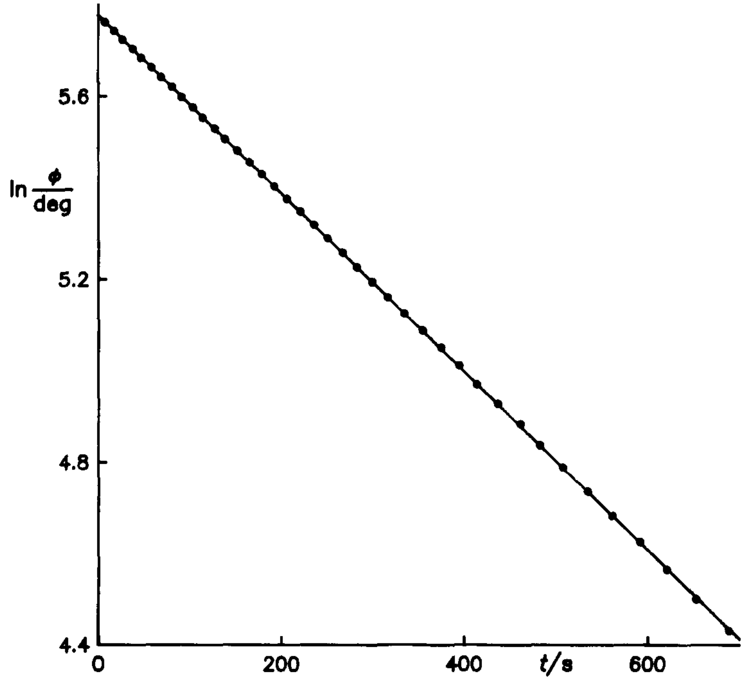

Figure 3. Logarithm of the angle Φ (see figure 1) versus time after a rotation of the torsion wire suspension.

wire also depends on the field strength (see equation (8)), and therefore no advantage results from the use of smaller field strengths.

These deviations lead to a lower limit for the torsion constants and, therefore, to a lower limit for the liquid crystal volume. We were able to measure the rotational viscosity of smaller samples (10 mm N.M.R. tube diameter, sample volume 1 cm^3) with an error of about 5 per cent. If the influence of the non-cylindrical sample vessel is taken into account in the evaluation of γ_1, it may be possible to reduce the minimum amount of liquid crystal required for a measurement.

Equation (7) predicts a non-logarithmic rotational movement to the equilibrium position for small values of a. We have therefore determined χ_a from the oscillation period of the sample, and found $\chi_a = 1{\cdot}35 \times 10^{-6}$ (SI), nearly independent of temperature at low temperatures. This leads to a value of $1/a = 0{\cdot}008$ for the correction term in equation (7) for the conditions usually used ($B = 1{\cdot}5$ T, $V = 8$ cm^3, and $D = 1{\cdot}56 \times 10^{-7}$ Nm (70 μm wire)). This correction is too small to give deviations from a logarithmic dependence. There should be a difference of only about 1 per cent between the rotational viscosity and its effective value determined by experiment.

In order to have a further check on the dependence of $\gamma_{1,\mathrm{eff}}$ on the field strength, we have performed relaxation experiments in magnetic fields of different strengths. Figure 4 shows that the dependence $(\gamma_{1,\mathrm{eff}} - \gamma_1) \propto 1/B^2$, which is predicted by equation (10), is observed within the errors of measurement. However, it should be noted that the slope of the line is only half the theoretical slope, $\gamma_1 \mu_0 D/\chi_a V$. This difference is probably caused by the fixed alignment of the director at the inner surface of the sample vessel leading to a hindered rotation of the director in the outer part of the sample and to a formation of disclinations. The magnetic coherence length of about 5 μm at 0·6 T in which these effects should take place is too small to explain

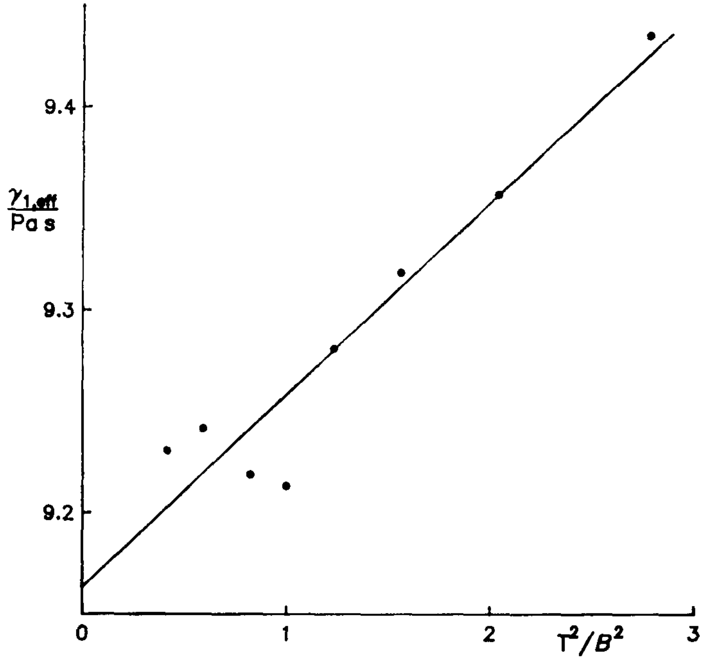

Figure 4. Effective rotational viscosity $\gamma_{1,\mathrm{eff}}$ as a function of $1/B^2$ at a temperature of $-30{\cdot}0$°C.

the observed deviation and leads to a different dependence on B ($(\gamma_{1,\mathrm{eff}} - \gamma_1) \propto 1/B$). However, it is known from measurements in rotating magnetic fields [9] that the plot of the viscous torque M versus angular velocity ω of the rotating field does not follow the theoretical dependence $M \propto \omega$ at high velocities, but shows a strong decrease of M if ω approaches the critical velocity ω_c. This effect arises when parts of the sample in the outer sample area which cannot follow the rotation of the magnetic field begin to tumble. Under our experimental conditions, the mean angular velocity corresponds to a critical field $B_c = 0{\cdot}5$ T. Since the low field strengths in figure 4 are comparable to this critical field the observed deviations may be explained by this effect.

Figure 5 shows the temperature dependence of the rotational viscosity of liquid crystal ZLI 2248 over a range of seven orders of magnitude in γ_1. Measurements of γ_1 at higher temperatures were performed by the rotation method. At -25 and -30° C, both methods were used and differences of about 1 per cent were found. Recently, we were able to determine γ_1 above 10^6 Pa s in polymeric liquid crystals [10]. The whole temperature dependence of the rotational viscosity can be described by an equation [5, 6] which takes into account the influence of the order parameter in the neighbourhood of the clearing point (the pre-exponential term in equation (11)) and the excess exponential increase at low temperatures (the denominator in the exponential term):

$$\gamma_1 = A\left(1 - \frac{T}{T^*}\right)^{2\beta} \exp\left(\frac{B}{T - T_0}\right). \tag{11}$$

Here T^* is the temperature at which the order parameter would vanish in a second-order transition, and T_0 is the temperature at which the rotational movement of the molecules would be frozen in. Probably, this Vogel-type dependence on temperature

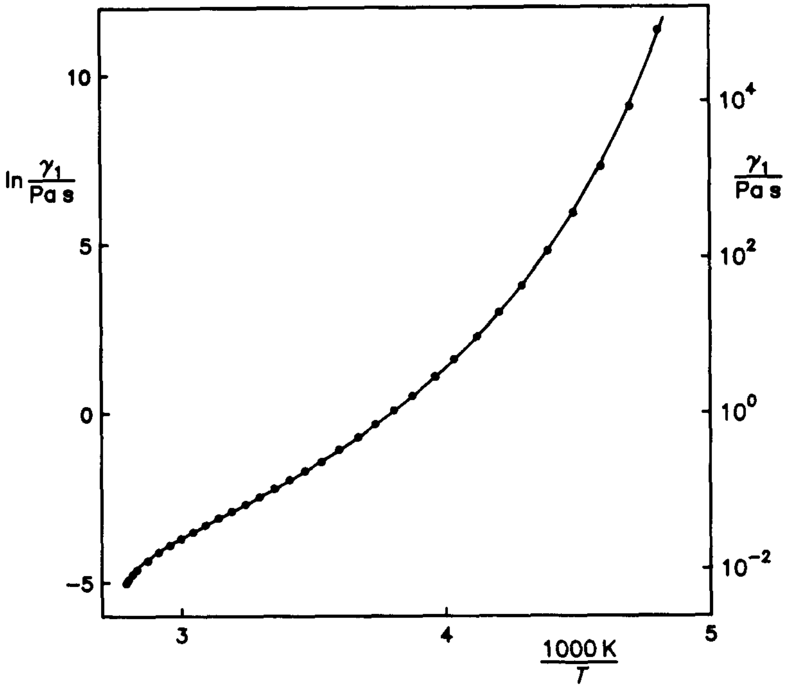

Figure 5. Temperature dependence of the rotational viscosity of liquid crystal ZLI 2248. The solid curve was calculated from equation (11) with $A = 4{\cdot}44 \times 10^{-4}$ Pa s, $\beta = 0{\cdot}145$, $T^* = 360{\cdot}11$ K, $B = 735{\cdot}19$ K and $T_0 = 169{\cdot}09$ K; these parameters were obtained by fitting equation (11) to the experimental data with the Marquardt algorithm.

is only valid for a limited temperature region. We assume that, at temperatures below T_0, γ_1 is also finite but shows a higher activation energy for the temperature dependence, as observed for the shear viscosity in isotropic liquids [11].

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