Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Direct Determination of the Five Independent Viscosity Coefficients of Nematic Liquid Crystals

Ch. Gähwiller [a]

[a] Physics Department, F. Hoffmann-La Roche & Co, 4002, Basle, Switzerland

Version of record first published: 28 Mar 2007.

To cite this article: Ch. Gähwiller (1973): Direct Determination of the Five Independent Viscosity Coefficients of Nematic Liquid Crystals, Molecular Crystals and Liquid Crystals, 20:3-4, 301-318

To link to this article: http://dx.doi.org/10.1080/15421407308083050

Molecular Crystals and Liquid Crystals. 1973. Vol. 20, pp. 301–318

Printed in Great Britain

Direct Determination of the Five Independent Viscosity Coefficients of Nematic Liquid Crystals

CH. GÄHWILLER

Physics Department
F. Hoffmann-La Roche & Co.
4002 Basle, Switzerland

Received June 5, 1972

Abstract—A novel experimental procedure combining the measurement of (i) the flow velocity and (ii) the change in birefringence induced by laminar flow in a magnetic field has been used to determine the complete set of the five independent shear-viscosity coefficients of nematic liquid crystals. The anisotropy of the magnetic susceptibility is obtained as well. Results are reported for *p'*-methoxybenzylidene-*p*-*n*-butylaniline (MBBA), *p*-*n*-hexyloxybenzylidene-*p'*-aminobenzonitrile (HBAB), and a 1:1:1-molar mixture of HBAB with *p*-*n*-butoxybenzylidene-*p'*-aminobenzonitrile and *p*-*n*-octanoyloxybenzylidene-*p'*-aminobenzonitrile.

1. Introduction

Viscosity measurements have been performed on liquid crystals since long ago, principally on the nematic mesophase.[1] It is only in the past few years however, that a consistent continuum theory describing the fundamental hydrodynamic properties of liquid crystals has been formulated by Ericksen[2] and Leslie.[3] A more general derivation of this theory has been given since by Forster *et al.*[4] and by Huang.[5]

The stresses produced by shear in a nematic liquid crystal depend on the relative orientation of the nematic axis and may be asymmetric, thus involving a torque. There appear five independent coefficients with the dimension of a viscosity in the dissipative part of the stress tensor, respectively seven if the two compressional viscosities are included. Several experimental methods have been used to determine these coefficients: viscometry with uniformly oriented samples,[6,7] absorption of ultrasonic shear waves,[8,9] spectroscopy of the light scattered by the long wavelength fluctuation

of the director.[10] So far a complete set of these coefficients has been reported only for p, p'-dimethoxy-azoxybenzene (p-azoxyanisole, PAA)[10] and at room temperature for p'-methoxybenzylidene-p-n-butylaniline (MBBA).[11]

In the present work we have determined all five viscosity coefficients over the entire nematic phase of

(i) p-n-hexyloxybenzylidene-p'-aminobenzonitrile (HBAB),

(ii) a 1 : 1 : 1-molar mixture of HBAB with p-n-butoxybenzylidene-p'-aminobenzonitrile and p-n-octanoyloxybenzylidene-p'-aminobenzonitrile,[12] and

(iii) MBBA.

These compounds are nematic over the range of 55–101.7 °C, 20–97.5 °C, and 18–43.0 °C respectively. We have developed a novel experimental procedure combining the determination of the change in birefringence induced by a laminar flow through a capillary of rectangular cross section with the measurement of the flow velocity. Uniform orientation (other than wall or flow induced) of the nematic in various directions was achieved with a magnetic field. This method allowed also the determination of the anisotropy of the magnetic susceptibility. The basic equations necessary for the analysis of the data are presented in Sec. 2. In Sec. 3 we describe in detail the experimental methods and the results are discussed in Sec. 4.

2. Laminar Flow in a Magnetic Field

The stability of laminar flow of a nematic in a magnetic field has been discussed in detail by Ericksen[13] and Leslie.[14] We shall recall here the most essential features pertinent to the determination of the viscosities. Suppose a nematic flowing in the z-direction between two glass plates normal to the X-axis. A uniform orientation of the molecules is achieved by means of a magnetic field in a fixed direction given by the unit vector

$$\mathbf{L} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta) \tag{1}$$

where θ is defined as the angle between the director and the flow direction, and ϕ as the angle between the direction of the velocity gradient and the projection of the director on the xy-plane.

The velocity in the nematic is

$$\mathbf{v} = (0, 0, u(x)). \tag{2}$$

With this geometry the xz and zx components of the dissipative part of the stress tensor as given by Leslie become

$$\sigma_{xz} = \frac{1}{2}\frac{\mathrm{d}u}{\mathrm{d}x}[(2\alpha_1 \cos^2\theta - \alpha_2 + \alpha_5)\sin^2\theta\cos^2\phi + (\alpha_3 + \alpha_6)\cos^2\theta + \alpha_4] \tag{3}$$

and

$$\sigma_{zx} = \frac{1}{2}\frac{\mathrm{d}u}{\mathrm{d}x}[(2\alpha_1 \cos^2\theta - \alpha_3 + \alpha_6)\sin^2\theta\cos^2\phi + (\alpha_2 + \alpha_5)\cos^2\theta + \alpha_4]. \tag{4}$$

Here the α's have the dimension of a viscosity, they are related through the Parodi–Onsager relation[15]

$$\alpha_2 + \alpha_3 = \alpha_6 - \alpha_5. \tag{5}$$

The effective viscosity η, i.e. the viscosity of an isotropic liquid which leads to the same frictional forces as the nematic, is defined by

$$\sigma_{xz} = \eta\frac{\mathrm{d}u}{\mathrm{d}x}. \tag{6}$$

Hence

$$\begin{aligned}\eta &= \eta(\theta, \phi)\\ &= (\eta_1 + \eta_{12}\cos^2\theta)\sin^2\theta\cos^2\phi + \eta_2\cos^2\theta + \eta_3\sin^2\theta\sin^2\phi\end{aligned} \tag{7}$$

where

$$\begin{aligned}\eta_1 &= \tfrac{1}{2}(-\alpha_2 + \alpha_4 + \alpha_5)\\ \eta_2 &= \tfrac{1}{2}(\alpha_3 + \alpha_4 + \alpha_6)\\ \eta_3 &= \tfrac{1}{2}\alpha_4\\ \eta_{12} &= \alpha_1 .\end{aligned} \tag{8}$$

These four viscosities η_i can be determined directly by properly choosing the angle θ and ϕ. η_1 and η_2 are the effective viscosities measured when the director is parallel to the velocity gradient or to the flow direction, respectively, η_3 is obtained when the director is normal to the shear plane. The largest contribution from the η_{12}-term to the effective viscosity occurs for $\theta = 45°$ and $\phi = 0$. In this case we have

$$\eta_{45°} = \tfrac{1}{2}(\eta_1 + \eta_2) + \tfrac{1}{4}\eta_{12}. \tag{9}$$

So far we have assumed that the orientation of the molecules imposed by the magnetic field is not affected by the shear flow. This approximation is certainly justified for very small shear rates. We proceed now to calculate the departure of the alignment caused by the shear torque for two different orientations of the magnetic field, namely parallel to the direction of flow and normal to the glass plates, respectively. In both cases the director lies parallel to the shear plane ($\phi = 0$) and the torque acting on it is perpendicular to that plane.

(a) **H** PARALLEL TO z-AXIS

The torque density exerted by the magnetic field H is

$$m_H = \tfrac{1}{2}\Delta\chi H^2 \sin 2\theta \tag{10}$$

where $\Delta\chi$ is the anisotropy of the magnetic susceptibility. The torque exerted by the flow shear is

$$m_s = \sigma_{xz} - \sigma_{zx} = (\kappa_1 \sin^2\theta + \kappa_2 \cos^2\theta)\frac{du}{dx} \tag{11}$$

Here $\kappa_1 = -\alpha_2$ and $\kappa_2 = \alpha_3$ are the coefficients relating the torque to the shear rate when the director is parallel to the velocity gradient or to the direction of flow, respectively.

For small variations $\theta(x)$ from the uniform alignment $\theta = 0$ the velocity profile $u(x)$ can be approximated by the usual parabolic dependence

$$u(x) = u_0\left(1 - \frac{4x^2}{d^2}\right) \tag{12}$$

where u_0 is the velocity halfway between the two plates at $x = 0$ and d the plate separation. At equilibrium the torque exerted by the magnetic field compensates the torque induced by the shear, i.e. $m_H + m_s = 0$. By solving this equation we obtain

$$\tan\theta \cong \frac{8\kappa_2 u_0 x}{\Delta\chi H^2 d^2}. \tag{13}$$

In this derivation we have neglected the contribution of the elastic restoring forces to the torque exerted on the director. Theoretical estimates made with the known moduli of p, p'-dimethoxy-azoxy-

benzene (PAA) show that this approximation is justified. It is only within two thin transition layers at the glass surfaces, where some boundary conditions are to be satisfied, that the elastic forces become important. For PAA the thickness of those layers turned out to be only a few percent of the plate separation.

When the nematic is at rest the optical path difference between the ordinary and extraordinary component of polarized light shining perpendicularly through the glass plates is

$$\Gamma_0 = (n_e - n_o)d \tag{14}$$

where n_o and n_e are the ordinary and extraordinary refractive indices, respectively. With shear flow this path difference becomes

$$\Gamma = \int_{-d/2}^{+d/2} (n(\theta) - n_o)\,\mathrm{d}x \tag{15}$$

where

$$\frac{1}{n^2(\theta)} = \frac{\sin^2\theta}{{n_o}^2} + \frac{\cos^2\theta}{{n_e}^2}. \tag{16}$$

Together with Eq. (13) we obtain

$$\Delta\Gamma_{\parallel} = \Gamma - \Gamma_0 = -\frac{8n_e}{3d}\left(\frac{{n_e}^2}{{n_o}^2} - \right)\left(\frac{\kappa_2}{\Delta\chi}\right)^2\left(\frac{u_0}{H^2}\right)^2. \tag{17}$$

If the magnetic field is made equal to zero a stable, zero-torque flow condition is possible when $m_s = 0$. This occurs for

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

where

$$\tan^2\theta_0 = -\frac{\kappa_2}{\kappa_1}. \tag{18}$$

θ_0 is called the flow alignment angle, it is independent of shear rate and exists only if $\kappa_1 > 0$ and $\kappa_2 < 0$. For thermodynamic reasons[3] the condition $\kappa_1 > 0$ is always satisfied in nematics constituted of rodlike molecules for which η_1 is greater than η_2.

In a flow alignment configuration the change in optical path difference when θ varies from zero to $\pm\theta_0$ is

$$\Delta\Gamma_0 = -\tfrac{1}{2}n_e d\left(\frac{{n_e}^2}{{n_o}^2} - 1\right)\tan^2\theta_0. \tag{19}$$

$\Delta\Gamma_0$ is independent of the shear rate provided the thickness of the transition layers at the glass plates and halfway between—where $\theta(x)$ varies from $+\theta_0$ to $-\theta_0$—is negligible compared to the plate separation.

(b) **H** PARALLEL TO x-AXIS

For this geometry we define $\psi = \frac{1}{2}\pi - \theta$ ($\psi = 0$ if the nematic is at rest). Similarly to the case $\mathbf{H} \| z$ we get for small angle $\psi(x)$

$$\tan\psi = \frac{8\kappa_1 u_0 x}{\Delta\chi H^2 d^2} \tag{20}$$

and for the difference in optical path

$$\Gamma_\perp = \frac{8n_o}{3d}\left(1 - \frac{n_o^2}{n_e^2}\right)\left(\frac{\kappa_1}{\Delta\chi}\right)^2\left(\frac{u_0}{H^2}\right)^2. \tag{21}$$

When $\psi = 0$ we have $\Gamma = 0$.

Therefore by measuring $\Delta\Gamma_0$, $\Delta\Gamma_\parallel(u_0, H)$, and $\Gamma_\perp(u_0, H)$ it is possible to determine the quantities κ_2/κ_1, $\kappa_1/\Delta\chi$, and $\kappa_2/\Delta\chi$. Using relation (5), which takes here the form

$$\eta_1 - \kappa_1 = \eta_2 - \kappa_2 \tag{22}$$

one obtains κ_1, κ_2, and $\Delta\chi$ separately.

3. Experimental Procedure

1. MEASUREMENT OF THE APPARENT VISCOSITY $\eta(\theta, \phi)$

For this purpose special capillaries with a rectangular cross section were used in order to achieve an essentially one-dimensional velocity distribution. These capillaries were typically 5 cm long, 4 mm wide and their thickness varied between 0.2 and 0.4 mm. They were made out of two microscope slides assembled with a hard epoxy bakable up to 150 °C. Two mylar strips having the same length as the capillary were used as spacers and prevented the formation of irregular epoxy boundaries along the edges. Two glass tubings a few cm long and of 4 mm inside diameter were likewise cemented at the two ends of the rectangular section. As shown on Fig. 1 two types of assembly were used in order to provide the four independent orientations in the magnetic field. They were placed in aluminium blocks, the temperature of which was controlled within $\frac{1}{10}$ °C by a

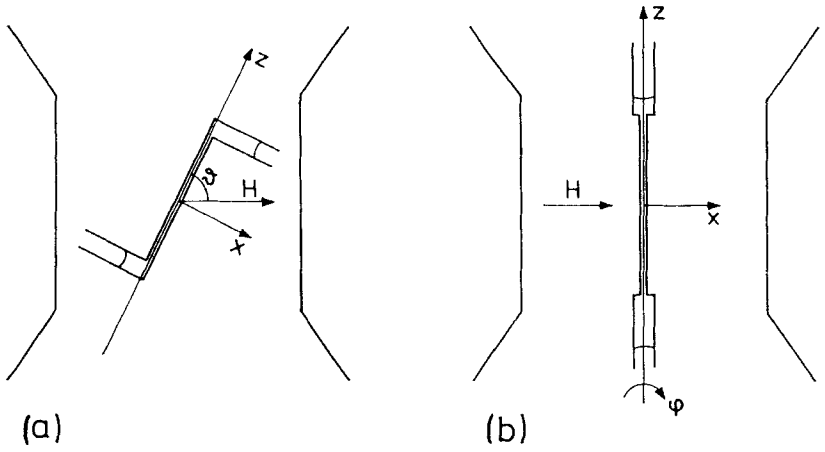

Figure 1. Top view of the flow cells positioned between the poles of an electromagnet. In (a) the angle θ is varied, in (b) the angle ϕ.

circulating fluid from a bath thermostat. About 0.3 cm^3 of liquid was necessary to fill the capillary for the meniscuses to appear in the two round tubes. Great care was given to ensure that the two meniscuses were at the same level in order to eliminate the effect of gravity. Flow motion was induced by applying a slight pressure difference Δp between the two ends of the capillary. Typical values for Δp ranged between 2 and 10 mm H_2O. They could be maintained at a constant level over a long period of time by controlling with needle valves the pressure in two buffer containers. The average flow speed was determined by timing the motion of one meniscus. For calibration purposes the viscosity of one compound, namely MBBA, was also measured in the isotropic phase with a conventional Oswald viscometer.

At very low flow speed the measured viscosities in the nematic phase were independent of the shear rate. Also no disclinations nor turbulences were observed in the capillary. If the flow speed was increased above a critical value, which depended upon the strength of the magnetic field, the apparent viscosity changed to a new value which was the same for all orientations of the magnetic field.[11] In this case the initially uniform orientation of the nematic broke up into a multitude of domains and the nematic became turbid. All measurements reported in this paper were taken at low shear rates

(less than 20 s^{-1}) in a magnetic field of 6 kOe under stable flow conditions. They were reproducible within 2–3%. Furthermore they did not vary more than a few percent when different capillaries with thicknesses ranging from 0.2 to 0.4 mm were used. We estimate at 7% the overall calibration error, taking into account that the width of the rectangular cross section was not infinite and that the surface tension at the meniscuses contributed also to the frictional forces.

2. Measurement of the Flow Induced Change in Birefringence

(a) **H** *parallel* z-*axis*

This geometry was used to measure both $\Delta\Gamma_0$ and $\Delta\Gamma_\parallel(u_0, H)$. A beam from a He–Ne laser shone perpendicularly through the broad faces of the rectangular section of the capillary which was placed between crossed polarizers. Hence the intensity of the light transmitted by the analyzer was a function of the optical path difference Γ in the flow cell, it passed through a minimum each time Γ equalled an integer number of wavelengths. The glass surfaces of the capillary were " rubbed " parallelly to the direction of flow prior to assembly in order to achieve a uniform orientation of the molecules in this direction at the glass walls. With this procedure ratios as large as 100:1 between maxima and minima in the transmitted light intensity were obtained when Γ varied by several wavelengths.

In order to determine the flow alignment angle θ_0 the nematic was first made to flow with the magnetic field on (6 kOe). As this field was turned off the angle θ varied from 0 to $\pm\theta_0$ (except for a thin layer halfway between the glass plates and within the two adsorption layers at the surfaces). The optical path difference changed by the amount $\Delta\Gamma_0$ which was measured by recording the oscillations of the transmitted light intensity on a storage scope. 2-3 sec later the magnetic field was switched on again and the change $-\Delta\Gamma_0$ was recorded. Values reproducible within 5% were obtained for $\Delta\Gamma_0$ which did not depend upon the shear rate. $\Delta\Gamma_0$ was found to be slightly smaller only if the flow speed was very small and consequently the flow alignment incomplete. θ_0 can be calculated using Eq. (19). Typically we obtained $\Delta\Gamma_0 \sim 3\text{–}5\,\lambda$ and $\theta_0 \sim 5\text{–}15°$ for a cell thickness of 0.35 mm.

Without magnetic field the flow conditions remained stable for at least 30 sec. After a while disclinations appeared at the ends of the rectangular section of the capillary—perhaps because of the discontinuity in the cross section—and were carried by the flow into the laser beam. This caused large fluctuations in the light intensity.

The measurement of $\Delta\Gamma_{\parallel}$ as function of magnetic field and flow velocity was performed with a similar optical arrangement. The magnetic field was set at a constant magnitude between 3 and 6 kOe. A controlled pressure difference Δp was applied and the resulting flow speed determined. Δp was then rapidly made equal to zero in order to achieve again uniform orientation of the nematic in the field direction. This was accompanied by a change equal to $-\Delta\Gamma_{\parallel}$ in the optical path difference causing a variation in the transmitted light intensity. $\Delta\Gamma_{\parallel}$ was measured by reading the setting of a calibrated Brace–Köhler compensator placed between flow cell and analyzer necessary to adjust the light intensity back to the level present before the shear flow was stopped. With this method it was possible to measure variations in Γ as small as $\lambda/100$. Typically $\Delta\Gamma_{\parallel}$ was of the order of $\lambda/10$. Note that Γ_0, the optical path difference at zero shear, was of the order of 150λ for a cell thickness of 0.35 mm (see below). Γ_0 was therefore extremely sensitive to temperature fluctuations and to impurity gradients in the nematic. This is why we choose to measure $\Delta\Gamma_{\parallel}$ at the moment the shear flow was turned off in order to avoid any drift in Γ_0 due to those spurious effects. By measuring the variation in Γ_0 as function of temperature we obtained the accurate temperature dependence of the birefringence $\Delta n = n_e - n_o$ which is particularly important near the clearing point.

(b) **H** *parallel* x-*axis*

Here the magnetic field is oriented parallelly to the laser beam. The inner surfaces of the rectangular capillary were coated with a layer of an emulgator, lecithin or triton X-100, in order to achieve a perpendicular orientation of the molecules within the adsorption layers. For this purpose a solution of the emulgator in ethanol was blown through the capillary after its assembly. With the magnetic field on and no shear flow the extinction of the light passing through the analyzer was almost complete ($\Gamma = 0$). The path difference $\Gamma_{\perp}$

was measured by recording the variation in intensity as the flow speed was gradually increased at constant field strength. Typically $\Gamma_\perp$ reached a few wavelengths under similar experimental conditions as in the previous measurements of $\Delta\Gamma_\parallel$.

The refractive indices n_o and n_e have been determined in a separate experiment. The ordinary index n_o was measured with a conventional Abbe refractometer. The difference $\Delta n = n_e - n_o$ was determined by measuring the increase in optical path difference Γ as the orientation of the molecules varied gradually from a perpendicular ($\Gamma = 0$) to a parallel ($\Gamma = \Gamma_0$) orientation. For this purpose the nematic was placed between two glass plates coated with the emulgator and the magnetic field slowly increased in a direction parallel to the plates. Γ_0 was measured for several cell thicknesses ranging from 0.1 to 0.2 mm. This allowed us to determine the thickness of the transition layers at the glass surface within which the orientation of the molecules could not be made parallel to the field. These layers turned out to be 3μ thick in a field of 9 kOe. The values of the refractive indices measured at different temperature for HBAB and the 1:1:1-mixture are collected in Table 1. For MBBA the results were within 5% of the data reported in the literature.[15]

TABLE 1 The Ordinary and Extraordinary Refraction Indices for HBAB and the 1:1:1-mixture at Different Temperatures

T	HBAB		1:1:1-mixture	
°C	n_o	n_e	n_o	n_e
25			1.513	1.827
40			1.511	1.808
60	1.510	1.790	1.510	1.784
70	1.511	1.776	1.512	1.770
80	1.513	1.758	1.514	1.751
90	1.517	1.734	1.519	1.724
95	1.520	1.716	1.527	1.699
97	1.523	1.708	1.534	1.678
97.5			1.536	1.666
100	1.527	1.685	1.578	
101	1.529	1.668		
101.5	1.530	1.659		
105	1.579		1.576	
115	1.575		1.572	

4. Results and Discussion

1. The Viscosity Coefficients η_i

The viscosity coefficients η_1, η_2, and η_3 measured on MBBA, HBAB and the 1:1:1-mixture are plotted in function of temperature on Figs. 2–4. The temperature scale is linear in $1/T$ in order to emphasize the usual $e^{W/kT}$ dependence of viscosities. The activation energy W turns out to have the same value over the isotropic range

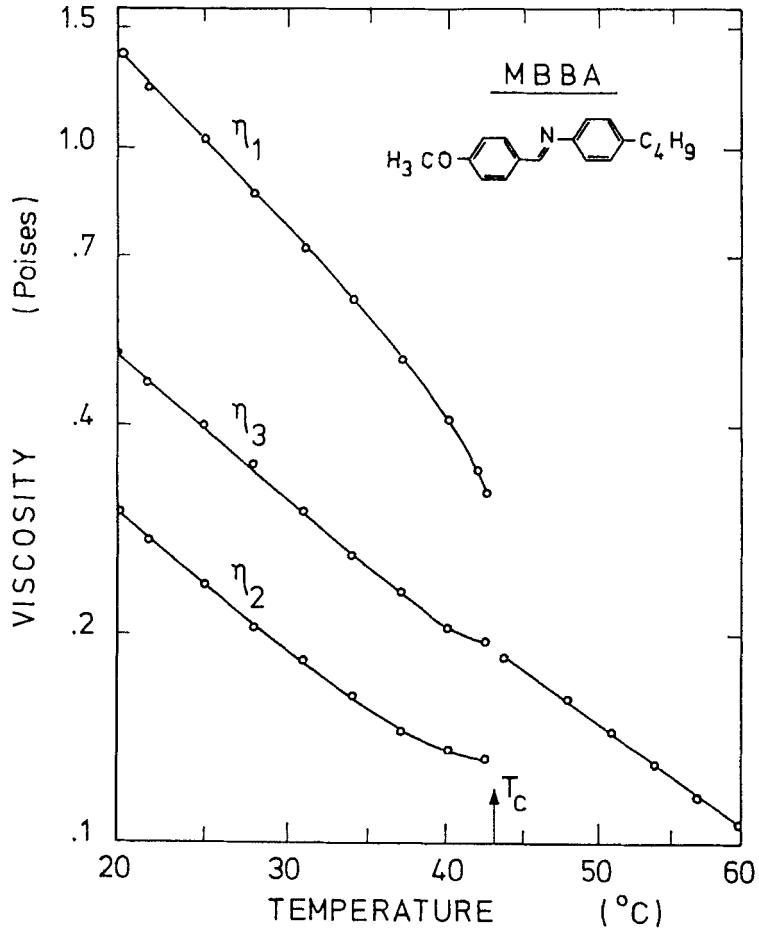

Figure 2. The viscosity coefficients η_1, η_2, and η_3 of MBBA as function of temperature. The temperature scale is linear in T^{-1}.

for all three materials, namely $W = 0.32 \pm 0.01$ eV. In the nematic phase we observe a strong anisotropy in the viscosities ($\eta_1 \simeq 5\eta_2$). It is smallest just below the transition temperature (low degree of order) and increases with decreasing temperature.

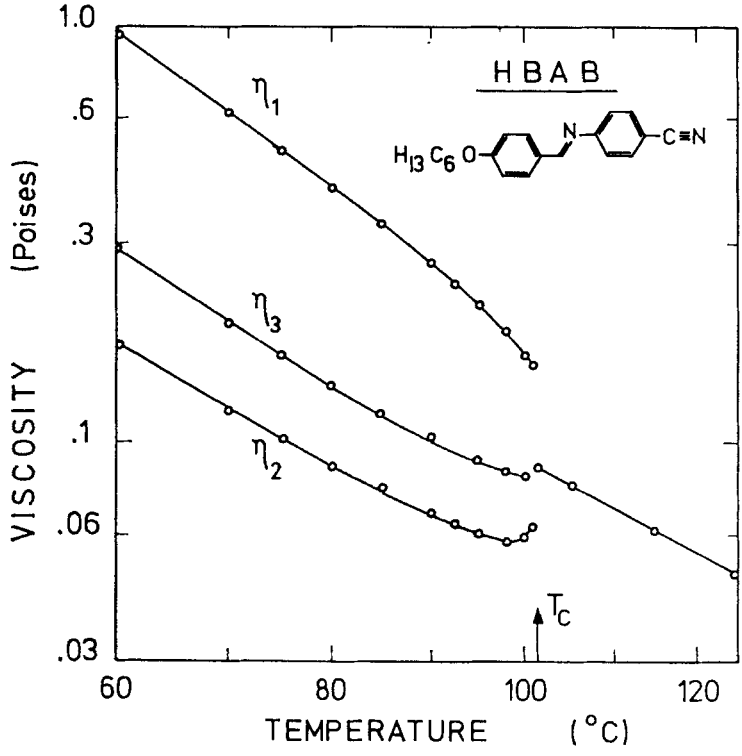

Figure 3. The viscosity coefficients η_1, η_2, and η_3 of HBAB as function of temperature. The temperature scale is linear in T^{-1}.

The viscosity coefficients of the 1:1:1-mixture are essentially identical to the viscosities measured at the same temperature on HBAB. This is to be expected since the three constituents of the mixture are chemically very similar so that the molecular interaction does not change much as one kind of molecules is replaced by another. The main advantage of the mixture—which is an eutectic—is that the temperature range of the mesophase is extended to room temperature. We observe a marked increase in activation energy as the

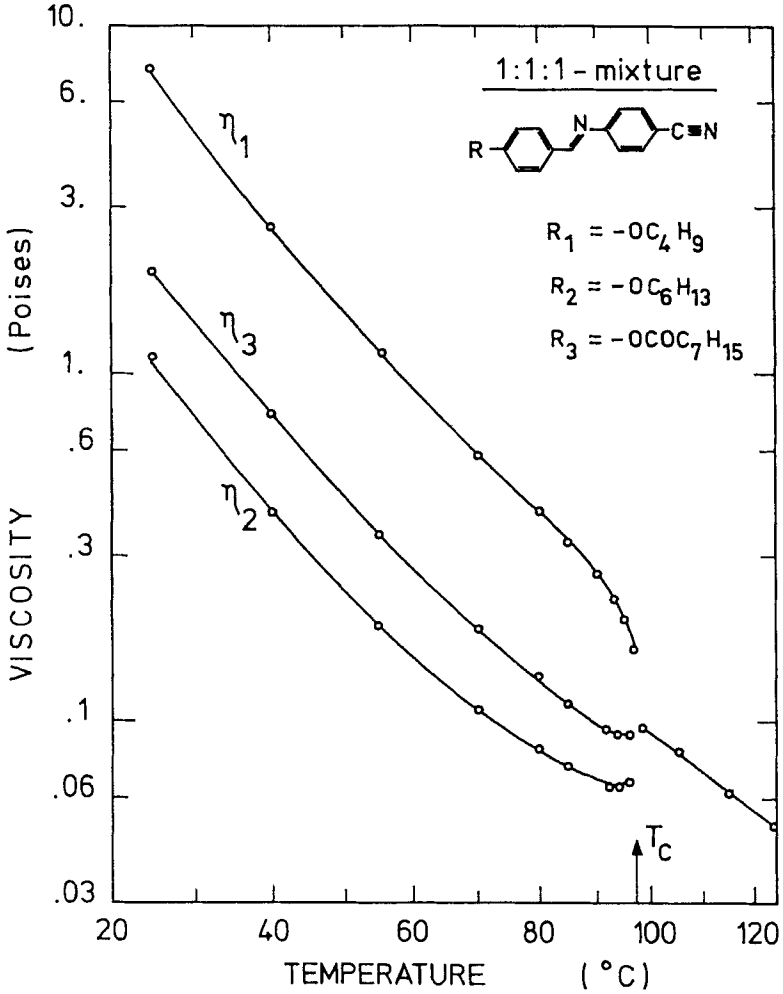

Figure 4. The viscosity coefficients η_1, η_2, and η_3 of the 1:1:1-mixture. The temperature scale is linear in T^{-1}.

temperature is lowered well below the clearing point. For the 1:1:1-mixture we have $W = 0.51 \pm 0.02$ eV between 25 and 50 °C.

The coefficient η_{12} seems to be comparatively small because its contribution to the apparent viscosity was only a few percent in the most favorable geometry ($\theta = 45°$, $\phi = 0$). We obtained $\eta_{12} = 6 \pm 4$ cp for both MBBA at $T = 25$ °C and HBAB at $T = 80$ °C. The temperature dependence was within the indicated error brackets.

For the 1:1:1-mixture we got $\eta_{12} = 70 \pm 40$ cp at 25 °C and $\eta_{12} = 5 \pm 4$ cp at 70 °C. Note that according to (9) one measures $\eta_{12}/4$ rather than η_{12} which diminishes the absolute accuracy with which this coefficient can be determined.

2. The Shear-torque Coefficients κ_1 and κ_2

As reported earlier[16] flow alignment is observed over the entire nematic phase of MBBA. The angle θ_0 increases from a value of 5.4° at a temperature of 22 °C up to 17.5° at 42.5 °C ($T_c = 43.0°$). Similar values for θ_0 are obtained also for HBAB in the temperature range just below the clearing point. For this compound however, θ_0 falls off steeply with decreasing temperature and becomes equal to zero at $T = 91.8 \pm 0.2$ °C. Below this temperature the laminar flow breaks off in many irregular rotating domains and no stable flow-alignment configuration is observed. Phenomenologically this means that the coefficient κ_2 changes from a negative to a positive value as the temperature is lowered across that critical temperature. Exactly the same behaviour is found for the 1:1:1-mixture for which this critical temperature is $86.0 \pm 0.3°$. Hence HBAB appears to be the first known representative of a class of nematic liquid crystals for which flow alignment does not occur over the entire temperature range of the mesophase.

Using Eq. (18) we calculated the negative values of the ratio κ_2/κ_1 shown on Fig. 5 as function of temperature for the three compounds studied. The rapid increase of the flow alignment angle, and hence of $|\kappa_2/\kappa_1|$, with temperature near T_c is related to the decrease in the degree of order as the temperature comes close to the nematic–isotropic transition point.[17] In the isotropic (unordered) phase the long axes of the rodlike molecules align preferentially at an angle of 45° relative to the direction of flow. Hence it is likely that we see a continuation of the isotropic flow alignment in the nematic phase. This effect would be largest just below the transition temperature and it would decrease rapidly as the degree of order increases.

The ratio κ_2/κ_1 was also determined from the two independent measurements of $\Delta\Gamma_\parallel$ and $\Gamma_\perp$ as function of magnetic field and flow velocity which yield $\kappa_2/\Delta\chi$ and $\kappa_1/\Delta\chi$ respectively. This method gave good agreement with the previously obtained values of κ_2/κ_1

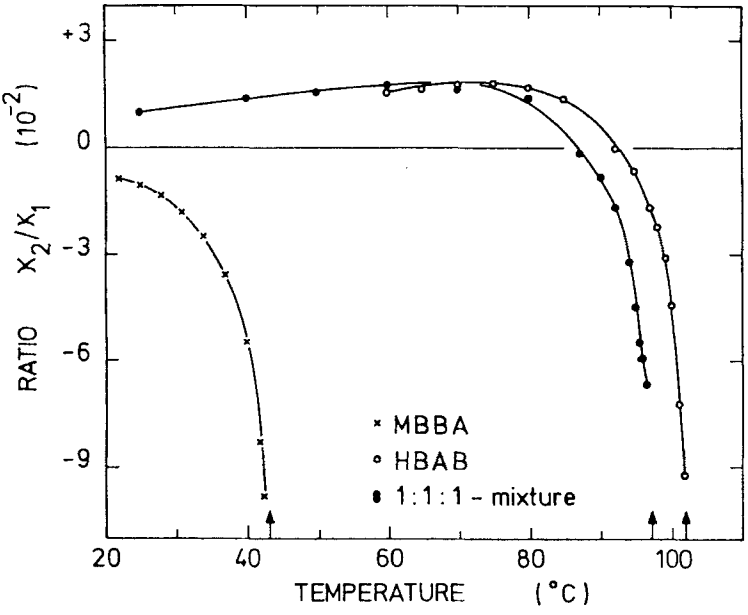

Figure 5. The ratio κ_2/κ_1 as function of temperature for MBBA, HBAB, and the 1:1:1-mixture.

and could be equally applied over the temperature range where flow alignment does not occur. In this range κ_2/κ_1 varies only slowly with temperature as shown on Fig. 5 for HBAB and the 1:1:1-mixture.

The main physical difference between the MBBA and the HBAB molecules is the presence of a large dipole moment ($\sim$4 debyes) associated with the C≡N triple bond. It has been suggested[16] that it is the additional contribution from the permanent dipole–dipole interaction—of the order of kT—to the interaction energy between HBAB molecules which causes the disappearance of flow alignment in this compound. The interaction through permanent electric dipole in MBBA is smaller by more than an order of magnitude and seems negligible.

Using Eq. (22) and the viscosities η_1 and η_2 the two coefficients κ_1 and κ_2 can be determined separately. They are plotted for MBBA as function of temperature on Fig. 6. Figure 7 shows the coefficient κ_1 for HBAB and the 1:1:1-mixture, here also very similar values are obtained for the two compounds. Finally from the measurement of

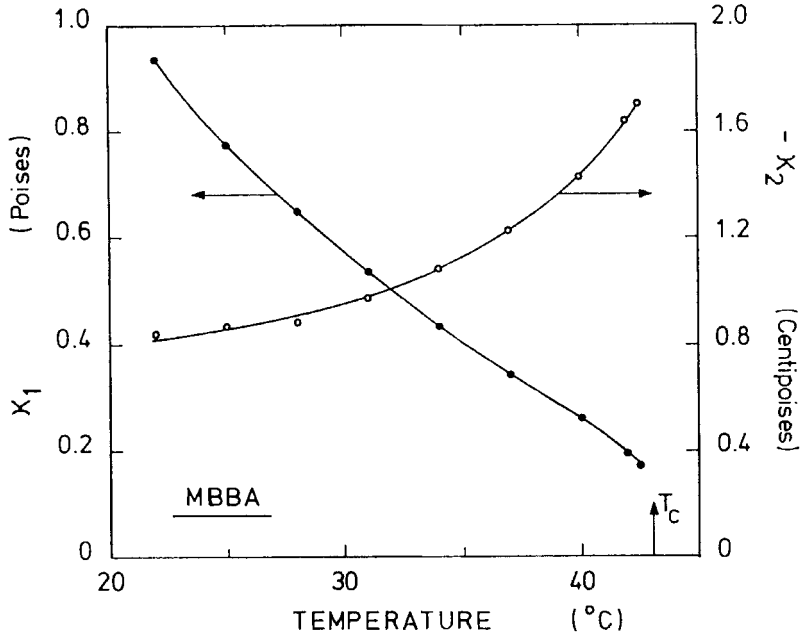

Figure 6. The shear-torque coefficients κ_1 (dots) and κ_2 (open circles) for MBBA as function of temperature.

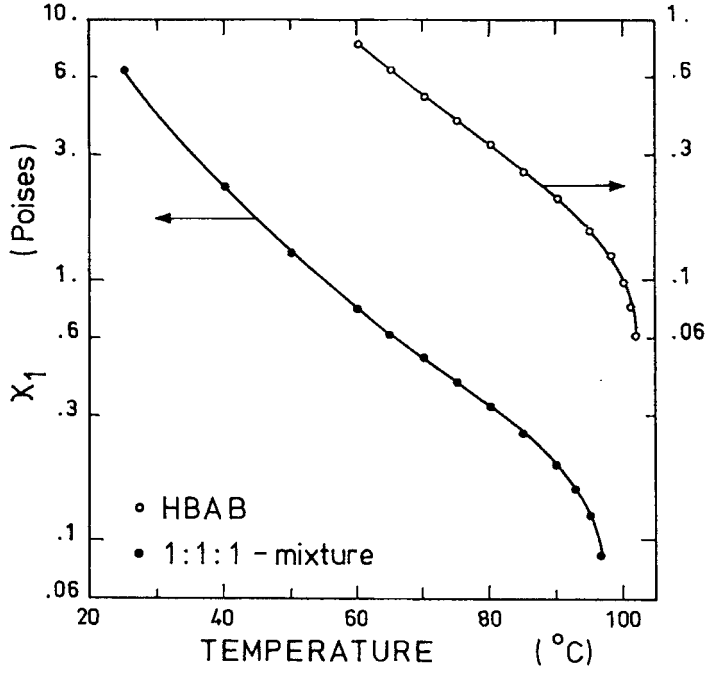

Figure 7. The shear-torque coefficient κ_1 for HBAB (right ordinate) and the 1:1:1-mixture (left ordinate) as function of temperature.

$\kappa_1/\Delta\chi$ we determined the anisotropy of the magnetic susceptibility shown for the three materials on Fig. 8. For MBBA we get $\Delta\chi = (0.95 \pm 0.07) \cdot 10^{-7}$ at 25 °C. This is in excellent agreement with the value $\Delta\chi = 0.89 \cdot 10^{-7}$ obtained by Gasparoux and Prost[18] by the method of a rotating magnetic field.

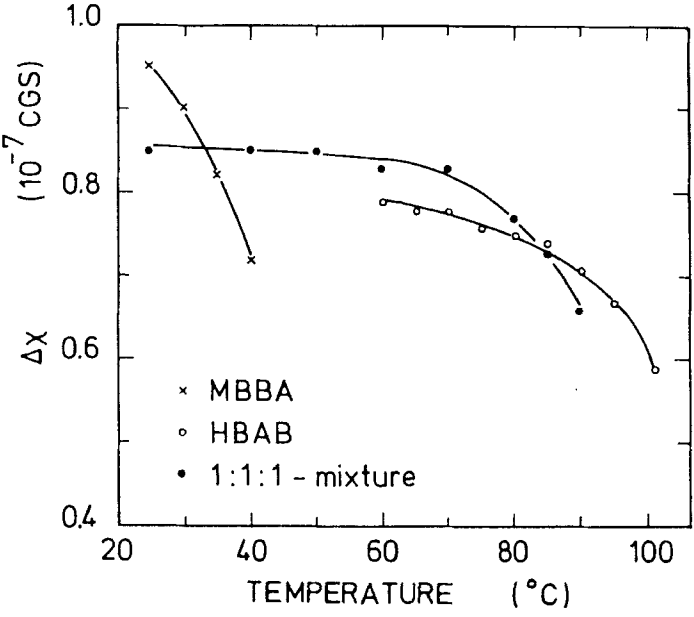

Figure 8. The anisotropy of the magnetic susceptibility $\Delta\chi$ as function of temperature for MBBA, HBAB, and the 1:1:1-mixture.

To conclude we can say that this method which combines viscometry using a capillary of rectangular cross-section and optical interferometry appears, because of its simplicity, extremely suitable for the determination of the viscosities in nematic liquid crystals. In particular it yields very accurate data for the shear-torque coefficient κ_2(resp. α_3) and, compared to the other methods, eliminates any ambiguity about its sign. Furthermore the method is also attractive for the determination of $\Delta\chi$.

Acknowledgements

The author would like to thank W. Helfrich for many helpful suggestions and A. Boller and H. Scherrer for the careful synthesis of the liquid crystals.

REFERENCES

1. Porter, R. S. and Johnson, J. F., in *Rheology, Theory and Applications*, ed. Eirich, F. R., Vol. IV, Academic Press, New York and London, 1967, pp. 317–345.
2. Ericksen, J. L., *Arch. Ration. Mech. Anal.* **4**, 231 (1960); *Phys. Fluids* **9**, 1205 (1966).
3. Leslie, F. M., *Quart. J. Mech. Appl. Math.* **19**, 357 (1966).
4. Forster, D., Lubensky, T. C., Martin, P. C., Swift, J. and Pershan, P. S., *Phys. Rev. Letters* **26**, 1016 (1971).
5. Huey–Wen Huang, *Phys. Rev. Letters* **26**, 1525 (1971).
6. Michailoff, G. M. and Zwetkoff, W. N., *Acta Physicochimica* (*URSS*) **10**, 775 (1939).
7. Miesowicz, M., *Nature* **158**, 27 (1946).
8. Martinoty, P. and Candau, S., *Mol. Cryst. and Liq. Cryst.* **14**, 243 (1971).
9. Kemp, K. A. and Letcher, S. V., *Phys. Rev. Letters* **27**, 1634 (1971).
10. Orsay Liquid Crystal Group, *Mol. Cryst. and Liq. Cryst.* **13**, 187 (1971).
11. Gähwiller, C., *Phys. Letters* **36A**, 311 (1971).
12. RCA US Patent No. 3 597 044.
13. Ericksen, J. L., *Arch. Ration. Mech. Anal.* **23**, 266 (1966).
14. Leslie, F. M., *Rheol. Acta* **10**, 91 (1971).
15. Brunet-Germain, M., *C.R. Acad. Sci., Paris, Serie B* **271**, 1075 (1970).
16. Gähwiller, C., *Phys. Rev. Letters* **28**, 1554 (1972).
17. Helfrich, W., *J. Chem. Phys.* **56**, 3187 (1972).
18. Gasparoux, H. and Prost, J., *J. Physique* **32**, 953 (1971).