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F. -J. Bock[a]; H. Kneppe[a]; F. Schneider[a]
[a] Physikalische Chemie, Universität Siegen, Siegen, F.R. Germany

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Rotational viscosity of nematic liquid crystals and their shear viscosity under flow alignment

by F.-J. BOCK, H. KNEPPE and F. SCHNEIDER
Physikalische Chemie, Universität Siegen, D-5900 Siegen, F.R. Germany

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The influence of molecular properties on the rotational viscosity, γ_1, of nematic liquid crystals is studied. The shear viscosity under flow alignment, η_S, is determined for the same liquid crystals. A significant correlation between both quantities is found. An equation is presented which allows the calculation of γ_1 from η_S with an error of about 20 per cent for the liquid crystals studied.

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1. Introduction

Response times of liquid crystal displays are proportional to the rotational viscosity, γ_1 [1]. Because of its strong temperature dependence the rotational viscosity is the most important quantity for the development of liquid crystal displays for low-temperature applications. As the experimental determination of γ_1 is more complicated than that of the shear viscosity under flow alignment, η_S, the shear viscosity is commonly used for a comparison of the viscous properties of liquid crystals at low temperatures. However, a correlation between γ_1 and η_S has never been confirmed in general. The only paper on this subject has been presented by Gerber and Schadt [2] for liquid crystals with terminal cyano groups.

We have studied the rotational viscosity for a large number of liquid crystals with different molecular structure in order to obtain information on the influence of the alkyl chain length, the ether oxygen in an alkyloxy chain, different ring systems, and the central linking group. Because of the time-consuming syntheses and measurements the study was restricted to carbocyclic two-ring systems. In addition, we have measured the shear viscosity under flow alignment for the same liquid crystals and have tested various methods to correlate γ_1 and η_S.

2. Experimental

The rotational viscosity was determined from the torque which acts on a sample rotating in a magnetic field with constant field strength (1·4 T) and fixed direction. The experimental set-up has previously been described in detail [3]. About 8 g of the liquid crystal were used for the measurement of γ_1. The density was determined in a dilatometer.

Shear viscosity under flow alignment was determined in Ostwald viscometers with capillary radii of 0·39 or 0·68 mm. The inner surface of the capillary was not prepared for a uniform alignment of the liquid crystal.

Liquid crystals used in this investigation were either commercial products (5PCH and ZLI1565 from Merck AG; 5CBP, 6CBP and 5OCBP from Hoffmann–La Roche) or were synthesized by us. Transition temperatures and acronyms are shown in table 1.

Table 1. Nematic–isotropic transition temperatures T_{NI} and acronyms of the liquid crystals studied.

Liquid crystal	Acronym	T_{NI}/°C
4′-Methoxybenzylidene-4-*n*-butylaniline	1O·4	46·4
4′-*n*-Ethoxybenzylidene-4-*n*-butylaniline	2O·4	79·0
4′-*n*-Propyloxybenzylidene-4-*n*-butylaniline	3O·4	58·8
4′-*n*-Butyloxybenzylidene-4-*n*-butylaniline	4O·4	75·2
4′-*n*-Pentyloxybenzylidene-4-*n*-butylaniline	5O·4	69·6
1-*n*-Pentyl-4-[4-cyanophenyl]-bicyclo-[2.2.2]octane	5BCO	101·2
4-Cyano-1-[trans-4-*n*-pentylcyclohexyl]-benzene	5PCH	55·0
4-Cyano-4′-*n*-pentylbiphenyl	5CBP	35·5
4-Cyano-4′-*n*-hexylbiphenyl	6CBP	29·9
4-Cyano-4′-*n*-pentyloxybiphenyl	5OCBP	68·2
4′-*n*-Butyloxyphenyl 4-*n*-pentylbenzoate	5–O4	58·0
4-*n*-Pentyl-4′-*n*-butyloxytolan	5,4OTOL	79·4
4,4′-Di-*n*-pentylazoxybenzene	5,5AZO	67·6
4-*n*-Pentyl-4′-*n*-butyloxyazoxybenzene†	5,4OAZO	103·3
4-*n*-Pentyl-4′-*n*-butyloxyazobenzene	5,4OAZ	86·6
4-*n*-Pentylbenzoic acid	5BENZ	124·5
Mixture of substituted cyclohexyl-benzenes	ZLI1565	86·5–98·0

† Mixture of isomers.

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3. Experimental results

3.1. *Rotational viscosity*

The rotational viscosities of the liquid crystals are shown in figures 1 and 2 as a function of temperature. A comparison of the rotational viscosities is difficult because of the dependence on the order parameter, *S*, which varies considerably in the neighbourhood of the nematic–isotropic transition. This dependence can be described by an equation of the type [4, 5]

$$\gamma_1 = S^2 f(T). \tag{1}$$

The temperature dependence of the order parameter is not known for most of the liquid crystals studied. Therefore, we have used the equation

$$S = [1 - (T/T^*)]^{\beta} \tag{2}$$

to describe the order parameter. The exponent β and the characteristic temperature, T^*, were determined from the temperature dependence of the rotational viscosity. We found characteristic temperatures 0·1–0·6 K greater than the nematic–isotropic transition temperatures in agreement with results from direct measurements of the order parameter. The values for the exponents (0·13–0·15) are rather low. This may be due to the neglect of higher-order terms in equation (1).

Figure 3 shows the reduced rotational viscosities

$${}^{1}\gamma_1 = \frac{\gamma_1}{S^2} \tag{3}$$

as a function of temperature. Except for 4O·4 and 5O·4 which show a divergence before the transition to the low-temperature smectic phase, all liquid crystals show a nearly linear temperature dependence in this representation. The slight curvature is also observed for the shear viscosity of isotropic liquids and can be described by the introduction of a temperature T_0 at which the viscosity diverges and which depends

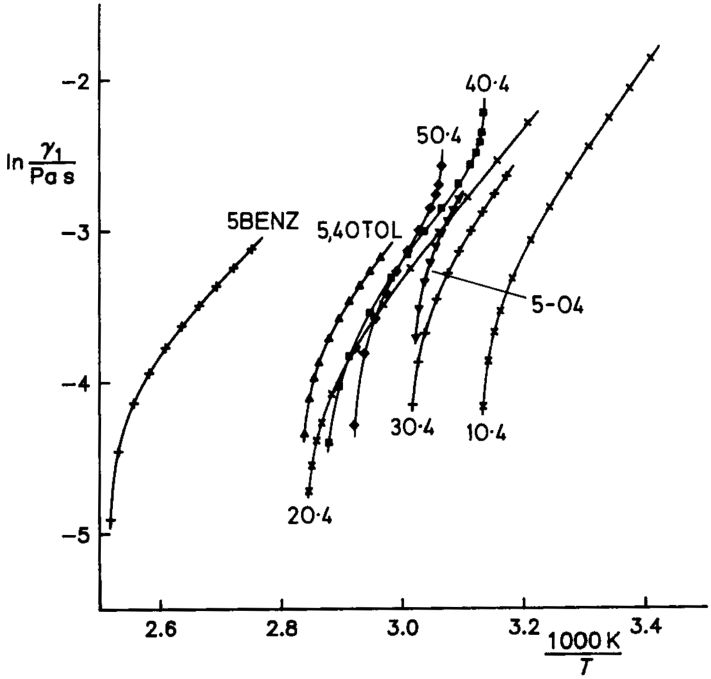

Figure 1. Temperature dependence of the rotational viscosity, γ_1.

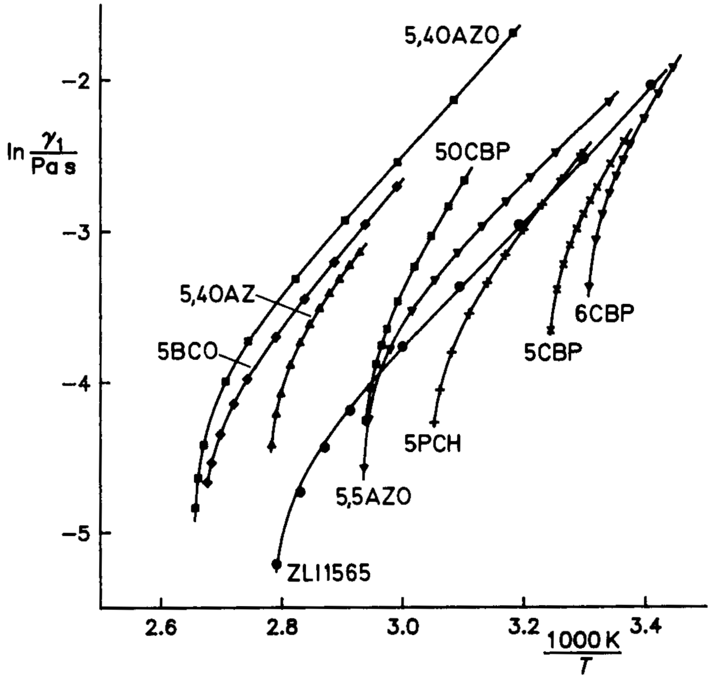

Figure 2. Temperature dependence of the rotational viscosity, γ_1.

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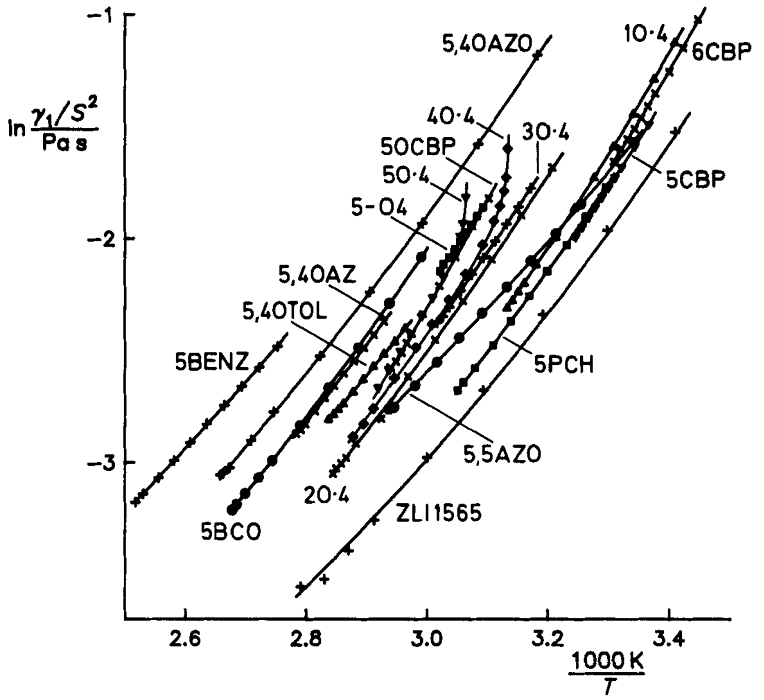

Figure 3. Temperature dependence of the reduced rotational viscosity, γ_1/S^2.

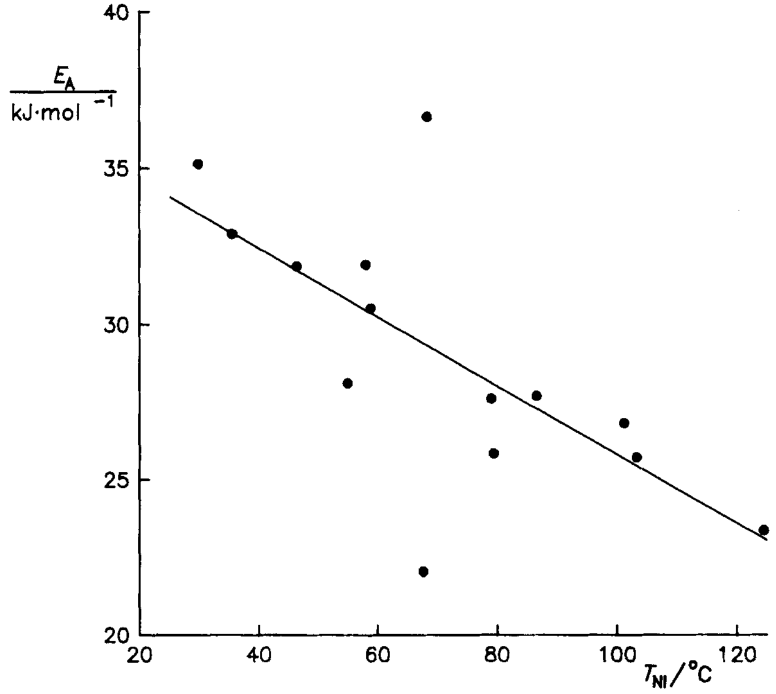

Figure 4. Activation energy of ${}^1\gamma_1$ at the nematic–isotropic transition as a function of T_{NI}.

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on the glass transition temperature of the liquid. Extension of Vogel's equation by an order parameter term gives [5]

$$\gamma_1 = A(1 - T/T^*)^{2\beta}\exp[B/(T - T_0)]; \tag{4}$$

this has been used for the calculation of the solid lines in figures 1 to 3. A more detailed discussion of equation (4) is given in [5] and [6].

The activation energy for the temperature dependence of ${}^1\gamma_1$ can be calculated from equation (4). The value at the nematic–isotropic transition

$$E_A = R\left(\frac{d\ln{}^1\gamma_1}{d(1/T)}\right)_{T_{NI}} = \frac{RBT_{NI}^2}{(T_{NI} - T_0)^2} \tag{5}$$

is shown in figure 4 as a function of the nematic–isotropic transition temperature. Only 5,5AZO and 5OCBP show large deviations from a linear dependence. As 4-methoxy-4′-*n*-butylazoxybenzene [5] also shows a lower activation energy, whereas 5,4OAZO gives the usual value we were not able to explain the deviation for 5,5AZO. The high activation energy for 5OCBP may be due partly to the very small temperature range of the nematic phase which does not allow a precise determination of the activation energy.

The range of viscosity values at constant temperature is rather small (1 : 2·5). Liquid crystals with larger cores give considerably higher rotational viscosities, for example, the viscosity ratio of ethylhydroquinone di-4-*n*-hexylbenzoate [7] to 1O·4 amounts to 10. The rotational viscosity of 5BENZ lies between that of two- and three-ring liquid crystals as the hydrogen bonding leads to a very stable dimer the length of which is comparable with a three-ring system. The very low rotational viscosity of ZLI1565 results from the content of very short and non-polar cyclohexylbenzenes.

The dependence of the rotational viscosity on the alkyl chain length can be studied in the homologous series of azomethins (cf. figure 5). A comparison with figure 1 shows that the observed odd–even effect for γ_1 only results from the alternating nematic–isotropic transition temperatures. High nematic–isotropic transition temperatures give high order parameters and high rotational viscosities at constant temperature. Figure 5 shows that the reduced viscosities exhibit only a large difference between 1O·4 and 2O·4 whereas the higher homologues give nearly equal values. An additional methylene group in a long alkyl chain has two opposing effects. It increases the volume of the molecule but also its flexibility.

Diogo and Martins [8] found similar effects in the homologous series of di-alkyloxy-azoxybenzenes: an alternating effect in γ_1 due to the alternation of the order parameter with the nematic–isotropic transition temperature and an alternation of the constant A in their equation

$$\gamma_1 = AS^2\exp[BS^2/(T - T_0)].$$

The difference in the results may have two different reasons. Firstly, there may in fact be a different behaviour in these homologous series as two alkyl chains are varied in the di-alkyloxy-azoxybenzene series in contrast to one in the *m*O·*n* series. Secondly, the equation used by Diogo and Martins is different from equation (4) which is strongly supported by experimental [5] and theoretical [4] studies. It is possible that the S^2 term in the exponent of their equation leads to the alternation of the constant factor.

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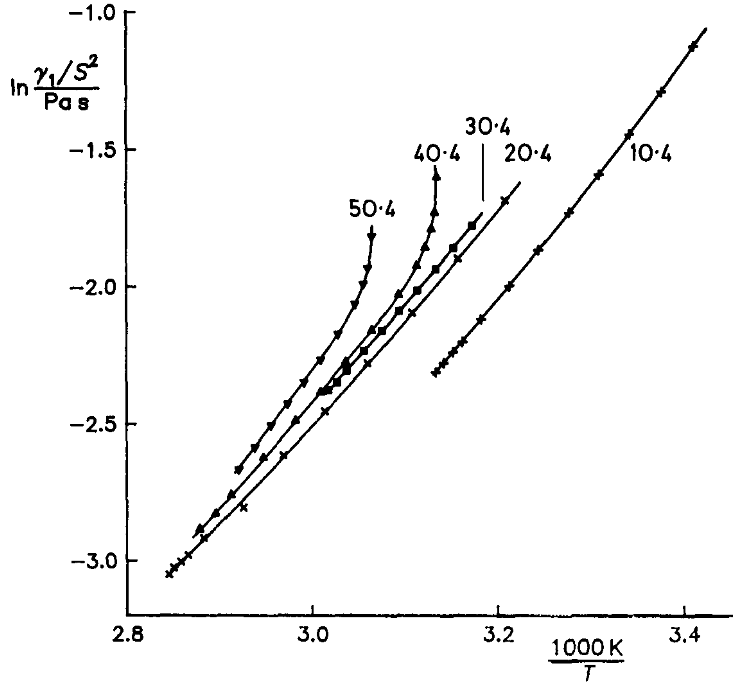

Figure 5. Temperature dependence of the reduced rotational viscosity γ_1/S^2 for the azomethins *m*O·4.

The different influence of alkyl and alkyloxy chains can be studied by comparing the liquid crystals 6CBP/5OCBP and 5,5AZO/5,4OAZO, respectively (cf. figure 3). The ratio of the reduced rotational viscosities at constant temperature is about 1 : 2, i.e. replacement of a methylene group by an oxygen increases the rotational viscosity by a factor of two. Gerber and Schadt [2] have also observed this effect when studying cyanobiphenyl liquid crystals. An increased resonance stabilization and increased association of the molecules caused by the ether oxygen was proposed as a possible explanation for this effect. As we have observed the same effect on azoxybenzenes, the explanation by an association effect cannot be valid in general. We also assume that the interaction of the lone-pair electrons of the oxygen with the π-electrons of benzene is the primary reason. This interaction restricts the free rotation of the first methylene group with respect to the O-benzene axis and leads to an increased viscosity.

A comparison of the reduced rotational viscosities of 5CBP, 5PCH and 5BCO with different ring systems shows that the first two exhibit nearly equal viscosities whereas the value for 5BCO is two times larger. Although 5BCO is somewhat shorter than 5CBP and 5PCH, respectively, it exhibits a considerably higher hydrodynamic diameter perpendicular to the long molecular axis. This should lead to a higher viscosity. We do not believe that a different degree of association of these molecules influences strongly the rotational viscosity, as 1O·4 and the associated 6CBP give nearly equal viscosities.

A comparison of the reduced rotational viscosities of 5BENZ, 5,4OAZO, 5,4OAZ, 5–O4, 5,4OTOL and 5O·4 allows us to estimate the influence of the central group on the rotational viscosity. For 5BENZ, the reduced rotational viscosity has to be increased by a factor of two in order to take into account the missing oxygen atom in one side chain.

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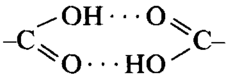
We find the following sequence:



$$-C\begin{matrix}OH\cdots O\\ O\cdots HO\end{matrix}C- > -N{=}N(O)- > -N{=}N- > -CO{-}O- \approx -C{\equiv}C- \approx -CH{=}N-.$$

This sequence can be explained partly by differences in polarity, molecular length, lateral dimension, restriction of intramolecular rotation and rigidity. However, we have found no arguments for the relations $-N{=}N- > -CO{-}O-$ and $-C{\equiv}C- \approx -CH{=}N-$.

3.2. *Shear viscosity*

The shear viscosity of the liquid crystals is shown in figures 6 and 7 as a function of temperature. In the isotropic phase, it is a linear function in this representation. The activation energies are shown in table 2. The dependence on nematic–isotropic transition temperature is similar to that of the activation energy for ${}^1\gamma_1$ in the nematic phase. Strong deviations from this linear dependence are shown by 5OCBP and 5BENZ (too high) as well as 5,5AZO and ZLI1565 (too low).

Table 2. Activation energies for the temperature dependence of the shear viscosity in the isotropic phase.

Liquid crystal	$E_A/\mathrm{kJ\,mol^{-1}}$
1O·4	33
2O·4	26
3O·4	34
4O·4	30
5O·4	30
5BCO	27
5PCH	29
5CBP	34
6CBP	36
5OCBP	34
5–O4	31
5,4OTOL	25
5,5AZO	23
5,4OAZO	25
5,4OAZ	26
5BENZ	26
ZLI1565	21

Flow alignment in the nematic phase usually leads to a director orientation which is nearly parallel to the flow direction. At low temperatures the same temperature dependence as for η_2 is observed. The viscosity values also agree, for example, 1O·4 at 20°C: $\eta_S = 0{\cdot}036$, $\eta_1 = 0{\cdot}189$, $\eta_2 = 0{\cdot}031$ and $\eta_3 = 0{\cdot}055\,\mathrm{Pa\,s}$ [9]. Only in the neighbourhood of the nematic–isotropic transition does the deviation from flow direction increase up to $\approx 15°$ which leads to a stronger influence of η_1 and to the characteristic temperature dependence shown in figures 6 and 7.

Exceptions to this general rule are shown by 5O·4 and 4O·4 because of their smectic phases. Figure 8 represents the temperature dependence for 5O·4 with a larger number of measurements. Directly below the nematic–isotropic transition 5O·4 shows flow alignment and, therefore, the normal temperature dependence. The flow alignment angle, θ_S, decreases with decreasing temperature and flow alignment disappears

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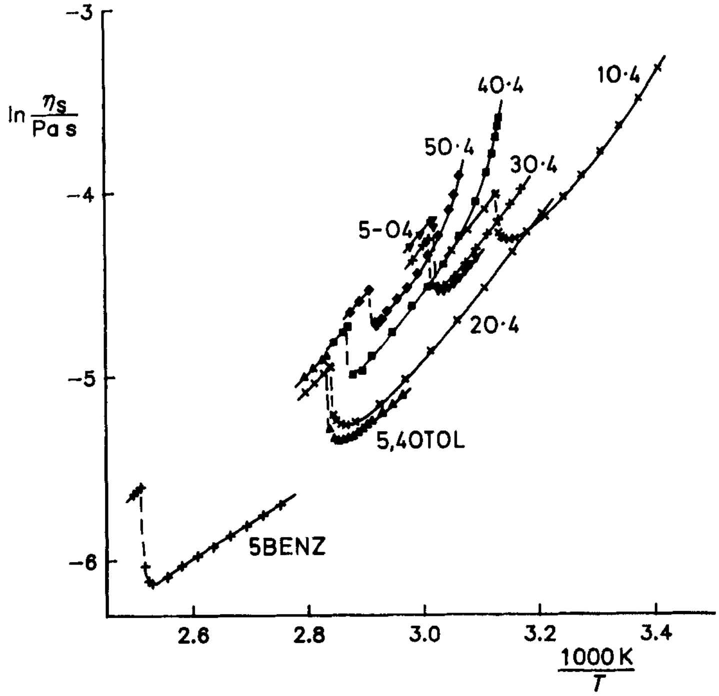

Figure 6. Temperature dependence of the shear viscosity in the nematic phase under flow alignment and in the isotropic phase.

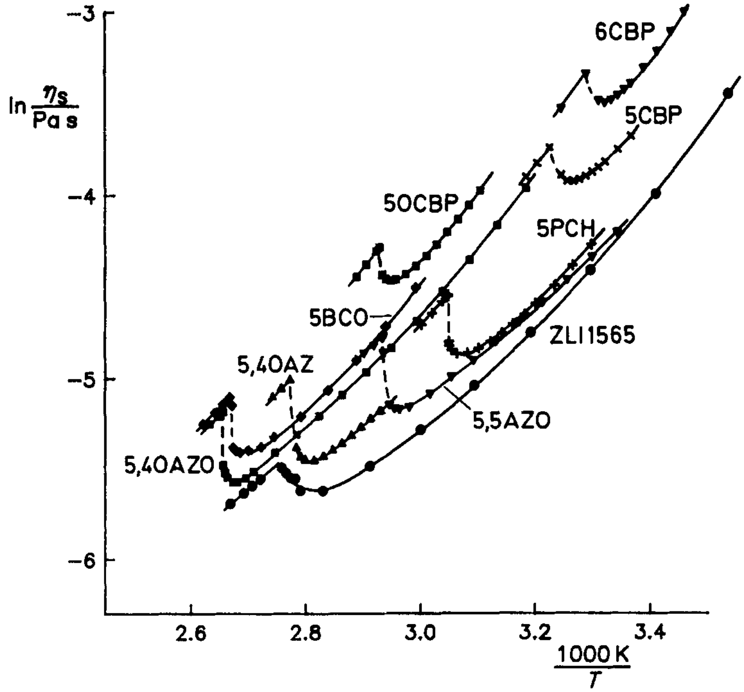

Figure 7. Temperature dependence of the shear viscosity in the nematic phase under flow alignment and in the isotropic phase.

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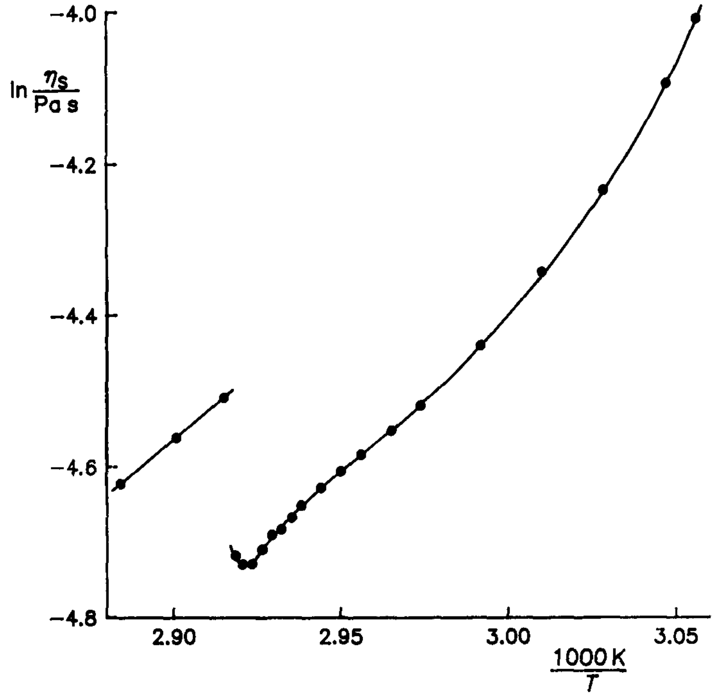

Figure 8. Temperature dependence of the shear viscosity in the nematic phase under flow alignment and in the isotropic phase for 5O·4.

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some degrees below the nematic–isotropic transition due to the low-temperature smectic phase. The director is now rotating in the shear plane and the shear viscosity corresponds to a mean value of η_1 and η_2 leading to an enhanced increase of the shear viscosity some degrees below the nematic–isotropic transition. Then the normal temperature dependence of the mean value of η_1 and η_2 is observed. Finally, the divergence of η_2 leads to a strong increase in the shear viscosity.

4. Determination of the rotational viscosity from shear viscosity measurements

In general, nematic liquid crystals show flow alignment. According to the Leslie–Ericksen theory [10, 11], the shear viscosity under flow alignment and the rotational viscosity are given by

$$\begin{aligned}\eta_s &= \eta_2 + (\eta_1 - \eta_2)\sin^2\theta_S,\\ &= \eta_2 - \alpha_3,\\ &= \tfrac{1}{2}(\alpha_4 + \alpha_6 - \alpha_3), \qquad (6)\\ \gamma_1 &= \alpha_3 - \alpha_2, \qquad (7)\end{aligned}$$

if a small term resulting from the viscosity coefficient η_{12} is neglected. α_i are the independent Leslie coefficients, i.e. η_S and γ_1 are also independent quantities. Figure 9 confirms that there is no direct correlation between these two quantities. Thus, the viscosity ratio η_S/γ_1 is considerably higher for ZLI1565 than for 5BENZ, i.e. a liquid crystal with a higher shear viscosity may still have a smaller rotational viscosity in comparison to other liquid crystals.

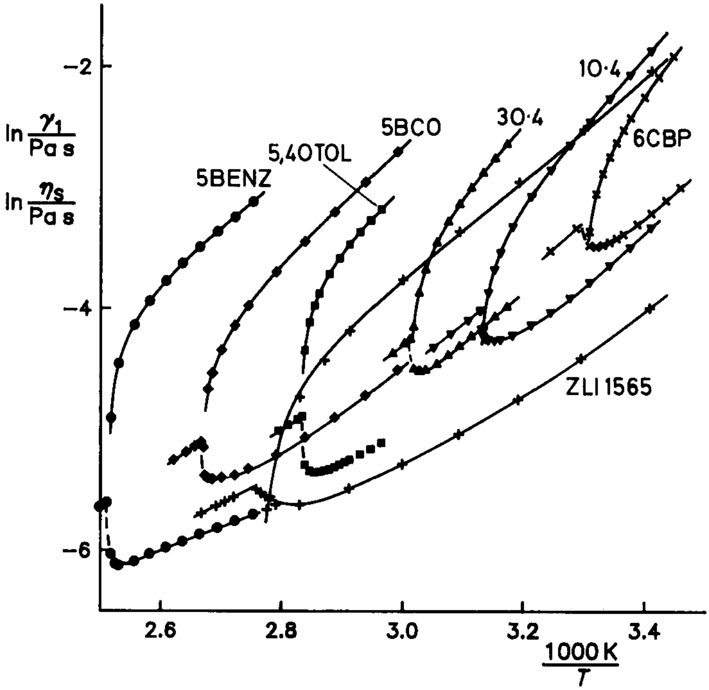

Figure 9. Temperature dependence of the rotational viscosity γ_1 and the shear viscosity η_S.

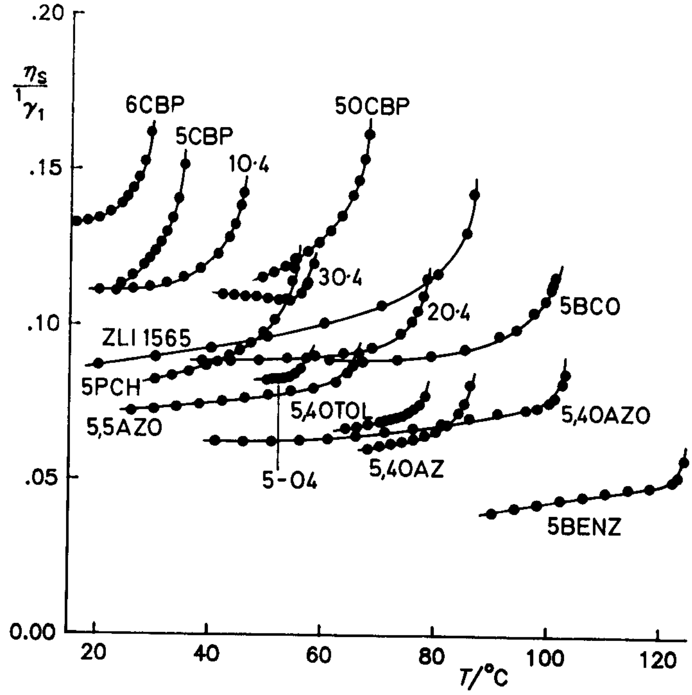

Figure 10. Temperature dependence of the viscosity ratio, $\eta_S/{}^1\gamma_1$.

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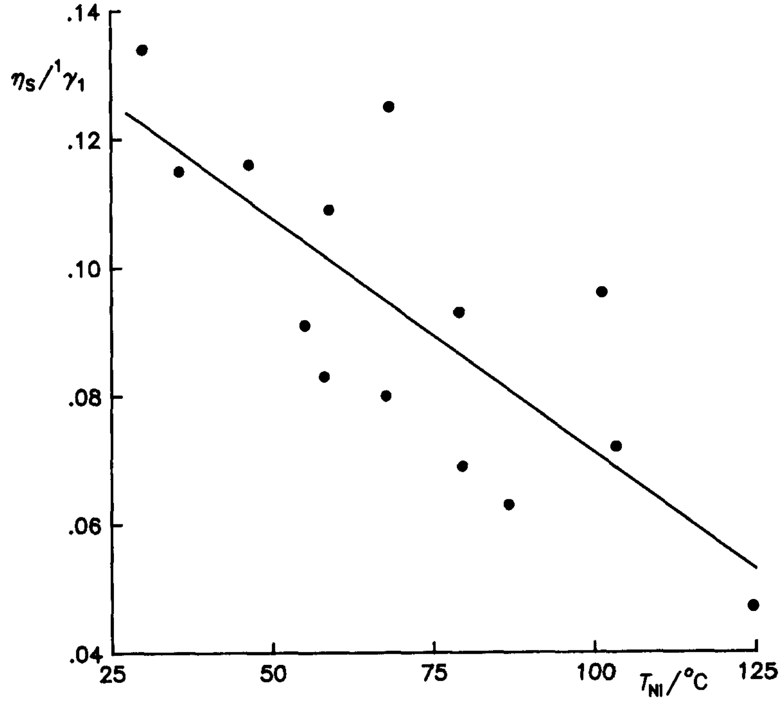

Figure 11. Viscosity ratio, $\eta_S/{}^1\gamma_1$, 10 K below the nematic–isotropic transition as a function of the nematic–isotropic transition temperature T_{NI}.

A microscopic model developed by Hess [12] leads to relations between the Leslie coefficients. The result for the ratio $\eta_S/{}^1\gamma_1$ is

$$\frac{\eta_S}{{}^1\gamma_1} = \frac{2}{15} a_6 R^2 + \frac{4}{105} R^2 S - \frac{1}{2} S^2, \tag{8}$$

where the first order parameter term can be neglected and a_6 is a constant which may depend on the liquid crystal but not on temperature. R describes the form anisotropy

$$R = \frac{l^2 - b^2}{l^2 + b^2}, \tag{9}$$

where l is the length of the molecule and b its diameter perpendicular to the long axis. Equation (8) predicts that the ratio $\eta_S/{}^1\gamma_1$ should show no exponential temperature dependence but only a weak dependence due to the order parameter terms. As R should be nearly constant, a_6 is the only term which could vary significantly for different liquid crystals. Figure 10 shows that the temperature dependence predicted by equation (8) is qualitatively correct. Furthermore, a_6 depends only slightly on the liquid crystal. As it seems to decrease with increasing nematic–isotropic transition temperature we have plotted (cf. figure 11) the ratio $\eta_S/{}^1\gamma_1$ at 10 K below the nematic–isotropic transition as a function of T_{NI}. The observed correlation is significant but not very good. The correlation between the isotropic shear viscosity, η_{iso}, and ${}^1\gamma_1$ at the nematic–isotropic transition (cf. figure 12) is somewhat better. The slope is about unity, i.e. the rotational viscosity is strongly related to the viscosity in the isotropic phase.

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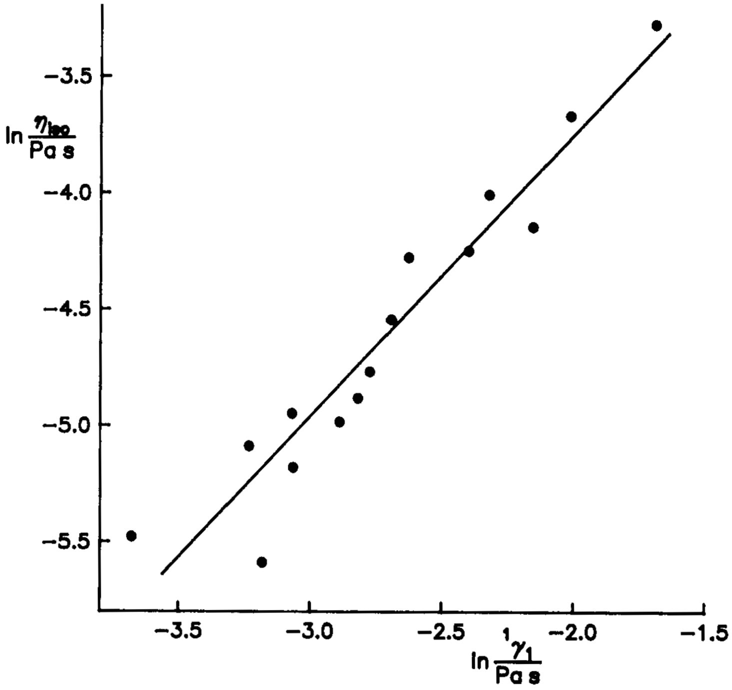

Figure 12. Isotropic shear viscosity at T_{NI} versus reduced rotational viscosity at T_{NI} in a double logarithmic plot.

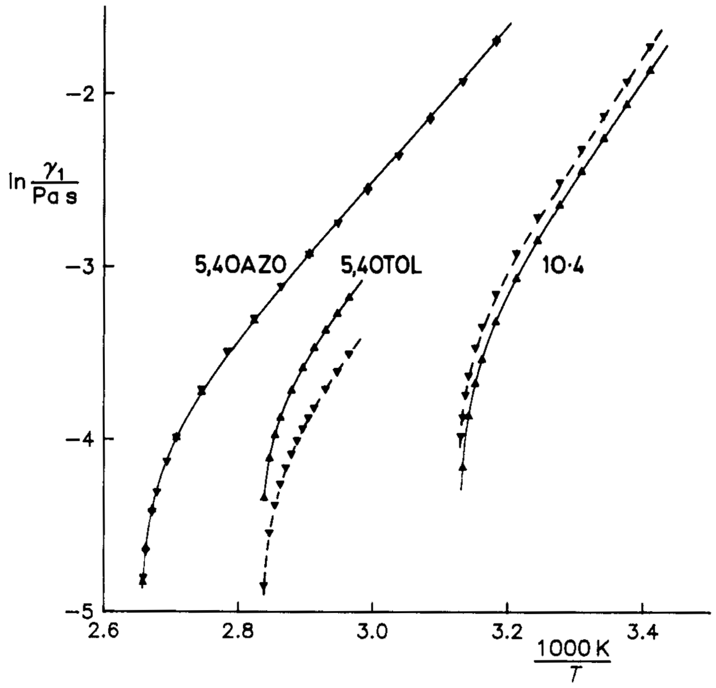

Figure 13. Measured (▲, ——) and calculated (▼, – – –) rotational viscosity as a function of the inverse temperature. The curves coincide for 5,4OAZO.

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Both correlations can be used to determine the rotational viscosity from shear viscosity measurements. The correlation between η_{iso} and ${}^1\gamma_1$ allows the calculation of ${}^1\gamma_1$ at the nematic–isotropic transition. Calculation of γ_1 at lower temperatures has to be performed with mean values for T^*, T_0, β and B. For liquid crystals with broad nematic phases, it is better to use shear viscosity measurements in the nematic phase. As the ratio $\eta_{\mathrm{S}}/{}^1\gamma_1$ still shows a slight temperature dependence we have used the expression $\eta_{\mathrm{S}}/\gamma_1 S^{-x}$ with x equal to 0·35 for the calculation

$$\frac{\eta_{\mathrm{S}}(T)}{\gamma_1 S^{-x}(T)} = \frac{\eta_{\mathrm{S}}(T_{\mathrm{NI}} - 10\,\mathrm{K})}{\gamma_1 S^{-x}(T_{\mathrm{NI}} - 10\,\mathrm{K})}$$

$$= 0{\cdot}1076 - 5{\cdot}048 \times 10^{-4}(T_{\mathrm{NI}}/^{\circ}\mathrm{C}), \qquad (10)$$

$$\gamma_1(T) = \left(1 - \frac{T}{T_{\mathrm{NI}} + 0{\cdot}35\,\mathrm{K}}\right)^{0{\cdot}35} \frac{\eta_{\mathrm{S}}(T)}{0{\cdot}1076 - 5{\cdot}048 \times 10^{-4}(T_{\mathrm{NI}}/^{\circ}\mathrm{C})}, \qquad (11)$$

in which the characteristic temperature $T^* = T_{\mathrm{NI}} + 0{\cdot}35\,\mathrm{K}$ for the representation of the temperature dependence of the order parameter has been used. Figure 13 shows a comparison between experimental and calculated values covering the range from good agreement (5,4OAZO) to bad agreement (5,4OTOL). Usually, deviations of up to 20 per cent are observed. A fit of the adjustable parameters within a group of similar liquid crystals should lead to a better agreement.

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References

[1] Jakeman, E., and Raynes, E. P., 1972, *Physics Lett.* A, **39**, 69.
[2] Gerber, P. R., and Schadt, M., 1982, *Z. Naturf.* (*a*), **37**, 179.
[3] Kneppe, H., and Schneider, F., 1983, *J. Phys.* E, **16**, 512.
[4] Hess, S., 1975, *Z. Naturf.* (*a*), **30**, 1224.
[5] Kneppe, H., Schneider, F., and Sharma, N. K., 1982, *J. chem. Phys.*, **77**, 3203.
[6] Schad, Hp., and Zeller, H. R., 1982, *Phys. Rev.* A, **26**, 2940.
[7] Kneppe, H., and Schneider, F., 1983, *Molec. Crystals liq. Crystals*, **97**, 219.
[8] Diogo, A. C., and Martins, A. F., 1981, *Molec. Crystals liq. Crystals*, **66**, 133.
[9] Kneppe, H., and Schneider, F., 1981, *Molec. Crystals liq. Crystals*, **65**, 23.
[10] Leslie, F. M., 1968, *Archs ration. Mech. Analysis*, **28**, 265.
[11] Ericksen, J. L., 1969, *Molec. Crystals liq. Crystals*, **7**, 153.
[12] Hess, S., 1984, *Z. Naturf.* (*a*), **39**, 22.