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Rotary Motion of Molecules about their Short Axis by Dielectric and Splay Viscosity Measurements

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Rotary Motion of Molecules about their Short Axis by Dielectric and Splay Viscosity Measurements

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Low frequency dielectric dispersion and splay viscosity were measured on four liquid crystalline materials. The relaxation times determined from dielectric dispersion measurements were compared with that calculated from

$$\tau = \frac{\zeta}{2kT}$$

where $\zeta = 8\pi\gamma_1 c^3 f(c/r)$, γ_1 being the splay viscosity and $f(c/r)$ the Perrin factor. The activation energies were determined and analysed for the above mentioned and other materials.

1 INTRODUCTION

The connection between the microscopic parameters, i.e. the diffusion constant or rotational relaxation time, and the macroscopic parameters, i.e. the viscosity coefficients is a puzzling question since the discovery of the Einstein–Stokes formula for translational and Debye formula for rotational diffusion motion. The discrepancy between the diffusion coefficients calculated with the help of viscosity data and the directly measured one was about a factor of 5–100 in spite of Perrin[1] modification which attempts to take into account the effect of the non-spherical form of the molecules. In spite of the doubts which are always present in such a comparison, it is useful to draw a parallel between the parameters determined from different experiments.

In liquid crystals we can directly measure the relaxation time for the rotation of the molecules about their short axis by dielectric relaxation measurements and determine the twist of splay viscosity coefficients by electrooptic methods. Rondelez *et al.*[2] compared the dielectric relaxation

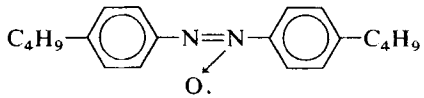
frequency of PAA and MBBA with the calculated one with the help of the twist viscosity parameter and found agreement. Recently Luckhurst *et al.*[3] have compared these data for MBBA at different temperatures, and demonstrated some differences.

In this paper we measure the splay viscosity coefficients and the low frequency dielectric relaxation times on four materials having different geometrical form, and dipoles in different positions on the molecules. Supposing the generalised form for the Debye formula we shall calculate the relaxation time and compare then with the directly measured one. The appropriate viscosity parameters have been determined by measuring the decay time of the splay deformation, which is also characterised (at small deformations) by the $\gamma_1 = \alpha_3 - \alpha_2$ viscosity parameter, where α_2 and α_3 are the Leslie coefficients.[4]

2 MATERIALS

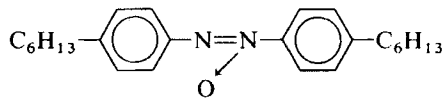
We have chosen the following four materials:

p-p'-di-butyl-azoxy-benzene,



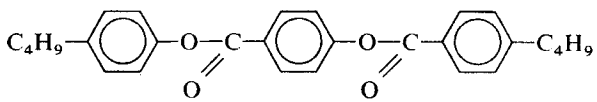
which is nematic in the 19–31°C range

p-p'-di-hexyl-azoxy-benzene



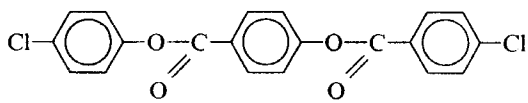
which is nematic in the 29–54°C range

di-butyl derivative of phenyl-benzoyloxy-benzoate



which is nematic in the 76–179°C range

and the di-chlorine derivative of phenyl-benzoyloxy-benzoate



which is nematic in the 146–240°C range (and on subsequent cooling to 105°C).

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Together with PAA and MBBA we get a great variety of materials for comparison concerning the length of the molecules and position of dipoles in the molecule. The azoxy dipole moment is $\mu = 1.7$ D, the carboxyle-dipoles has a value $\mu = 1.9$ D and both make nearly the same angle of about 52° with the para-axes.

3 SPLAY VISCOSITY MEASUREMENTS WITH EXTERNAL ELECTRIC FIELD

The liquid crystal materials were placed between two transparent electrodes, in which the molecules were aligned (by surface treatment) parallel to the glass slides (homogeneous structure), so the optical axis of the system was initially in the xy plane: the materials measured by us have positive dielectric anisotropy, the electric field tends to align the molecules parallel to the field, to the z direction, producing a splay deformation. By measuring the birefringence, i.e., the phase difference between the ordinary and extraordinary components of light penetrating the cell, the tilt angle θ of the molecules can be determined.[5] The characteristic time after removing the electric field is

$$\tau_d = \gamma_1 \frac{L^2}{\pi^2 K_{11}} \tag{1}$$

The elastic constant K_{11} was determined by measuring the threshold voltage U_0 from

$$K_{11} = \frac{\varepsilon_a U_0^2}{\pi^2} \tag{2}$$

where ε_a is the dielectric anisotropy.

The measured temperature dependence of the γ_1 viscosities are shown on Figure 1. In this figure the PAA and MBBA data taken from[6] are also shown. For each material we obtained an exponential relationship in $1/T$ scale up to the near neighborhood of the phase transition temperatures T_{NI}. The activation energies determined from the linear parts of the curves are given in parentheses in the figure.

These data show that the activation energies are nearly the same if the length of the molecular core (that part of the molecule with the benzene rings) are the same, i.e. 0.55 eV for two and 0.33 eV for three benzene ring core, respectively. It is striking that:

The values of viscosity extrapolated to the phase transition points are nearly the same in both cases, viz. when the molecules have dipoles at both ends and in the other case (i.e. without dipole or only one dipole).

The viscosity values at molecules having dipoles at both ends are an order of magnitude smaller than in the other case.

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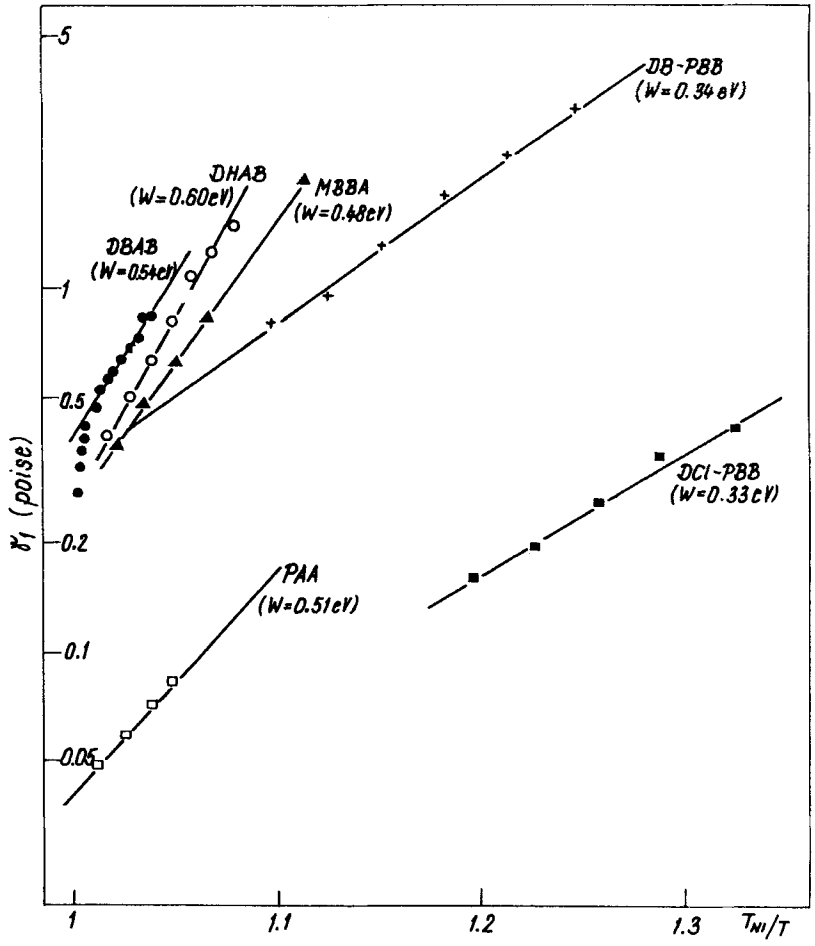

FIGURE 1 Semilog plot of the rotational viscosity $|\gamma_1|$ of six nematic liquid crystals as a function of T_{NI}/T, reciprocal reduced temperature.

4 DIELECTRIC RELAXATION TIME MEASUREMENTS

In a homogeneously oriented nematic material the uniaxial dielectric tensor has two components, viz. $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$.[4] These can be measured by taking the orienting magnetic field to be perpendicular or parallel to the alternating electric field. When molecules forming nematic mesophase have a nonzero dipole moment component along their long axis, a specific dispersion of $\varepsilon_{\perp}$ occurs at low frequencies which disappears in the isotropic liquid state.[7] This dispersion is connected with the reorientation of molecules

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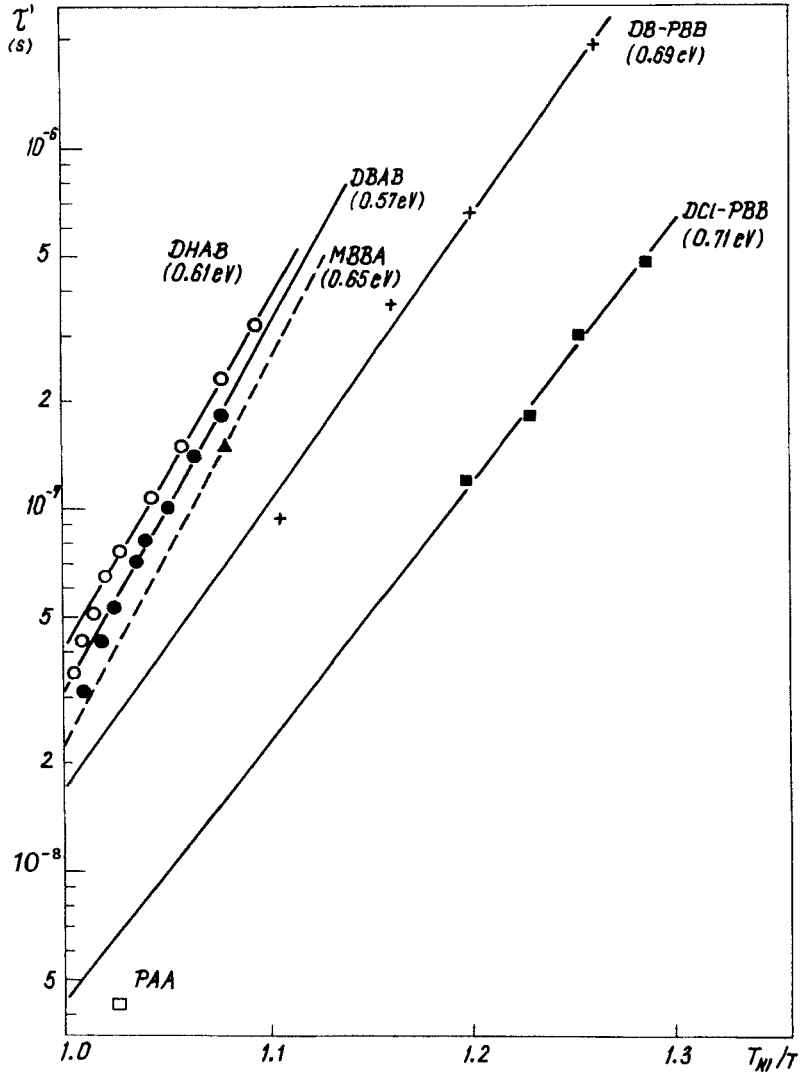

FIGURE 2 Semilog plot of the low frequency dielectric relaxation time τ' of six nematic liquid crystals as a function of reciprocal reduced temperature. The activation energies are in parentheses.

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about their short axes. Such motion is strongly hindered by the aligned neighbours of the molecule and is characterized by much higher relaxation time than the rotation around long molecular axis.

The substances were in a three-terminal parallel plate capacitor sample holder and were oriented by a 10 kOe magnetic field. The measurements in the 100 Hz–100 kHz frequency range were carried out using a General Radio 1615 A capacitance bridge, and those in the 100 kHz–10 MHz range using a Wayne Kerr B 602 bridge. In the 1–2 MHz frequency range a Hewlett Packard 250 B RX meter was applied. The temperature was regulated to within ± 0.1°C. In all cases the Cole–Cole plots were found to be semicircles with the centre lying on the real axes, so the characteristic relaxation time τ' could always be calculated according to the Debye equation for dielectric dispersion

$$\varepsilon(\omega) = \frac{\varepsilon_0 - \varepsilon_\infty}{1 + i\omega\tau'} \tag{3}$$

where ε_0 and ε_∞ are the static and high frequency limiting values of the dielectric constant, respectively.

The temperature dependence of the relaxation times is plotted in Figure 2. For each material we obtained a linear relationship (in log-lin scale) despite the fact that in the vicinity of the phase transition, a deviation similar to the viscosity can be seen.

Again, we obtained very close values of the activation energies (0.60 eV) for the compounds with two benzene rings. The three benzene ring esters have a slightly higher common activation energy with the values of about 0.7 eV, just the opposite to the case of viscosity.

Comparing the relaxation times on a reduced temperature scale, we can see that (similarly to viscosity, see Figure 1) the molecules having dipoles at both ends (PAA, DCl-PBB) have markedly smaller relaxation time values.

5 COMPARISON OF RELAXATION TIMES

The classical Debye formula

$$\tau = \frac{\zeta}{2kT} \tag{4}$$

gives us a possibility to compare the relaxation times determined by dielectric relaxation measurements with the calculated one with the help of γ_1 twist or splay viscosity data. In our case

$$\zeta = \begin{cases} 8\pi\gamma_1 a^3 & \text{for sphere and} \quad (5a) \\ 8\pi\gamma_1 c^3 f(c/r) & \text{for rotational ellipsoid} \quad (5b) \end{cases}$$

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Here, a is the radius of a sphere, c the half long axis of the ellipsoid, r is the radius of the rotational ellipsoid. [These were determined by means of a EUGON (Leybold, Courtauld) model.]

$$f(x) = \frac{2}{3}\frac{1-x^4}{\frac{2-x^2}{\sqrt{1-x^2}}\ln\frac{1+\sqrt{1-x^2}}{x}-1} \approx \frac{2}{3}\frac{1}{2\ln\frac{1+\sqrt{1-x^2}}{x}-1}$$

is the Perrin function.[1] The calculated relaxation time τ_y, viscosity γ_1, $f(x)$ and the geometrical parameters c and r with the τ' measured dielectric relaxation time at specific temperatures are shown in Table I for different materials.

TABLE I

Materials	c	r	$f(x)$	T°K	γ_1	$\tau_x \cdot 10^8$ s	$\tau' \cdot 10^8$ s
MBBA	10	3.1	0.25	295	1.25[a]	9.6	14.5[b]
PAA	8.9	2.9	0.26	398	0.06[a]	0.25	0.4[c]
DBAB	11	3.1	0.23	299	0.57	5.38	4.2
DHAB	13.5	3	0.20	315	0.64	9.1	10
DB-PBB	14.5	3.2	0.20	397	1.3	18	28
DC1-PBB	11.3	3.2	0.23	408	0.263	1.94	30

[a] From Ref. 6.
[b] From Ref. 2.
[c] From Ref. 8.

From Table I we are able to conclude that the calculated and the measured relaxation times agree rather well for the first five materials. We synthesized the DCl-PBB after this to separate the effect of tails, believing that the agreement will be even better. The experiment gave the opposite result, as can be seen in the last line of Table I. We can not explain the difference by the dipoles being at both ends (as was done previously). The effect of charge on Cl must therefore be considered. Bearing in mind the idea of the previously used geometry effect (5) we can say that the "Cl ions" of different molecules repulse each other so their effective length is larger than that geometrically calculated. In other words the molecules in DCl-PBB are moving not only between their neutral neighbours, but in an "ionised" liquid.

6 DISCUSSION

The splay viscosity as well as the low frequency dielectric relaxation process are connected with the rotation of the molecules around their short axis, and with the existence of nematic order. In both figures we can see similar temperature dependence, both parameters decline from the linear in the vicinity

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of the phase transition temperature. Similar results for twist viscosity[9] and for relaxation time[10] have already been found.

Regardless of this effect, the activation energies determined from the linear part of the curves characterising the processes can be compared. The activation energy values found from the viscosity and relaxation time measurements respectively, are nearly the same within the experimental error (± 0.04 eV) or the difference is about 0.1 eV for the compounds with two benzene rings, while for double esters such as DB–PBB and DCl–PBB we obtained values twice larger from relaxation times than from viscosity. The difference in activation energies shows that there is a difference between the two phenomena as well. In reality, in splay viscosity the rotation about the short axis is a "collective" rotation, in dielectric relaxation an individual one. The collective rotation means that when a molecule makes a rotation, the nearest neighbour has a hole to turn in, so the barrier is smaller. The difference between the activation energies are connected with the synchronized motion of holes which have an activation energy up to 0.1 eV.

The big difference in the case of the three benzene ring ester molecules (0.3 eV) can not be interpreted solely on the basis of hole motion. Probably these molecules during rotation about their short axes make a turn, a rotation, about their long axes as well. The activation energy of this type of motion for the same molecule has been measured,[11] the value 0.2 eV having been obtained. So the relatively large activation energy for these two esters in dielectric measurement is the sum of the three effects.

Taking into account the whole process we can now say that the values calculated according to the Debye formula (4) agree well with those measured by dielectric relaxation. The only exception is DCl–PBB, where the marked difference can be ascribed to the effect of "Cl ions." The twist and splay viscosity coefficients are appropriate parameters to calculate, according to the Debye formula, the rotational motion of molecules around their short axis.

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