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# Molecular Crystals and Liquid Crystals

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# Experimental Data on the Elasticities and Viscosities of Some Nematics

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EXPERIMENTAL DATA ON THE ELASTICITIES AND VISCOSITIES OF SOME NEMATICS

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(Submitted for publication September 1, 1978)

We have measured the elastic ratios of two types of nematic liquid crystals: 4 methoxy 4' azoxybenzene (N<sub>4</sub>) and p-p' dibutyl azoxy benzene (Dibab). The experiments involved the use of a light scattering technique and analysis of the scattered light versus the scattering angle. From these measurements and the results of other investigators (De Jeul), Prost<sup>2</sup>), Van Eck<sup>3</sup>) we were able to extract and to discuss the coefficients of elasticity and viscosity.

#### INTRODUCTION

There are several ways of obtaining information about the viscosities and elasticities of an nematic liquid crystal (n.l.c.). A very effective tool for this purpose is the Rayleigh light scattering technique. A laser beam is strongly scattered by an n.l.c. due to director fluctuations<sup>4)</sup>.

From an analysis of the light intensity measured versus the scattering angle, ratios of the elastic constants can be determined. In addition from the measured linewidths of the scattered light, visco-elastic ratios can be deduced<sup>3,4</sup>).

This letter describes such measurements on 4 methoxy 4' azoxy benzene ( $N_4$ ) and p-p' dibutyl azoxy benzene (Dibab) which have their clearing temperature  $T_c$  at 347 K and 304 K respectively. Visco-elastic and elastic ratios were determined from the experimental results using essentially De Gennes theory.

# THEORY AND MEASUREMENTS

The differential cross-section for light scattering from an nematic is given by 5):

$$\frac{d\sigma}{d\Omega} = V \cdot \{(\varepsilon_a \omega_0^2)/(4\pi c^2)\}^2 \cdot \sum_{\alpha=1,2} \frac{k_B \cdot T}{K_\alpha(q)} \cdot G_\alpha^2$$
 (1)

where V is the scattering volume,  $\epsilon_a$  the anisotropic dielectric constant, c the velocity of light,  $\omega_0$  the angular

frequency of light, T the absolute temperature and  $k_B$  is Boltzmann's constant. In addition  $K_{\alpha}(q) = K_{\alpha\alpha}q^{-2} + K_{33}q//^2$  ( $\alpha = 1, 2$ ) where  $K_{ii}$  are the three elastic constants associated with the splay, twist and bend deformation respectively;  $q_i$  and  $q_i$  are the normal and parallel components of the scattering vector q with respect to the director  $n_0$ .  $G_{\alpha} = i_{\alpha}f_{0} + f_{\alpha}i_{0}$  ( $\alpha = 1, 2$ ) is a geometrical factor, where i and f are unit vectors giving the polarizations of the incoming and scattered light respectively. The subscripts  $\alpha$  and 0 indicate components with respect to an orthonormal system of reference defined by  $\frac{1}{2} = \frac{1}{2} = \frac{1}{2} \times \frac{1$ 

an orthonormal system of reference defined by  $\vec{e}_0 = \vec{n}_0$ ,  $\vec{e}_2 = (\vec{n}_0 \times \vec{q})/|\vec{n}_0 \times \vec{q}|$  and  $\vec{e}_1 = \vec{e}_2 \times \vec{e}_0$ .

If one takes  $\vec{f}$  normal to the observation plane defined by the wave vectors  $\vec{k}_0$  and  $\vec{k}_s$  of the incoming and the scattered light respectively,  $\vec{i}$  in the plane of observation and  $\vec{n}_0$  parallel to  $\vec{f}$ , eq. (1) becomes

$$\frac{d\sigma}{d\Omega} \sim 1/q \int_{\alpha=1,2}^{2} \cdot \sum_{\alpha=1,2}^{2} G_{\alpha}^{2} / K_{\alpha\alpha}$$
 (2)

If however  $\vec{n}_0$  is taken in the plane of observation normal to  $\vec{k}_0$ , and  $\vec{i}$  and  $\vec{f}$  remain in the same position with respect to the plane of observation as before eq. (1) becomes

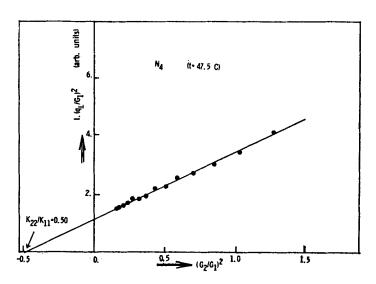
$$\frac{d\sigma}{d\Omega} \sim G_2^2/(K_{22}q_1^2 + K_{33}q_{//}^2)$$
 (3)

From intensity measurements taken as a function of the scattering angle  $\theta$  we can derive two elastic ratios with the help of eqs. (2) and (3) by plotting  $I \cdot (q_1^2/G_1^2)$  versus  $(G_2^2/G_1^2)$ , and  $G_2^2/(q_1^2)$  versus  $(q_1^2/q_1^2)$  respectively, where I is the scattered light intensity measured with a photomultiplier tube.

Figures 1a, b show the two results for  $N_4$ . Both show a straight line, and from the intercept with the abscissa we can immediately read the elastic ratios.

In figure 2 we have plotted the elastic ratios of  $N_4$  versus reduced temperature  $(T-T_c)/T_c$ . Note that only close to the n-i transition a slight temperature dependency does occur.

Using the results of  $\operatorname{Prost}^2$  who measured  $\gamma_1$  of  $\operatorname{N}_4$  as a function of temperature we have calculated  $\operatorname{K}_{22}$  from the visco-elastic ratio  $\gamma_1/\operatorname{K}_{22}$  obtained from the spectra of the light intensity fluctuations<sup>3</sup>). Then the values for  $\operatorname{K}_{11}$  and  $\operatorname{K}_{33}$  could be obtained separately from the measured elastic ratios. Figure 3 gives the results of the twist, splay and bend elasticities as a function of reduced temperature. We have added the results of Aronishidze et al.<sup>6</sup>), who have measured the twist elasticity with doped  $\operatorname{N}_4$  material (open triangles in figure 3).



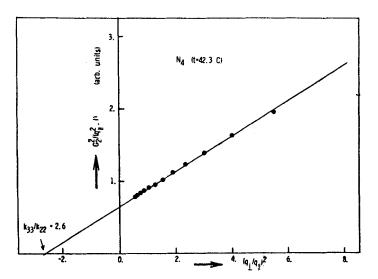


FIGURE 1a, b. The linear behaviour between  $I(q|/G_1)^2$  versus  $(G_2/G_1)^2$  and  ${G_2}^2/({q//}^2 \cdot I)$  versus  $(q|/q//)^2$  respectively.

# 42 D. C. VAN ECK and M. PERDECK

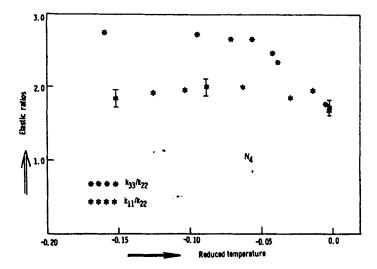


FIGURE 2. The elastic ratios  $(K_{33}/K_{22})$  and  $(K_{11}/K_{22})$  of  $N_4$  plotted versus reduced temperature.

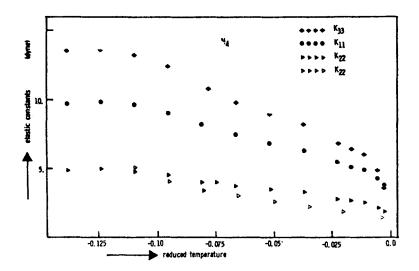


FIGURE 3. The splay ( $K_{11}$ ), twist ( $K_{22}$ ) and bend ( $K_{33}$ ) elastic constant of  $N_4$  versus reduced temperature.

In addition we have calculated the three principal viscosities which are connected with the visco-elastic ratios obtained from the spectra of the scattered light fluctuations 3,4).

We have the twist viscosity 
$$n_{twist} = \gamma_1 = \alpha_3 - \alpha_2$$
  
the splay viscosity  $n_{splay} = \gamma_1 - \alpha_3^2/n_b$  (4)  
the bend viscosity  $n_{bend} = \gamma_1 - \alpha_2^2/n_c$ 

where  $\alpha_2$  and  $\alpha_3$  are the Leslie coefficients and  $\eta_b$  and  $\eta_c$  the positive Miesowicz constants of an n.l.c. Figure 4 shows an example for Dibab. Here we have used the results of De Jeul) and Van Eck<sup>3)</sup> who measured the elasticities and the viscoelastic ratios respectively.

### **DISCUSSION**

Our study of the "scattering" viscosities shows that in all cases  $\eta_{bend} << \gamma_1$  and  $\gamma_1$  is of the order of  $\eta_{splay}.$  From eqs. (4) it follows that  $(\eta_{bend} - \gamma_1)$  must be negative. Our results are in good agreement with this requirement. On the other hand the quantity  $\eta_{splay} \div \gamma_1 = -\alpha_3^2/\eta_b$  also requires a negative sign. In all measurements we know there is a slight-inconsistency between measurement and theory, because the

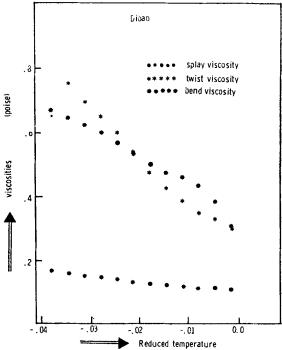


FIGURE 4. The splay, twist and bend viscosities for Dibab versus reduced temperature.

measurements show that  $\gamma_1$  -  $\eta_{splay}$  becomes negative (fig. 4). This inconsistency can only be removed by assuming that for all practical purposes  $\alpha_3$  can be put equal to zero in our equations. Then eq. (4) becomes

$$\eta_{\text{splay}} = \eta_{\text{twist}} = -\alpha_2 
\eta_{\text{bend}} = -\alpha_2 - \alpha_2^2/\eta_c$$
(5)

This simplification implies that we can obtain one elastic ratio ( $K_{11}/K_{22}$ ) directly from the visco-elastic ratios. These measurements give us another method to obtain elastic ratios.

Figure 5 shows the thus obtained results for Dibab compared with the measurements of De Jeul) who determined the elastic ratios from the measurements of Frederick transitions.

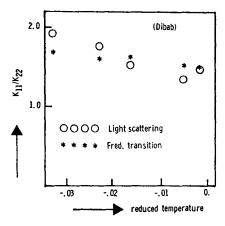


FIGURE 5. Comparison of the elastic ratio  $(K_{11}/K_{22})$  obtained from spectral light-intensity measurements (circles) and measurements of the Frederick-transition (asterisks) respectively versus reduced temperature.

Our conclusion is that there are several methods of measuring elastic ratios with the help of the light scattering technique.

#### ACKNOWLEDGEMENT

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