CORRELATION BETWEEN TWIST VISCOSITY AND DIELECTRIC RELAXATION IN NEMATIC LIQUID CRISTALS (*)

A. C. Diogo and A. F. Martins
Centro de Física da Matéria Condensada (INIC)
Av. Gama Pinto 2, 1699 Lisboa Codex, Portugal

(Received 16 June 1980)

ABSTRACT — We compare experimental data on the low-frequency dielectric relaxation time $\tau_{\parallel}^{(1)}$ with data on the twist viscosity γ_1 for the nematic phase of the elements with $n = 4$ to 7 in the homologous series of 4,4'-di-n-alkoxyazoxybenzenes, using the relation

$$\tau_{\parallel}^{(1)} \simeq 1/\nu_0 = (\pi^2 V^* / kT) \cdot \gamma_1$$

which was proposed by us in a previous paper; here, V^* is a molecular volume and T is the temperature.

This relation is verified to within the experimental uncertainties in all cases studied.

1 — INTRODUCTION

In previous papers [1], we proposed a molecular statistical theory of the twist viscosity in nematic liquid crystals which involves the frequency ν_0 of the rotational jumps performed by the nematic molecules about an axis normal to their preferred orientation **n**, between two equilibrium positions separated by π radians. This quantity was related to the twist viscosity coefficient γ_1 by the following expression [1]:

$$\frac{1}{\nu_0} = \frac{\pi^2 V^*}{k T} \cdot \gamma_1 \tag{1}$$

(*) Presented at the Second Conference of the Portuguese Physics Society (Porto, April 16-18, 1980).

where V^* is the molecular volume at the temperature T, as extrapolated from the isotropic phase, and *k* is the Boltzmann constant. It was suggested in ref. [1] that

$$\frac{1}{\nu_o} \simeq \tau_{\parallel}^{(1)} \tag{2}$$

or

$$\gamma_1 \simeq \frac{k\,T}{\pi^2\,V^*} \cdot \tau_{\parallel}^{(1)} \tag{3}$$

which is a relation between twist viscosity and dielectric relaxation since $\tau_{\parallel}^{(1)}$ is the low-frequency dielectric relaxation time, measured when the electric field **E** is parallel to the nematic director **n**. This low frequency relaxation observed in nematics, was attributed [2] to the reorientation of the component of the molecular dipole parallel to the long molecular axis, which is hindered by the nematic mean-field potential. Therefore, a check of relation (3) may provide information about the molecular processes that contribute both to the low frequency dielectric relaxation and to the twist viscosity.

The validity of relation (3) was demonstrated in ref. [1] for the case of p-azoxyanisol, which is the first element in the homologous series of 4,4′-di-n-alkoxyazoxybenzenes (nOAB). Here, the result of [1] is extended to the elements of this series with aliphatic chains ranging from n=4 (butoxy) to n=7 (heptyloxy). In the next section we compare the values of $1/\nu_o$ computed from our experimental data on the twist viscosity [3] with the dielectric relaxation times $\tau_{\parallel}^{(1)}$ quoted from refs [4-6], and discuss the results. Section 3 displays our main conclusion together with a suggestion for further work.

2 — EXPERIMENTAL DATA AND DISCUSSION

Figures 1 to 4 show the plots of log $\tau_{\parallel}^{(1)}$ and log $(1/\nu_o)$ versus $1/T$, respectively for the homologues 4OAB, 5OAB, 6OAB, and 7OAB. The dielectric data are quoted from refs. [5] and [6], and ν_o was computed from our data on twist viscosity [3], using expression (1). In computing ν_o we used the actual molecular volume in the nematic phase V_N [7], instead of V^*, due to the lack of enough data on the density of these materials in the isotropic phase. This

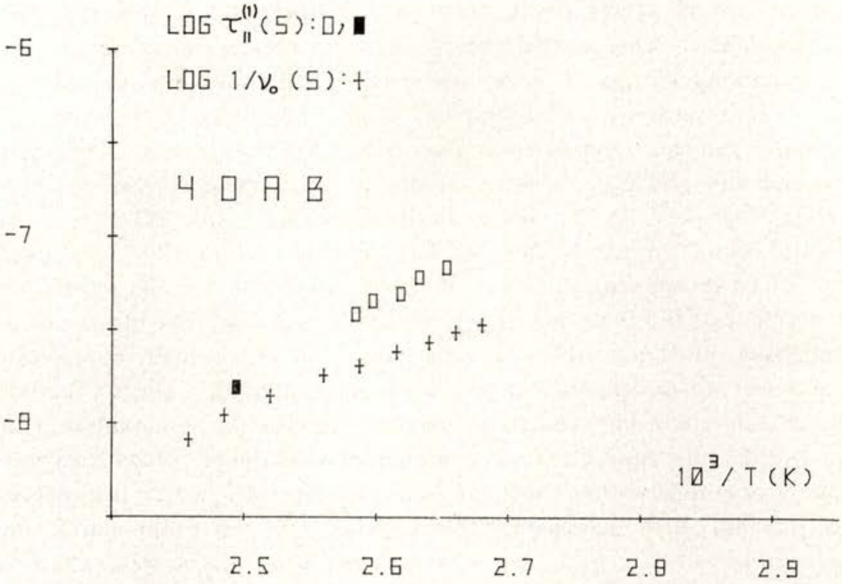

Fig. 1 — Log $\tau_{\parallel}^{(1)}$ and log $1/\nu_o$ versus $10^3/T$ for 4OAB. Data points: + : values of $1/\nu_o$ computed from the twist viscosity data of [3]; ■: $\tau_{\parallel}^{(1)}$ quoted from [5]; □ : $\tau_{\parallel}^{(1)}$ quoted from [6].

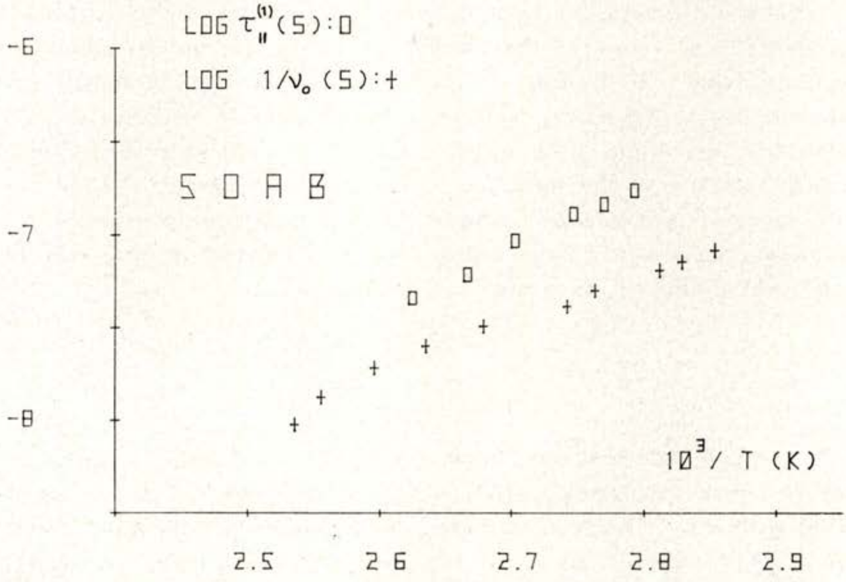

Fig. 2 — Log $\tau_{\parallel}^{(1)}$ and log $1/\nu_o$ versus $10^3/T$ for 5OAB. Data points: + : values of $1/\nu_o$ computed from the twist vicosity data of [3]; □ : $\tau_{\parallel}^{(1)}$ quoted from [6].

approximation seems to be not very important due to the smallness of the density jump at the nematic-isotropic phase transition.

Looking at figs. 1 to 4, one sees that the simple expression (2) is in reasonably good agreement with experience along the full nematic range of these materials. In the low temperature region of the nematic phase of these materials, $\tau_{\parallel}^{(1)}$ appears to increase slightly faster than $1/\nu_o$ as the temperature decreases. This effect may be partly due to the use of the nematic molecular volume $V_N(T)$ instead of $V^*(T)$ in the computation of ν_o, because the thermal expansion coefficient of the isotropic phase is usually less than that of the nematic phase. Most probably, however, this will not explain completely the observed discrepancy, and a sounder explanation should include some differences between twist viscosity and dielectric relaxation. One such difference may stand on the distinct sensitivities of both experimental methods to the short range molecular order, which is expected to increase with decreasing temperature. On the other hand, the calculation of $\tau_{\parallel}^{(1)}$ from the observables in dielectric relaxation is always based on some model and is subject to a number of approximations that are difficult to control. The values obtained are model-dependent to an extent that could be used to explain the observed discrepancy [8].

The agreement between $1/\nu_o$ and $\tau_{\parallel}^{(1)}$ shown by figs. 1 to 4 supports our view [1] that a simple model of molecular jumps between the two minima of the nematic mean-field potential can account for the essential features of both the twist viscosity and the dielectric relaxation, although it may be somewhat surprising due to the complexity of the microscopic behaviour involved in these two processes. This is specially true in the high temperature region of the nematic phase, near the nematic-isotropic transition temperature, where $1/\nu_o$ and $\tau_{\parallel}^{(1)}$ have nearly the same value.

3 — CONCLUSION

We conclude that the available dielectric relaxation data about $\tau_{\parallel}^{(1)}$ in the nematic materials 4OAB, 5OAB, 6OAB and 7OAB is compatible with eq. (3) which is based on a molecular statistical theory of $\gamma_1(T)$ proposed by us [1, 3]. Our viscosity measurements discussed here are the first set of data on γ_1 obtained from one homologous series of nematic liquid crystals. In order to test more closely the

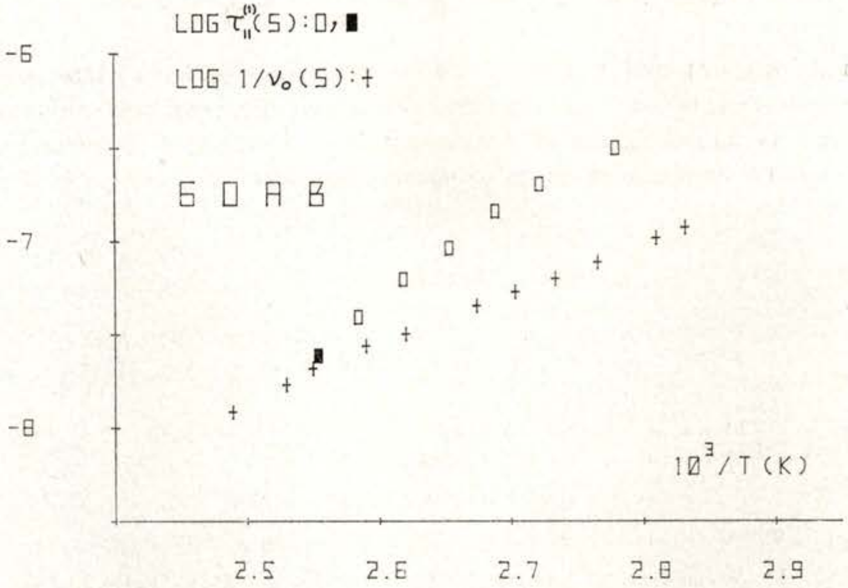

Fig. 3 — Log $\tau_{\parallel}^{(1)}$ and log $1/\nu_o$ versus 10^3/T for 6OAB. Data points: + : values of $1/\nu_o$ computed from the twist viscosity data of [3]; ■ : $\tau_{\parallel}^{(1)}$ quoted from [5]; □ : $\tau_{\parallel}^{(1)}$ quoted from [6].

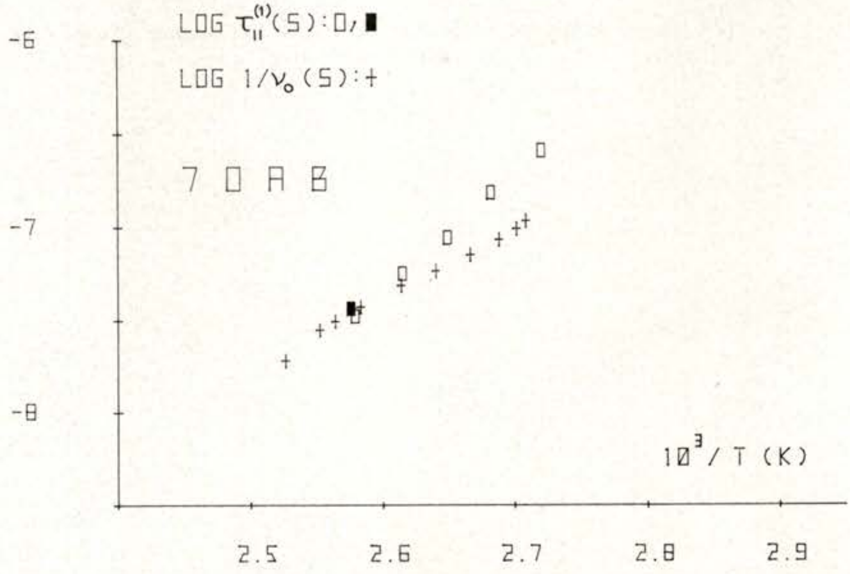

Fig. 4 — Log $\tau_{\parallel}^{(1)}$ and log $1/\nu_o$ versus 10^3/T for 7OAB. Data points: + : values of $1/\nu_o$ computed from the twist viscosity data of ref [3]; ■ : $\tau_{\parallel}^{(1)}$ quoted from [5]; □ : $\tau_{\parallel}^{(1)}$ quoted from [6].

relations (2) and (3) it should be interesting to have systematic measurements on both dielectric relaxation and twist viscosity, as well as measurements of the density, as a function of temperature, for other homologous series of nematic liquid crystals.

REFERENCES

[1] A. F. MARTINS and A. C. DIOGO, *Portgal. Phys.*, **9**, 129 (1975); A. F. MARTINS, A. C. DIOGO and N. P. VAZ, *Ann. Physique* **3**, 361 (1978).

[2] G. MEIER and A. SAUPE, *Mol. Cryst.*, **1**, 515 (1966); A. J. MARTIN, G. MEIER and A. SAUPE, *Symp. Farad. Soc.* n.° 5, 119 (1971).

[3] A. C. DIOGO and A. F. MARTINS, to be published.

[4] W. MAIER and G. MEIER, *Z. Naturforschg.* **16-a**, 1200 (1961).

[5] H. WEISE and A. AXMANN, *Z. Naturforschg.* **21-a**, 1316 (1966); A. AXMANN, *Z. Naturforschg.* **21-a**, 615 (1966).

[6] A. MIRCEA-ROUSSEL and F. RONDELEZ, *J. Chem. Phys.*, **63**, 2311 (1975).

[7] V_N was computed through the density data of F. LINSERT, Master Thesis, Halle (1945).

[8] See for instance W. H. DE JEU, *Solid State Physics, Suppl.* **14**, 109 (1978).