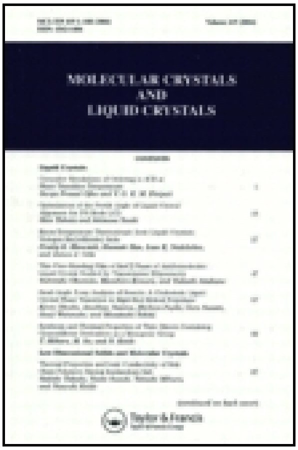

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A Study of the Dielectric Relaxation in Nematic Liquid Crystals using the Freedericksz Transition Technique

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We have used the Freedericksz transition technique to study the low frequency dielectric relaxation of nematic liquid crystals arising from the orientational relaxation of the long axis component of the molecular dipoles. The experiments have been done in two geometries: (i) the splay deformation produced by an AC electric field in a homogeneously aligned sample and (ii) the effect of a crossed AC electric field on the bend deformation produced by a magnetic field in a homeotropically aligned sample. The experiments have been done on (a) 4′-*n*-hexyl-4-cyanobiphenyl (6CB) and (b) *trans*-*p*-*n*-nonyloxy-α-methyl-*p*′-cyanophenyl cinnamate (90MCPC). In 6CB the relaxation occurs in the neighbourhood of 5 MHz (at room temperature). In 90MCPC the dielectric anisotropy changes sign in the neighbourhood of 1 MHz (at 54°C) to become negative at higher frequencies. We have also observed electrohydrodynamic instabilities in 90MCPC, with the domain sizes comparable to sample thickness at frequencies in the neighbourhood of dielectric isotropy.

INTRODUCTION

Due to the long range orientational order in a nematic liquid crystal, reorientations of the anisotropic molecules about their short axes are relatively difficult in such a medium. As a consequence, the relaxation of the long axis component of the dipole moment ($\mu_{\parallel}$) is retarded. A simple theory for the retardation factor g was proposed by Meier and Saupe.[1] The retarded relaxation time is given by

$$\tau_r = g\tau_0 \tag{1}$$

where τ_0, the Debye relaxation time in the absence of retardation is given by

$$\tau_0 = \zeta/2k_B T \tag{2}$$

where ζ is a friction coefficient, k_B the Boltzmann constant and T the absolute temperature. Further, we have

$$g = \frac{k_B T}{q_{\text{nem}}}\left\{\exp\left(\frac{q_{\text{nem}}}{k_B T}\right) - 1\right\} \tag{3}$$

where q_{nem} arises from the long range orientational order in the medium, and can in principle be derived from molecular models.[1] Hence the relaxation frequency can be written, to a very good approximation, as

$$f_r \propto \exp\left\{-\frac{q_{\text{nem}} + q_{\text{visc}}}{k_B T}\right\} \tag{4}$$

where q_{visc} is the activation energy associated with ζ. If an alternating electric field of a frequency greater than f_r is applied to the medium, the long axis component of the dipole moment of the *molecule* ($\mu_{\|}$) is no longer able to follow the external field and hence ε_1, the dielectric constant of the *medium* measured with the electric field parallel to the director decreases considerably. On the other hand ε_2 whose major contribution comes from the component of the dipole moment perpendicular to the long axis ($\mu_{\perp}$) does not exhibit the low frequency relaxation.

We have studied the frequency dependence of the dielectric anisotropy $\Delta\varepsilon(=\varepsilon_1 - \varepsilon_2)$ in two compounds both of which exhibit strong positive low frequency dielectric anisotropies.

EXPERIMENTAL

We have studied the dielectric relaxation by measuring the Freedericksz transition fields for elastic deformation of suitably prepared nematic samples. Two geometries have been employed:

i) A homogeneously aligned sample, i.e., a sample with the director parallel to the plane of the substrates, is contained between two tin oxide coated glass plates. The homogeneous alignment is achieved by the oblique coating of silicon on the plates.[2] If V_c is the threshold field for distortion,

$$k_{11} = \frac{\Delta\varepsilon V_c^2}{\pi^2} \tag{5}$$

where k_{11} is the splay elastic constant. Hence

$$\Delta\varepsilon \propto \frac{1}{V_c^2} \tag{6}$$

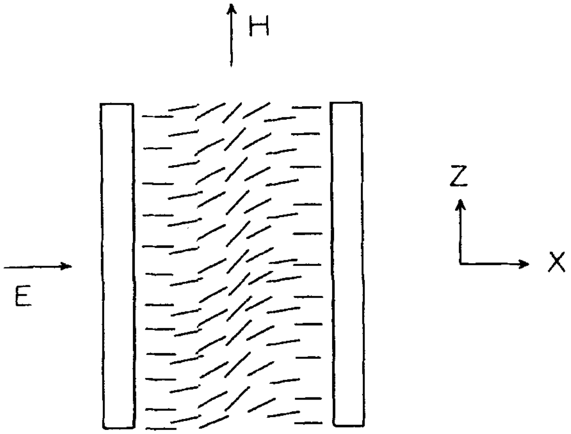

FIGURE 1 Schematic diagram of the experimental set up to study dielectric relaxation of nematic liquid crystals using bend elastic constant measurements.

i.e., as we approach the relaxation frequency, V_c should increase, and if $\Delta\varepsilon$ becomes negative, there is no deformation of the sample if electrohydrodynamic effects are absent.

ii) A homeotropically aligned sample is taken between two tin oxide coated glass plates. The Alignment is achieved by treating the glass plates with a dilute solution of ethyl tetra methyl ammonium bromide in chloroform. The sample is mounted between the pole pieces of an electromagnet such that the undistorted director is normal to the magnetic field (Figure 1). A known voltage V is applied between the electrodes and the magnetic field H_e necessary to start a deformation in the sample is noted. Then, we get

$$k_{33} = \frac{\Delta\chi d^2 H_e^2}{\pi^2} - \frac{\Delta\varepsilon V^2}{\pi^2} \tag{7}$$

where k_{33} is the bend elastic constant, $\Delta\chi$ the anisotropy of the *volume* diamagnetic anisotropy of the medium and d the thickness of the sample. We can write a similar expression for the threshold magnetic field H_0 when $V = 0$. Using this, we get

$$\Delta\varepsilon = \Delta\chi d^2\left(\frac{H_e^2 - H_0^2}{V^2}\right). \tag{8}$$

In deriving (6) and (8), we have assumed that piezoelectric effects arising from the shape anisotropy of the molecules do not contribute to the Freedericksz transition fields.[3] As Gruler[4] has argued, there will be a relaxation of the elastic constants k_{11} and k_{33} if the deformation is changing sign with the frequency of the applied fields. We have in the present case a static

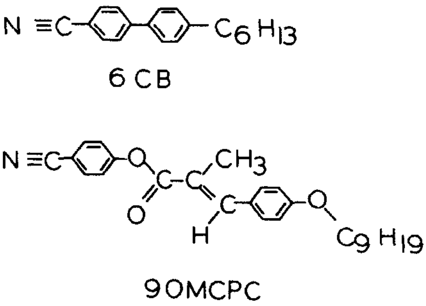

FIGURE 2 Molecular structures of 4′-*n*-hexyl-4-cyanobiphenyl (6CB) and *trans-p-n*-nonyloxy-α-methyl-*p*′-cyanophenyl cinnamate (9OMCPC).

deformation above the threshold, and the molecular dipoles will be following the applied electric field below f_r. Hence during one half cycle of the applied field, the shape anisotropy favours the dipolar orientation in one half of the sample while in the other half of the sample with opposite curvature (see Figure 1) the orientations due to the shape anisotropy and the dipole moment will be opposing each other. However, *at* the Freedericksz transition, the distortion in the medium is negligibly small and hence the Freedericksz transition field itself is not affected by the shape anisotropy (i.e., piezoelectric) effects. Hence we can assume that (6) and (8) truly represent the variation in dielectric anisotropy.

In both the geometries, the sample was mounted in a suitable oven whose temperature could be measured to an accuracy of ±0.02° using a copper-constantan thermocouple. The deformation was detected visually, using an appropriate optical set up. Other experimental details have been given elsewhere.[5]

We have studied two compounds, viz., 6CB[6] and 9OMCPC[7] whose structural formulae are shown in Figure 2. Both are colourless compounds, the former having the nematic–isotropic transition at 28.8°C and the latter at 70.3°C.

RESULTS AND DISCUSSION

In order to check Eq. (7) we have plotted in Figure 3, H_e^2 vs. V^2 for two compounds, viz., 6CB and 8OCB (4′-*n*-octyloxy-4-cyanobiphenyl). In accordance with Eq. (7), we get linear variations.

Values of V_c^2 (geometry i) and $(H_e^2 - H_0^2)/V^2$ (geometry ii) are plotted as functions of the frequency (marked on a logarithmic scale) in Figure 4 for 6CB at room temperature. In this case, H_e^2 is always greater than H_0^2,

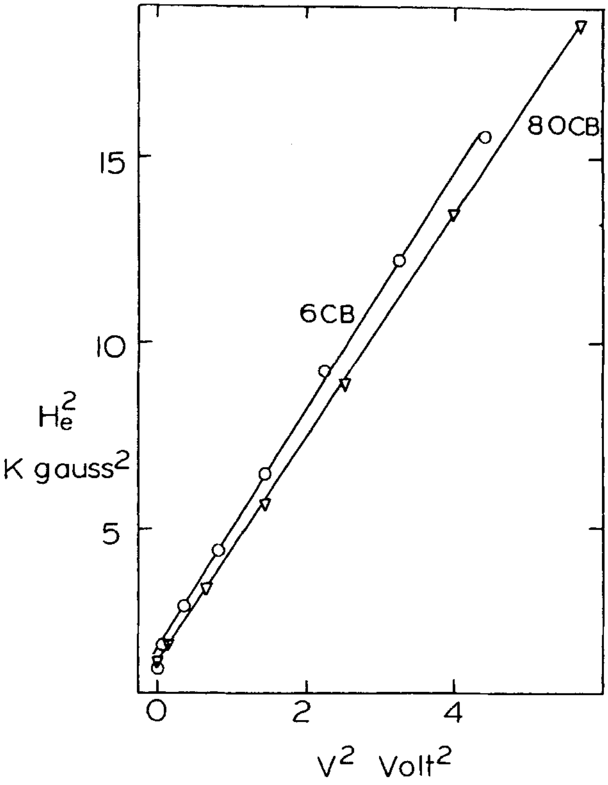

FIGURE 3 Verification of the linear dependence of H_e^2 on V^2 in 4′-*n*-hexyl-4-cyanobiphenyl (6CB) and 4′-*n*-octyloxy-4-cyanobiphenyl (8OCB).

i.e., $\Delta\varepsilon$ is always positive though it reduces to a small value beyond the relaxation frequency $f_r \simeq 5$ MHz. This behaviour is easily understood in terms of the molecular structure (Figure 2). There is practically no perpendicular component of the dipole moment and the dielectric anisotropy is strongly positive at low frequencies due to the nitrile group. Beyond f_r, the dielectric anisotropy is essentially determined by the molecular polarizability which has a positive anisotropy.

The results on 90MCPC for three temperatures are displayed in Figure 5. In this case, beyond a certain frequency f_0 (in the neighbourhood of f_r), $H_e < H_0$, i.e., $\Delta\varepsilon$ becomes negative (see Eq. (8)) and f_0 decreases with decrease of temperature (Figure 5). There have been several earlier observations on the sign reversal of $\Delta\varepsilon$ due to the relaxation of $\varepsilon_\parallel$, both in single compounds[8,9] as well as in mixtures.[10-12] de Jeu and Lathouwers[8] have demonstrated that in such cases the calculated activation energy does not change if f_r is

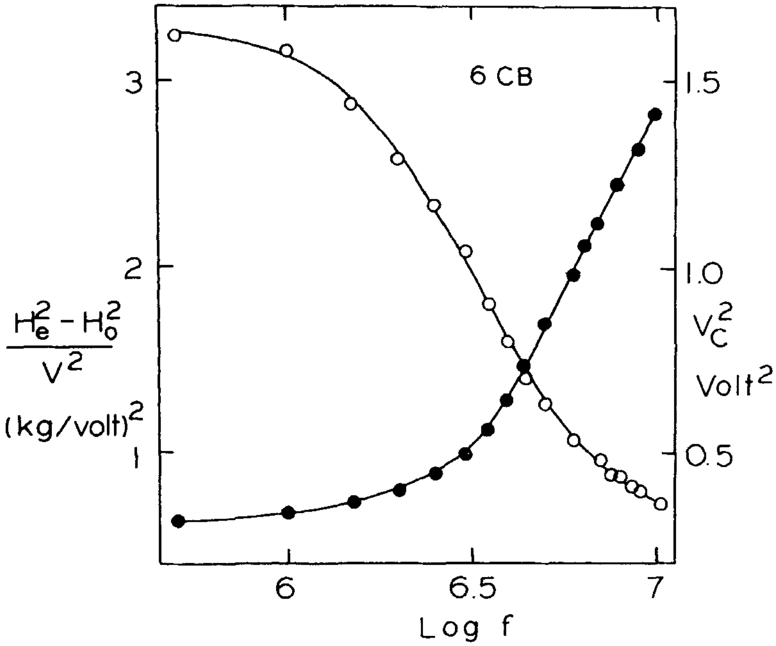

FIGURE 4 Dielectric relaxation in 4′-*n*-hexyl-4-cyanobiphenyl. Open circles refer to $(H_e^2 - H_0^2)/V^2$ and filled circles to V_c^2.

replaced by f_0 in relation (4). Moreover, since f_0 should be close to f_r, we can for our present purposes identify f_0 with f_r. We have plotted $\log f_r$ versus $1/T$ in Figure 6. The resulting straight line plot has a slope which is proportional to the total activation energy $Q = q_{\text{nem}} + q_{\text{visc}}$ (see relation (4)). We get for 90MCPC $Q \simeq 1$ eV.

90MCPC has a complicated molecular structure (Figure 2). The dipole moment of the nonyloxy end group contributes to both parallel and perpendicular components. The $\overset{\overset{\displaystyle O}{\|}}{-C-}O-$ has an essentially long-axis component. The nitrile group is also practically parallel to the long axis. Beyond f_0 ($\simeq 1$ MHz) the perpendicular component predominates in determining the dielectric properties of the medium, and $\Delta\varepsilon$ becomes negative.

From equation (5) $V_c^2 \propto k_{11}/\Delta\varepsilon$ and since $k_{11} \propto s^2$ where s is the order parameter and $\Delta\varepsilon \propto s$, V_c^2 is higher for lower temperatures at low frequencies, far away from f_r (Figure 5). At the same frequency, we would expect that $(H_e^2 - H_0^2)/V^2$ which is proportional to $\Delta\varepsilon/\Delta\chi$ (see Eq. (8)) to remain independent of temperature, since both $\Delta\varepsilon$ and $\Delta\chi$ should vary as the order

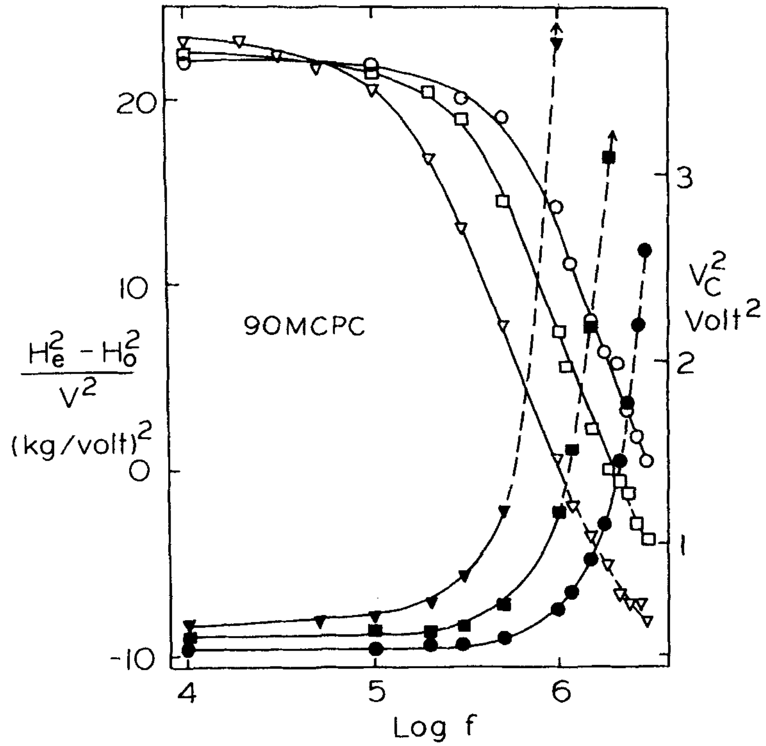

FIGURE 5 Dielectric relaxation in *trans*-*p*-*n*-nonyloxy-α-methyl-*p*′-cyanophenyl cinnamate at three temperatures in the nematic phase. The open symbols refer to $(H_e^2 - H_0^2)/V^2$ and the filled symbols to V_c^2. The temperatures of experiment are as follows: ▽, ▼: 54°C, □, ■: 60°C and ○, ●: 66°C. The dashed lines correspond to electrohydrodynamic instabilities rather than to elastic deformation.

parameter. However, we see from Figure 5 that $\Delta\varepsilon/\Delta\chi$ has a tendency to increase at lower temperatures.

The sign reversal of $\Delta\varepsilon$ in 90MCPC leads to some interesting results. In the k_{11}-geometry, as we approach f_0, we observe electrohydrodynamic patterns in the field of view. The pattern is rather similar to Williams domains, with the width of the flow cells being approximately equal to the thickness of the sample, even though the frequency ($\simeq 1$ MHz) of the exciting AC field is far above the charge relaxation frequency. The variation of V_c^2 indicated by the dashed line in Figure 5 corresponds to the threshold of the electrohydrodynamic instability in the medium rather than to that of elastic deformation. There have been similar observations, though at somewhat lower frequencies near f_0 of some mixtures.[13,14]

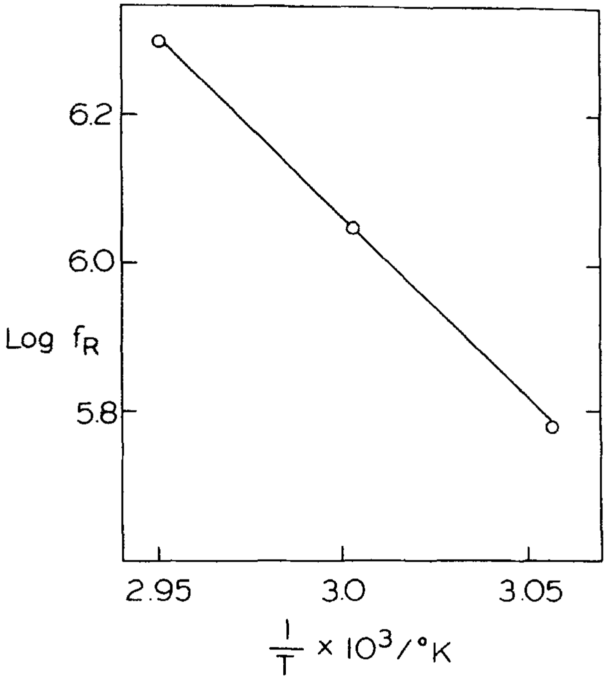

FIGURE 6 Variation of the relaxation frequency with temperature in 90MCPC.

Goossens[15] developed a theory of this effect by noting the formal similarity between the dielectric loss which peaks at f_r and conductivity in the sample. The conduction regime has been identified in an earlier study,[14] in which dynamic scattering was observed at voltages somewhat larger than the threshold voltage (V_{th}) for the appearance of domains. Further, V_{th} was found to increase as the frequency was increased above f_0, and, beyond a second frequency limit f_c, chevrons were also observed.

More recently, Smith *et al.*[16] have discussed electrohydrodynamic instabilities in nematics in considerable detail. They have particularly emphasized the role of ionic diffusion currents (which has been ignored by Goossens[15]) in determining the instabilities at these high frequencies ($\gtrsim 10$ KHz). The effect of the diffusion currents is to give rise to a *dielectric* regime with $k \simeq \pi/d$ (in which the *curvature* oscillates in phase with the applied field, while in the conduction regime, the charge density oscillates); see also Ref. 17. Also, even according to the theory of Smith *et al.*[16] an effective conduction regime for weakly positive materials can exist at high frequencies with $k \simeq \pi/d$. However, we have not made any detailed observations to distinguish between these two possibilities.

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