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Dielectric Studies of the Ordering Due to an External DC Electric Field in Nematic 4,4′-di-*n*-hexyloxyazoxybenzene

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Studies of dielectric permittivity changes under the action of a DC electric field on nematic 4,4′-di-*n*-hexyloxyazoxybenzene (DHAB) have been performed. Observations of time dependent processes occurring during the application of a voltage were made for samples of 0.5–2 mm thickness as a function of the applied voltage. The dielectric permittivity changes which are related to changes in the ordering of the samples were interpreted in dielectric as well as in electrohydrodynamic terms. Three voltage regions were distinguished which are characterised by ordering due to dielectric orientation, hydrodynamic laminar flow and turbulent flow.

1 INTRODUCTION

The Ericksen–Leslie theory[1] of liquid crystalline behaviour is based on the assumption of continuous changes from point to point of the ordering. Regions differing in directions of preferred orientation are not separated by sharp boundaries, except for disinclination lines. The interaction of external factors with molecules of anisotropic properties i.e. anisotropy of polarizability, electric or magnetic, permanent dipole moment, anisotropy of molecular shape[2] gives rise to macroscopical ordering of the sample. The ordering action may be exerted either by electromagnetic fields, by flow involving velocity gradients, or by surface effects. In the same way it is possible to order anisotropic molecules of any isotropic medium, however the required energy is much larger than in liquid crystals in which a local ordering exists due to molecular interactions.

In this work we present observations of ordering processes expressed in terms of electric permittivity changes due to the action of a static electric field.

The specimens under study were not subjected to any previous ordering actions or agents before the application of the electric field.

The electric field effect in liquid crystals cannot be understood in terms of dielectric behaviour of dipoles coupled with an ordering field. For the creation of hydrodynamic phenomena[3,4] the action of the field is much more complicated than implied by the existing theories of electric polarization of normal molecular media.

2 EXPERIMENTAL

The measurements were carried out on 4,4′-di-*n*-hexyloxyazoxybenzene (DHAB), produced by Merck, exhibiting a conveniently wide nematic range within 81–131°C and possessing a high chemical stability when heated. Samples remained satisfactorily unchanged when exposed to the action of static electric fields of high intensity and of long duration. During the experimental procedure the purity of a sample under test was continuously monitored by measuring its electric conductivity, found to be in the range $4 \cdot 10^{-11}$–$5 \cdot 10^{-10}\ \Omega^{-1}\ \mathrm{cm}^{-1}$.

DHAB with $\varepsilon_{\parallel} = 3.45$, $\varepsilon_{\perp} = 4.34$ at 2 MHz and 86°C[5] is characterized by a substantial negative dielectric anisotropy $\varepsilon_{\parallel} - \varepsilon_{\perp} = -0.89$ which suits satisfactorily the demands of the dielectric methods.

The measuring cell was a plan-parallel capacitor, made of invar. The circular electrodes were of area 3 cm^2 and the gap was adjustable over 0.5–2 mm. Thick specimens were examined in order to minimize the ordering due to the surfaces of electrodes. The cell was carefully thermostated in order to decrease as much as possible the convective flow along the vertically situated electrodes.

The cell was incorporated into a 2 MHz oscillator. The voltage of the measuring frequency was always lower than 10 V. In addition to the radiofrequency measuring field a DC voltage could be applied to the cell to change the electric permittivity of the medium under study. The resultant frequency shift depends on changes of the real part of electric permittivity. These shifts are converted into output voltage changes and recorded on a storage oscilloscope.[6]

The following measurements were performed:

1) At 86°C the time dependence $\Delta\varepsilon(t)$ was recorded for DC voltages ranging up to 3 kV. Each voltage acted long enough to attain a time independent steady value of ε.

2) Temperature dependence of the effect was measured at 2.5 kV within the whole nematic range. A special measuring cycle with shorter thermostation

was performed within the nematic range and in the isotropic phase in order to examine the role of the convective flow.

In order to relax the molecular system after an application of the field in all the experiments an arbitrary equilibration time of 15 min. separated two consecutive measurements.

3 RESULTS

3.1 Reproducibility

The results for different samples tested are completely reproducible as far as qualitative features are concerned. Slightly differing readings were sometimes observed resulting from differences in the initial ordering of samples as well as from changes in electric conductivity.

The readings depend in general on the duration and magnitude of the voltage applied previously to the sample. The equilibration time of 15 min. was sufficient in most cases to relax the system. In other cases only the maiden response from a freshly melted sample was taken into account.

3.2 The steady state of ε

Following the switching on of a DC voltage the permittivity of nematic DHAB approached a limiting value, which we have termed the steady state of ε. This

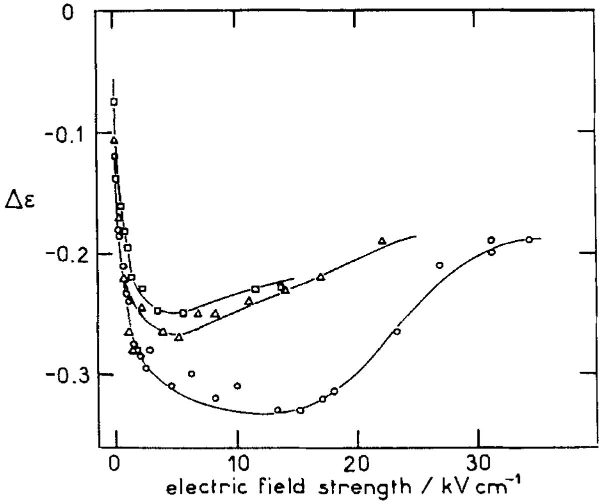

FIGURE 1 The steady state permittivity changes due to DC electric field at 86°C. Electrode gap: ○—0.96 mm, △—1.35 mm, □—1.88 mm.

state was completed within some 10^0–10^2 s depending on the voltage applied. All the observed $\Delta\varepsilon$ values were negative for the steady state (under the action of the DC field ε decreased), showing complicated dependence on electric field strength E and on the electrode gap (Figure 1).

Measurements of $\Delta\varepsilon$ at very low electric fields should in principle allow the determination of threshold voltage for the field effect. However the system under study showed fluctuations of ε affecting considerably the small $\Delta\varepsilon$ values at the lowest voltages. We had to extrapolate departing from values far beyond the threshold, arriving at a value $V_{th} = 3.6$ V, which does not much depend on the gap (Figure 2).

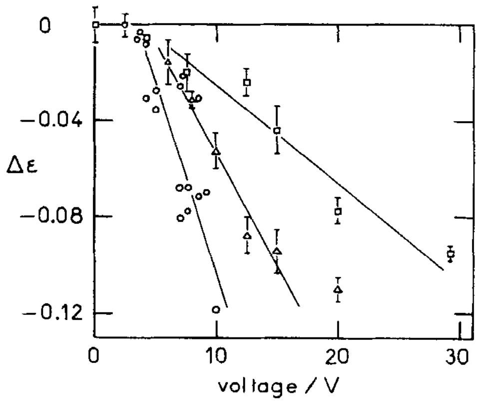

FIGURE 2 The steady state permittivity changes at low DC voltages. Electrode gap: ○—0.96 mm, △—1.35 mm, □—1.88 mm.

3.3 Transient effects

The time dependence of the electric field effect, the $\Delta\varepsilon(E, t)$ function, was recorded on a storage oscilloscope. In Figure 3 typical records are presented. The effect always begins with a short lived positive $\Delta\varepsilon$. The duration of this positive transient depends on the applied voltage and decreases sharply from about 40 s at 10 V down to about 10^{-3} s at 10^3 V. From Figure 4 it is seen that the lifetime of the positive effect depends very strongly on the voltage.

The positive transient is followed by a negative effect leading to the steady state of ε. At low voltages the negative effect depends monotonically on time (cf. Figure 3a), at larger voltages (50–1000 V) a minimum appears (Figure 3c) and in the region 1500–3000 V one or two additional minima are recorded. The results suggest that the time at which a minimum occurs is proportional to exp(− const V). Rather complicated transient effects were also observed after switching off the voltage or after its reversal.

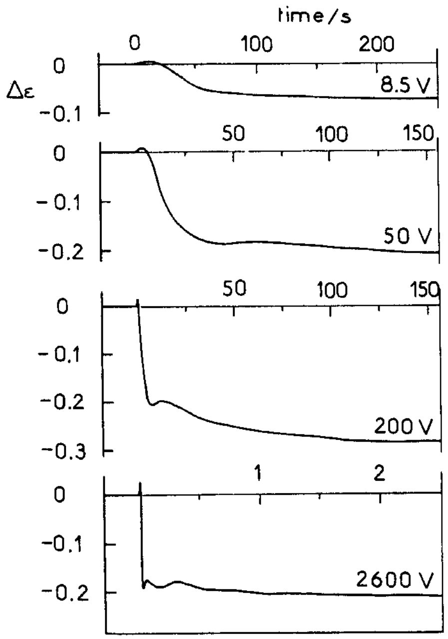

FIGURE 3 Time dependence of Δε (gap 0.96 mm, 86°C).

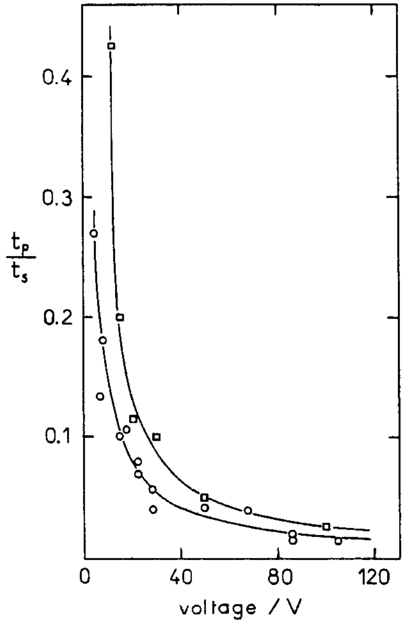

FIGURE 4 The ratio t_p/t_s as a function of applied voltage [t_p—duration of the positive effect; t_s—time of attaining the steady state of $\varepsilon(E)$].

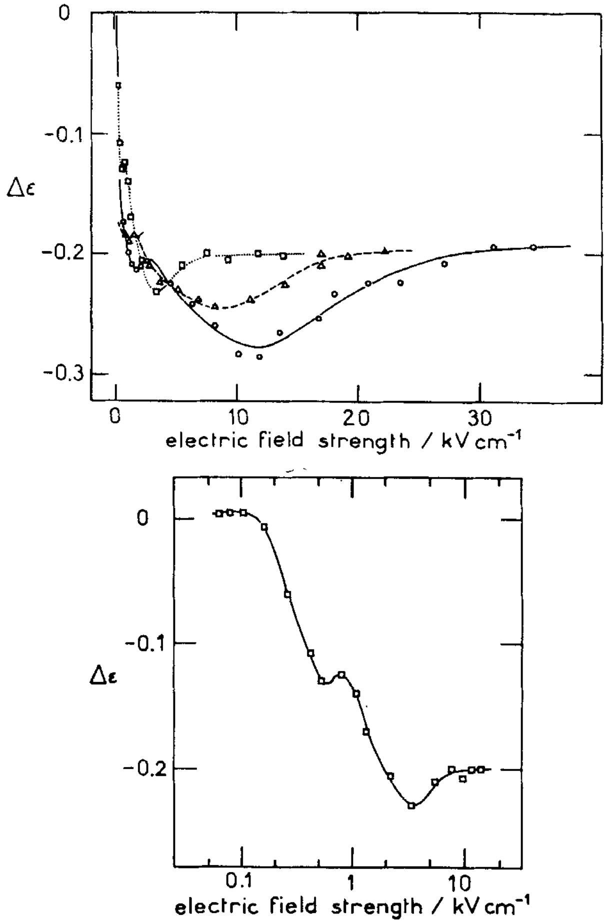

FIGURE 5 Δε values 10 s after the switching on of the electric field: a) gap: ○—0.96 mm, △—1.35 mm, □—1.88 mm; b) logarithmic plot for 1.88 mm gap.

Figures 5a, b show values of $\Delta\varepsilon(E)$ read from the oscillograms of Figure 3, 10 s after DC voltage was switched on. The local minima in $\Delta\varepsilon(E)$ correspond to minima in $\Delta\varepsilon(t)$ on the oscillograms (Figures 3c,d). The results in Figure 5a evidently depend on the electrode gap.

3.4 Fluctuations

Fluctuations of ε were always observable in the nematic state. For all the gap values the zero field fluctuations amounted up to ± 0.002. With fields up to 1 kV cm^{-1} for gaps 1.35 mm and 1.88 mm the fluctuations increased to some

±0.01. For higher fields there was a decrease. Similar fluctuations have been reported by Cummins *et al.*[7] in PCB (4,4′-*n*-pentyl-cyanobiphenyl) having $\varepsilon_{\parallel} - \varepsilon_{\perp} = 11$. For fields of 10–40 V cm^{-1} with a 1.7 mm gap the fluctuations were approximately ±0.7, what corresponds to the same part of $\varepsilon_{\parallel} - \varepsilon_{\perp}$ as in the case of DHAB.

3.5 Isotropic phase

There were no fluctuations of ε in the isotropic phase. The measured $\Delta\varepsilon(E)$ effects were much higher than expected for a purely molecular system. The effect appeared some 10^{-2} s after the switching on of the field. Its main contributions were probably due to electrohydrodynamical phenomena enhanced by the presence of small thermal gradient flow.

4 DISCUSSION

A microscopic state of a liquid crystal is described by the parameter of molecular order $s = \frac{1}{2}\langle 3\cos^2\theta - 1\rangle$ with θ being the angle between the long axis of a molecule and the local orientation director **N**.[2] On the other hand the macroscopic state of a sample can be described by the parameter of director ordering $S = \frac{1}{2}\langle 3\cos^2\phi - 1\rangle$, with ϕ being the angle between the director and an assumed axis. Thus for an ideal orientation along this axis we have $S = 1$, for a perpendicular arrangement $S = -\frac{1}{2}$, and for a completely random case $S = 0$.

In our discussion the state of ordering will be defined with respect to the electric field vector **E**. It can be shown that

$$S(E) = \frac{\varepsilon(E) - \bar{\varepsilon}}{\varepsilon_{\parallel} - \bar{\varepsilon}} = \frac{3}{2}\,\frac{\varepsilon(E) - \bar{\varepsilon}}{\varepsilon_{\parallel} - \varepsilon_{\perp}} \tag{1}$$

where $\bar{\varepsilon} = \frac{1}{3}(2\varepsilon_{\perp} + \varepsilon_{\parallel})$ is the electric permittivity of the statistically disordered state. The action of the electric field E changes the parameter S

$$\Delta S = S(E) - S(0) = \frac{3}{2}\,\frac{\varepsilon(E) - \varepsilon(0)}{\varepsilon_{\parallel} - \varepsilon_{\perp}} \tag{2}$$

This linear relation between ΔS and $\varepsilon(E) - \varepsilon(0)$ values allows to infer the ordering parameter changes from the experimental $\Delta\varepsilon(E)$ results taking into account the change of sign involved by the negative material constant $\varepsilon_{\parallel} - \varepsilon_{\perp}$ of DHAB.

A typical plot of $\Delta\varepsilon(E)$ can be generally divided in three voltage regions: below 10 V, from 10 to 10^3 V, and above 10^3 V. In the first region the effect is positive, in the second negative attaining a minimum, in the third the negative effect becomes independent of the applied voltage.

Region I. The positive effect for $\Delta\varepsilon(E)$ i.e. negative $\Delta S(E)$, corresponds to a process favouring an orientation of **N** perpendicular to **E**. In the case of total perpendicular orientation of initially disordered state, with $\varepsilon(0) = \bar{\varepsilon}$, we have

$$\Delta\varepsilon_{\rm I} = \varepsilon_\perp - \bar{\varepsilon} = -\tfrac{1}{3}(\varepsilon_\parallel - \varepsilon_\perp) \tag{3a}$$

amounting to $+0.30$ for DHAB. This positive effect is evidently caused by a dielectric mechanism of orientation, the lowest energy is attained in the state with molecular dipoles (being in DHAB perpendicular at each point to the director **N**) arranged parallel to the external electric field. The experimental maximum value of $\Delta\varepsilon$ is $+0.02$ only, indicating that the ideal orientation has not been achieved or even approached.

Region II. The effect $\Delta\varepsilon(E)$ is negative, i.e., $\Delta S(E)$ becomes positive. For complete ordering along the electric field we have

$$\Delta\varepsilon_{\rm II} = \varepsilon_\parallel - \bar{\varepsilon} = \tfrac{2}{3}(\varepsilon_\parallel - \varepsilon_\perp) \tag{3b}$$

which for DHAB would amount to -0.60. The measured lowest values are -0.30, indicating a partial orientation parallel to **E**. The mechanism now is presumably due to the field induced drift of ions which destroys the dielectric orientation and induces gradients of the flow velocity that favour orientation along **E**.[3,4] The flow remains partly laminar at voltages within the region II. Orientation due to flow appears after the time of ion cluster formation, cf. Figures 3, 4.

Region III. The measured $\Delta\varepsilon(E)$ values for sufficiently high voltages approach a limiting value of -0.20. The flow of ions becomes turbulent giving rise to vortices with axes perpendicular to the field direction.[4] For a sample which has completely undergone this process the permittivity is $\varepsilon_v = (\varepsilon_\parallel + \varepsilon_\perp)/2$ leading to

$$\Delta\varepsilon_{\rm III} = \varepsilon_v - \bar{\varepsilon} = \tfrac{1}{6}(\varepsilon_\parallel - \varepsilon_\perp) \tag{3c}$$

For DHAB the calculated value is -0.15, what is close to the observed $\Delta\varepsilon$. The difference (-0.05) can be explained by a discrepancy between $\varepsilon(0)$ and $\bar{\varepsilon}$ caused by residual alignment parallel to the electrodes due to convective flow along their planes. Figure 6 allows to estimate the influence of convective flow on $\varepsilon(0)$. An increase of flow affects evidently the values of $\Delta\varepsilon(E)$. The dashed line in Figure 6 corresponds to a transition from a state of ideal disorder [$\varepsilon(0) = \bar{\varepsilon}$] to a hypothetical vortice-like ordering by the electric field when all other types of ordering are excluded.

The separation of the effects into three regions reveals the different orientation mechanisms acting during the application of a DC field. The first mechanism of dielectric orientation is only temporarily present at the

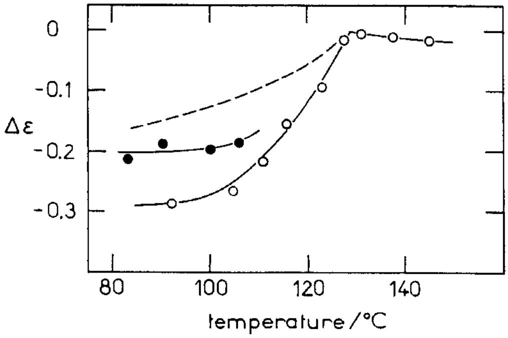

FIGURE 6 Temperature dependence of the steady state Δε, (2.5 kV, 1.88 mm gap). ●—sample very carefully thermostated (many h for each point), ○—thermostating less perfect (1 h for each point), ----calculated for orientation due to vortices only.

beginning and is later overwhelmed by electrohydrodynamic effects. None of the three mechanisms seems to exist in isolation, any resultant orientation is a superposition of all of them.

Ikeno *et al.*[8] presented a dielectric-hydrodynamic orientation model of nematics with negative anisotropy under the action of a DC electric field. This model differs from ours: the authors do not anticipate the formation of vortices. In their thin (ca. 100 μm) MBBA and EBBA samples the orientation by surfaces is probably a dominant factor limiting the turbulent flow.

Yanagisawa *et al.*[9] have investigated transient electric currents in MBBA. The reported current vs. time plots due to DC voltage of some kV are very similar to our $\Delta\varepsilon(t)$ plots. This supports the conduction induced orientation mechanism for high voltages.

The electrohydrodynamic phenomena due to charge injection and migration play a significant role in orientation of macromolecules in isotropic solutions. Tsuji and Watanabe[10] studied electrooptical properties of poly-γ-benzyl-L-glutamate in 1,2-dichloroethane. Following some seconds of DC excitation three maxima occurred in a typical birefringence transient record. Unusual birefringence transients have also been observed in the same system at concentrations as low as 0.5 g/l[11] These observations suggest some similarities in the orientation mechanism in so different substances as macromolecular isotropic solutions and pure nematic liquid crystals composed of rather small molecules.

Not much attention has been paid to experiments on thick disordered samples hitherto.[6–8, 12–14] Moreover not sufficient experimental details were given by some authors on their voltage application procedures involving equilibration time, hysteresis etc. orientational memory effects exhibited by particular samples. Without such information there remains always an ambiguity in comparing and discussing different data.

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