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Influence of Electric and Magnetic Fields on the Molecular Alignment in EBBA

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The effects of external dc and af electric fields of strengths up to 25 kV/cm on the nematic liquid crystal *p*-ethoxybenzylidene-*p*′-*n*-butyl aniline (EBBA) are investigated. The effectiveness of electric fields and of high magnetic fields in producing molecular alignment are compared. Changes in the molecular alignment are observed in terms of changes in the rf dielectric constant. These measurements are as fruitful as microwave measurements in studying the degree of ordering of molecules in bulk samples of liquid crystals. The threshold voltages for chevron formation in the dielectric regime are found to be considerably lower than the threshold voltages necessary to induce changes in dielectric constant in the same regime.

INTRODUCTION

Electric fields cause a number of interesting optical effects in nematic liquid crystals.[1,2] The type of effect depends upon the state of purity and on the sign of the dielectric and conductivity anisotropies of the material.[1,2] In materials having a conductivity of the order of 10^{-9} V/cm and a negative dielectric and positive conductivity anisotropy, af or dc electric field creates the following hydrodynamic instabilities.[3,4] At low strengths but above a threshold value of the electric field, the fluid deforms into a periodic structure and parallel striations are visible in the sample which are termed as domains.[5] At higher field strengths, the sample becomes highly turbulent and exhibits one of the more exploited electro-optic effects known as dynamic scattering.[6] The domains and the dynamic scattering are frequency dependent and are not observed beyond a critical frequency referred to as cut off frequency, f_c, which normally lies in the audio frequency region. It was found earlier[7,8] that for electric fields in the audio frequency region, the molecular axes tend to prefer an alignment along the field direction, forcing the dipoles into a perpendicular orientation with respect to the field. Such an alignment is anomalous with respect to dielectric constant and Carr[9–11] traced its origin to the interplay of dielectric and conductivity anisotropies which are of opposite sign and to the space-charge relaxation time. The anomalous behaviour is the consequence of the hydrodynamic instability caused by the electric fields. Theoretical justification for these ideas was provided by the works of Helfrich[12] and Dubois-Violette *et al.*[13] The latter work established that there occurs a second instability in the region beyond the cut-off frequency. Unlike the first instability, the second instability is purely of dielectric origin and hence the region above f_c is designated as the dielectric regime. In contrast, the low frequency region is termed the conduction regime.

Most of the work done so far on the electrohydrodynamic instabilities is confined to very thin samples only. Apart from Carr's work[9,10,14–17] not much is known about the behaviour of thick samples in the presence of high electric and magnetic fields. The present work is aimed at investigating in moderately thick samples of EBBA.

1) the electrohydrodynamic instabilities

2) the relative effectiveness of electric and magnetic fields on the orientation of molecules.

Dielectric measurements at 1 MHz were used to study changes in the molecular alignment in the presence of external fields. This simpler technique is useful for low loss materials and offers some advantages over the microwave measurements.[8–10,13–16] Smaller samples can be made use of and the results can be predicted with greater ease.

The H^1-NMR experiments on EBBA reported in an earlier paper[18] indicated that EBBA exhibits a "glassy" nature below 46°C. It is hoped that the present experiments would help to substantiate the NMR findings.

EXPERIMENTAL

The commercial EBBA sample obtained from Vari-Light Corporation (VLC) and Eastman Organic Chemicals (EOC) were subjected to fractional distillation under reduced pressure before use. Repeated distillations were done to minimize the ionic impurities. The distilled samples exhibit the phase in the range of 32°–75°C. The details of the dielectric cell and the experimental set up were similar to those reported earlier.[19] The cell was made up of two metal-coated glass plates separated by a U-shaped stainless stee wire frame. The frame makes electrical contact with only one conducting surface and serves as the earth lead. The diameter of the wire is 310 μm. Another short wire of the same diameter makes contact with the second plate and acts as the "live terminal". The assembly was epoxy sealed and held in between two thick brass plates screwed at the four corners. The brass plates have windows to permit visual observations. The stainless steel wire prevents chemical degradation of the sample due to interaction between it and the sample. The domains and chevrons were observed optically with the help of a long focal length travelling microscope.

Initially a cut off frequency of 56 Hz was observed for the VLC sample and it gradually increased with time. The cut off frequency of the EOC sample was 208 Hz and it could not be lowered even after a number of distillations. A comparison of "f_c" for these two samples suggests that the EOC sample contains ionic impurities which could not be removed by fractional distillation. This may perhaps largely depend on the method of synthesis of the compound.

The present work was carried only on the VLC sample at 32°C. The cut off frequency during the experiments was 96 Hz and the conductivity ratio $\sigma_{\|}/\sigma_{\perp}$ was 1.3 measured at 50 Hz.

RESULTS AND DISCUSSION

The first electrohydrodynamic instability in the conduction regime leading to the formation of domains occurs above a threshold voltage, which depends on the applied frequency. The theory[13] relates the frequency and the corresponding threshold voltages through the following equation:

$$V_{th}^2 = V_H^2\left[1 + (\zeta^2 - 1)\left(\frac{f}{f_c}\right)^2\right]\Big/\left[1 - \left(\frac{f}{f_c}\right)^2\right] \qquad (1)$$

Where V_H is the dc Helfrich voltage, ζ^2 is the Helfrich parameter, f_c is the cut off frequency and f is the frequency of the external electric field.

Figure 1 shows the variation of the threshold fields with frequency. The threshold fields gradually increase with frequency and in the vicinity of the f_c, 96 Hz, they attain very high values. The nature of the threshold field variation is qualitatively in good agreement with Eq. (1). In the conduction regime, the threshold fields for inducing dielectric and optical changes are identical. The Helfrich parameter ζ^2 of Eq. (1) involves many unknowns. From the experimental data at 60 Hz and using f_c = 96 Hz and V_H = 9V, a value of 17.5 is obtained for ζ^2 which satisfied the results at all frequencies in the conduction regime. However, 17.5 is a high value and so far such a high value is not reported in the literature. It may be due to the viscous

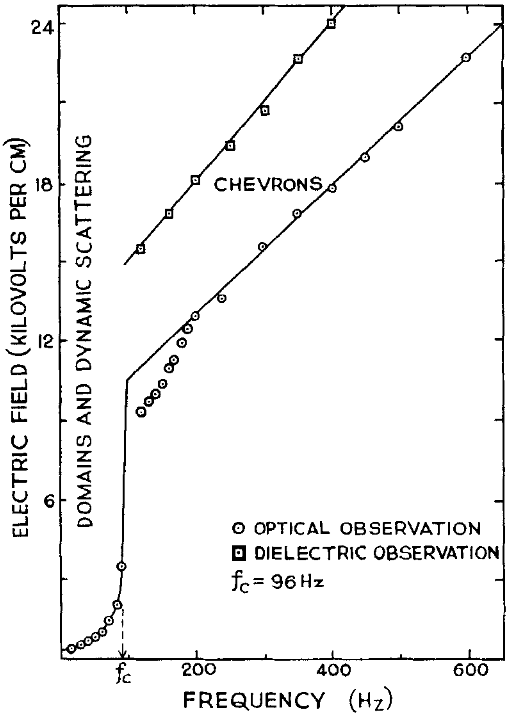

FIGURE 1 Threshold electric field for domain formation, chevron formation and dielectric constant change in EBBA as a function of frequency of the field $T = 32°C$.

nature of the sample[18] but however it is very difficult to assign any particular reason. Temperature variation of f_c was carried only to see whether there is any transition around 46°C from the viscous state to the normal state as was observed from NMR results. The variation is smooth and does not indicate any such transition.

The second hydrodynamic instability occurs in the dielectric regime and the threshold field is given by

$$\langle E_{th}^2 \rangle = Af \tag{2}$$

Where A is a constant.

In Figure 1 the curve above the cut off frequency 96 Hz satisfies the relation and is given by $E^2 = 1 \times 10^6$ f. There is a slight deviation of optical data points above f_c. The deviation was explained by Dubois-Violette *et al.*[13] The important observation is that the threshold fields in this regime for chevron formation are considerably lower than the threshold fields for inducing dielectric changes.

The relative effectiveness of E and H fields on molecular ordering

If the sample exhibits a negative dielectric and positive conductivity anisotropy, the electric and magnetic fields contest with each other in aligning the molecules when the fields are applied parallel to each other in the dielectric regime and perpendicular in the conduction regime. The changes resulting from such competition can be most effectively studied using the low frequency dielectric measurements, since they are directly related to the changes in orientation of molecular dipoles.

Figure 2 illustrates the competing influences of magnetic and electric fields in parallel configuration. The frequency of the applied field was held at 500 Hz which falls in the dielectric regime. The changes in the molecular ordering is observed with varying electrical field strengths for different magnetic field strengths. The molecules are initially aligned parallel to the magnetic field and hence to the electric field. The parallel orientation is shown by the lower dotted line corresponding to a dielectric constant

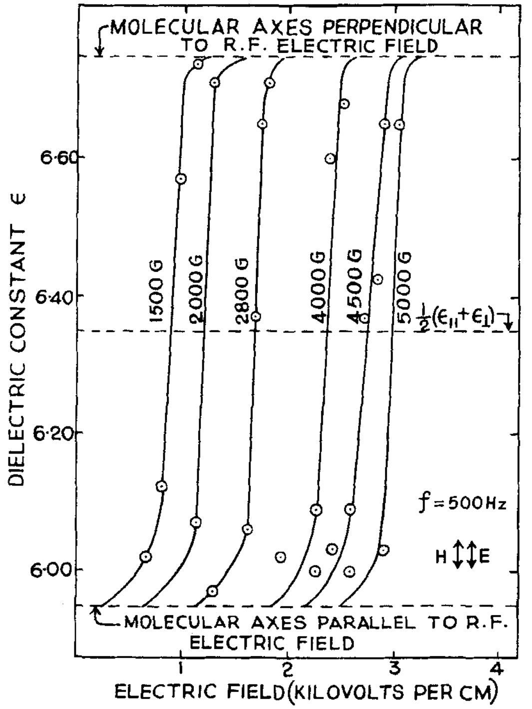

FIGURE 2 Dielectric constant ε of EBBA at 1 MHz as a function of externally applied 500 Hz electric field. The individual curves are for various values of a static magnetic field applied parallel to the external electric field and rf measuring field. $T = 32°C$.

$\varepsilon_{\parallel} = 5.95$ obtained using a magnetic field of 5 KG. As the electric field is increased, keeping the magnetic field at a particular value, the molecular dipoles turn into the direction of the electric field. They complete a 90° rotation within a small range of the electric field and the molecular axes attain a perpendicular alignment above it. The perpendicular orientation is designated by the upper dashed line corresponding to $\varepsilon_{\perp} = 6.75$ obtained using $H = 5$ KG applied perpendicular to the rf measuring field.

The effectiveness of the electric and magnetic fields on the molecular ordering can be compared for a value of the dielectric constant, $\varepsilon_{\text{random}} = (\varepsilon_{\parallel} + \varepsilon_{\perp})/2$ which represents random orientation of molecules in the plane of E and H. A value of 0.56 V/cm · G was obtained for E/H and this value is fairly independent of the magnetic field strength.

Since E/H is independent of H in the dielectric regime, the following equation used by Carr[9] should hold good

$$\frac{E}{H} = \frac{1}{300}\left[\frac{\Delta\mu}{\Delta\varepsilon}\right]^{1/2} \tag{3}$$

Using the values of $\Delta\varepsilon$ and $\Delta\mu$ determined for MBBA[20,21] a value of $E/H = 0.53$ is obtained from Eq. (3). This compares well with the ratio obtained for EBBA in the present work and indicates that the molecular alignment is purely due to dielectric anisotropy in this region.

Figure 3 shows the competing influences of external electric and magnetic fields in the conduction regime. The magnetic field was held constant at 5 KG and results are obtained for electric fields of different frequencies. For all frequencies, as long as the external electric field is zero, the molecules tend to line up parallel to the magnetic field and hence perpendicular to the rf field. When the strength of the electric field is increased above a threshold value the molecules prefer a parallel alignment with respect to the external electric field. There is not much difference in molecular behaviour when a dc electric field or a very low audio frequency field is used and also when the magnetic field is present or absent. The only difference is that there is a shift in the threshold voltage for anomalous alignment. However, the alignment brought about even by the dc electric field is not as complete as that due to a magnetic field. As the frequency of the external electric field approaches the cut off value, the threshold voltage for anomalous alignment increases and also the dielectric constant changes level off at higher electric field strengths. The latter indicates that the molecules are gradually preferring perpendicular alignment with respect to the electric field, the influence of conducting impurities being decreased. If the dashed line corresponding to $\frac{1}{2}(\varepsilon_{\parallel} + \varepsilon_{\perp}) = \varepsilon_{\text{random}}$ represents an average change orientation of 45° by the molecules with respect to either of the fields, the curve labelled $H = 5$ KG,

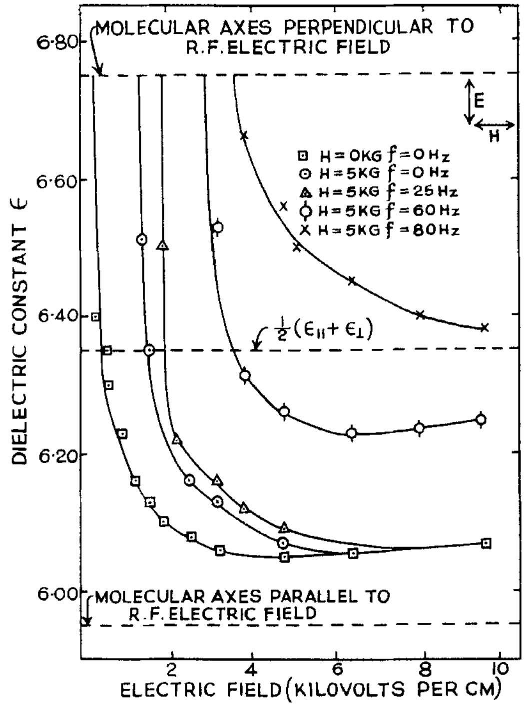

FIGURE 3 Dielectric constant ε of EBBA at 1 MHz as a function of externally applied electric field. The individual curves are for various values of the frequency of electric field. A static magnetic field of 5000 G was applied perpendicular to the external electric field, which was a parallel to the rf electric field. The temperature was 32°C.

$f = 60$ Hz shows that the molecules are making an angle $\theta \leq 45°$. The curve labelled $f = 80$ Hz and above shows that $\theta \geq 45°$, where θ is the average angle made by the nematic director with the rf electric field. The relative effectiveness of E and H can be compared here also at this $\varepsilon_{\text{random}}$ value of 6.35. The E/H ratio is found to be frequency dependent and indicates that there are other processes involved as was demonstrated by Carr's work.[9,11] If the frequency is increased beyond f_c in this crossed field configuration where conductivity anisotropy plays no part, the value of $\varepsilon = 6.75$ remains unchanged until the chevron regime is attained.

The changes in the molecular ordering due to external electric field of different frequencies in the presence of a magnetic field of strength 5 KG were shown in Figure 4. The changes in the molecular alignment are gradual for dc and low audio frequency fields, but the threshold strengths increase with the increase in frequency of the electric field. As the frequency of the electric field approaches the cut off value 96 Hz, the molecules prefer more and more

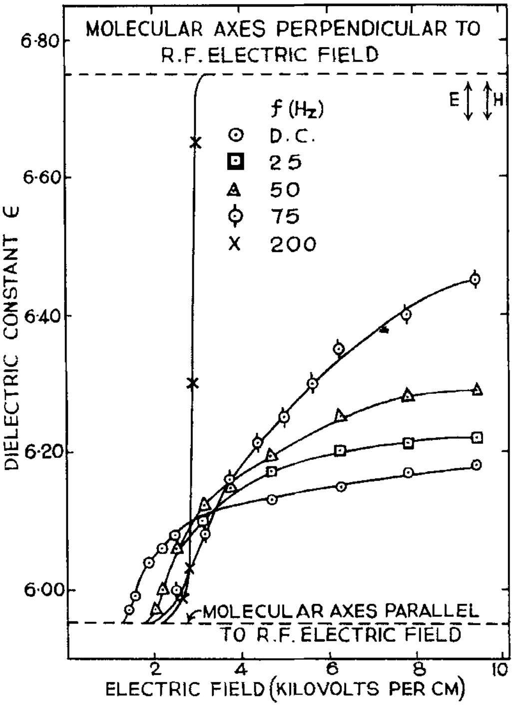

FIGURE 4 Dielectric constant ε of EBBA at 1 MHz as a function of externally applied electric field. The individual curves are for various values of the frequency of electric field. A static magnetic field of 5000 G was applied parallel to the external electric field which was parallel to the rf electric field. The temperature was 32°C.

a perpendicular orientation and above the cut off the molecules abruptly switch over to the perpendicular alignment with respect to the electric field as shown for 200 Hz electric field.

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