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Effects of dielectric and conductivity anisotropies on molecular alignment in a liquid crystal

E. F. Carr and W. T. Flint
Physics Department, University of Maine, Orono, Maine 04473

J. H. Parker
Husson College, Bangor, Maine 04401
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The relative effectiveness of electric and magnetic fields for producing molecular alignment in a nematic liquid crystal has been investigated while changing the magnitudes of the dielectric and conductivity anisotropies. The comparison was made for an ordering of the molecules such that the average angle that a molecule makes with the magnetic field is 45°. The dielectric anisotropy was changed from $\epsilon_{\parallel}' - \epsilon_{\perp}' = -0.2 - 1.0$. A relationship involving dielectric, conductivity, and magnetic permeability anisotropies was found to be satisfied in a range of magnetic field strengths of 3–6 kG. If the torque due to the conductivity anisotropy was greater than the torque due to the dielectric anisotropy, stable Williams domains were likely to be observed, but if it was less, stable Williams domains were unlikely to occur. This has been shown earlier for materials exhibiting a negative dielectric anisotropy but this work emphasizes materials with a positive dielectric anisotropy.

INTRODUCTION

The relative effectiveness of electric and magnetic fields for producing molecular alignment in a liquid crystal has been investigated while changing the magnitudes of the dielectric and conductivity anisotropies. It has been shown earlier[1] that if an electric field is applied perpendicular to a magnetic field and adjusted such that the average angle that the molecules make with the magnetic field is 45°, the following relation appears to be satisfied for a small range of fields:

$$[c + (\epsilon_{\parallel}' - \epsilon_{\perp}')]E^2 = 9\times 10^4(\mu_{\parallel} - \mu_{\perp})H^2 \, ; \tag{1}$$

$\epsilon_{\parallel}' - \epsilon_{\perp}'$ and $\mu_{\parallel} - \mu_{\perp}$ are the differences in the static dielectric constants and magnetic permeabilities, respectively parallel and perpendicular to the nematic director (direction preferred by the long molecular axes). The quantity c is associated with a mechanism involving space charge and conductivity anisotropy and is negligible for frequencies corresponding to periods that are short compared to the space-charge relaxation time. E is in V/cm and H is in Oe (or G since $\mu \approx 1$).

A relation for the torque per unit volume due to the conductivity anisotropy has been derived by Helfrich.[2] If we assume that the nematic director makes an angle of 45° with the magnetic field when Eq. (1) is satisfied we may write

$$c = G\left(\frac{(\sigma_{\parallel}/\sigma_{\perp} - 1)}{(\sigma_{\parallel}/\sigma_{\perp} + 1)}(\epsilon_{\parallel}' + \epsilon_{\perp}') - (\epsilon_{\parallel}' - \epsilon_{\perp}')\right) , \tag{2}$$

where $\sigma_{\parallel}$ and $\sigma_{\perp}$ are the conductivities parallel and perpendicular to the director, respectively. If the temperature and all the properties of a material except the conductivity and dielectric anisotropies do not vary appreciably, G should be a constant. Approximations have been made in obtaining this relationship which include an angle of 45° for a distribution of angles that would average approximately 45°. It has been shown[3] that as $(\sigma_{\parallel}/\sigma_{\perp} - 1)$ varies from 0.2 to 0.55 with $\epsilon_{\parallel}' - \epsilon_{\perp}' = -0.21$, the G factor appears to be constant within the limits of experimental error. For the work reported here $(\epsilon_{\parallel}' - \epsilon_{\perp}')$ has been varied from −0.21 to +1.0.

It has been shown earlier,[4] that liquid crystals exhibiting a positive dielectric anisotropy ($\epsilon_{\parallel}' > \epsilon_{\perp}'$) can show molecular alignment due to ionic conduction and that there are conduction and dielectric regimes. These regimes are separated by a cutoff frequency as found in materials exhibiting a negative dielectric anisotropy. For the work reported here the dielectric anisotropy of p-azoxyanisole (PAA) was changed by adding very small amounts of p-[(p-methozybenzylidene)-amino] benzonitrile (PMBAB) which has a large positive dielectric anisotropy $\epsilon_{\parallel}' - \epsilon_{\perp}' \approx +15$. The amounts added should not change the viscosity appreciably.

EXPERIMENTAL

Measurements of the dielectric loss at a microwave frequency of 24.5 GHz were used to indicate the degree of molecular alignment. The techniques have been described earlier.[1] The externally applied electric field is always applied parallel to the weak microwave electric field when using these techniques. When the ac electric field was applied perpendicular to the static magnetic field and varied, a value of the dielectric loss corresponding to $\epsilon'' = \frac{1}{2}(\epsilon''_{\parallel} + \epsilon''_{\perp})$ was used to indicate the alignment which is associated with Eq. (1). $\epsilon''_{\parallel}$ and $\epsilon''_{\perp}$ represent the dielectric loss when the polarized microwave electric field is parallel and perpendicular to the nematic director, respectively. For frequencies above cutoff (dielectric regime) the dielectric anisotropy could be determined, because the quantity c in Eq. (1) is zero. Since it was shown earlier that the results did not depend appreciably on the magnitude of the conductivity but only on the ratio of the conductivities parallel and perpendicular to the director, samples with resistivities of approximately $10^7\ \Omega$ cm or larger were used. With the low resistivity the ratio of the conductivities could be easily measured at 100 Hz.

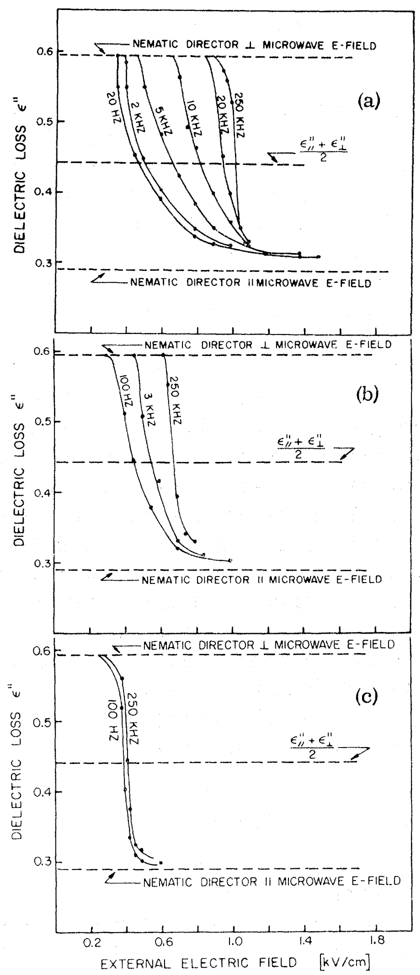

FIG. 1. Dielectric loss in PAA containing small amounts of PMBAB at a microwave frequency of 24.5 GHz and a temperature of 120 °C. A magnetic field of 1000 G was applied perpendicular to the microwave field and externally applied electric fields were parallel to the microwave field. $\sigma_{\parallel}/\sigma_{\perp} = 1.3$. (a) $\epsilon'_{\parallel} - \epsilon'_{\perp} = +0.16$, (b) $\epsilon'_{\parallel} - \epsilon'_{\perp} = +0.35$, (c) $\epsilon'_{\parallel} - \epsilon'_{\perp} = 1.0$.

It was usually necessary to stir the sample before making measurements of the conductivity and dielectric anisotropies.

For the observation of domains and dynamic scattering we used a typical optical cell, similar to that described by Williams.[5] Another cell was constructed which was identical to the cell used for the microwave measurements except that it was open at the top. This cell permitted optical observations perpendicular to the externally applied electric and magnetic fields. The cells were 2 × 7.5 mm in cross section and about 30 mm deep. Since they were open at the top direct observation with a microscope was possible. MBBA was used for these observations.

RESULTS AND DISCUSSION

Molecular alignment and dielectric anisotropy in ac fields

Figure 1 shows the effect of an ac electric field on the molecular alignment in a nematic liquid crystal exhibiting a positive ($\epsilon'_{\parallel} > \epsilon'_{\perp}$) dielectric anisotropy as ($\epsilon'_{\parallel} - \epsilon'_{\perp}$) is increased from 0.17 to 1.0. The nematic director was originally aligned perpendicular to the microwave field (maximum loss) with a 1000-G static magnetic field, but as the external ac electric field ($E \perp H$) was increased, the director underwent a rotation as indicated by a decrease in the dielectric loss. Figures 1(a) and 1(b) show that, for low values of the dielectric anisotropy, very low-frequency electric fields (conduction regime) are more effective in aligning the molecules than a 250-kHz field which is in the dielectric regime.

Figure 2 shows the effect on molecular alignment of a 100-Hz (conduction regime) electric field for different values of the magnetic field. Results at 20 Hz were identical to those at 100 Hz. The nematic material was PAA containing approximately 1.4 wt.% of PMBAB giving a dielectric anisotropy $\epsilon'_{\parallel} - \epsilon'_{\perp} = +0.14$ and a ratio of the conductivities $\sigma_{\parallel}/\sigma_{\perp} = 1.3$. The magnetic field was applied perpendicular to the 100-Hz electric field. As the electric field was increased for various values of the magnetic field a value of the dielectric loss was reached which corresponds to an average rotation of the directors of 45°. This value of the dielectric loss $\epsilon'' = \frac{1}{2}(\epsilon''_{\parallel} + \epsilon''_{\perp})$ is shown on the figure. The ratios E/H corresponding to this value of the loss are nearly constant, particularly in the 3–6 kG range which implies that Eq. (1) is satisfied.

Since the dielectric anisotropy of PMBAB is very large compared to PAA, the dielectric anisotropy could be easily altered by changing the amount of PMBAB in the sample without appreciably changing the viscosity. For each sample the

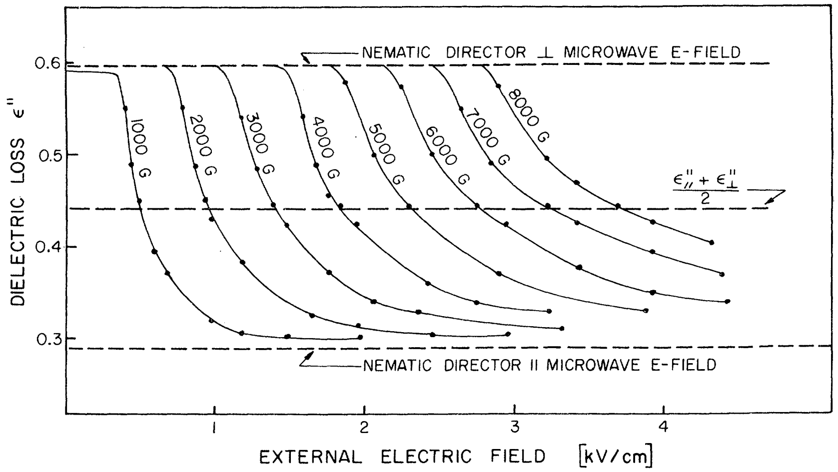

FIG. 2. Dielectric loss in PAA containing a small amount of PMBAB at a microwave frequency of 24.5 GHz as a function of a 100-Hz electric field. The individual curves are for various values of a static magnetic field applied perpendicular to the external electric field which was parallel to the microwave field. $T = 126\,°C$. $\sigma_{\parallel}/\sigma_{\perp} = 1.3$, and $\epsilon'_{\parallel} - \epsilon'_{\perp} = 0.14$.

ratio of E/H (conduction regime) was determined for a value of the dielectric loss of $\epsilon'' = \frac{1}{2}(\epsilon''_{\parallel} + \epsilon''_{\perp})$ in a magnetic field of 4 kG. The dielectric anisotropy and the ratio of conductivities $\sigma_{\parallel}/\sigma_{\perp}$ were also determined. These values were used in Eqs. (1) and (2) to obtain values of G which are shown in Fig. 3 as a function of the dielectric anisotropy. The quantity G appears to be nearly constant within the limits of experimental error for the range covered. For a dielectric anisotropy $\Delta\epsilon' > 1$, Fig. 1(c) shows that the alignment in the conduction regime is comparable to the alignment in the dielectric regime. For the work reported here $\sigma''_{\parallel}/\sigma_{\perp}$ varied between 1.2 and 1.4. For larger values of $\sigma''_{\parallel}/\sigma_{\perp}$ the effect due to ionic conduction would have been greater at $\Delta\epsilon' = 1$. It should be pointed out that approximations have been made for the quantity c in Eq. (2) and that this relation may not be satisfactory in the regions where the effect due to ionic conduction is large. Since the quantity G appears to be constant, the results shown in Fig. 3 provide good evidence that Eqs. (1) and (2) are satisfied for PAA in the range covered.

Molecular alignment in a dc electric field

Figure 4 shows the effect of a dc electric field on the molecular alignment for various values of the magnetic field. The dielectric anisotropy is $(\epsilon'_{\parallel} - \epsilon'_{\perp}) = +0.14$ and the ratio of the conductivities is $\sigma_{\parallel}/\sigma_{\perp} = 1.3$. The results are very similar to those in Fig. 2 which shows that the aligning mechanism employing dc fields is a reasonably well-behaved process. The most significant difference is probably the slope of the curves which indicates that there is more turbulence when employing dc fields. Since $(\epsilon'_{\parallel} - \epsilon'_{\perp})$ and $\sigma_{\parallel}/\sigma_{\perp}$ for the results in Fig. 4 are comparable to those in Fig. 2, the threshold for dc fields appears to be a little lower, but this cannot be seriously considered until more data are available.

Domains and molecular alignment in ac fields

It has been shown[6] that domains and light scattering can be observed in materials exhibiting a positive dielectric anisotropy using dc electric fields. It has also been shown more recently[4,7,8] for materials exhibiting small positive dielectric anisotropies that Williams domains and dynamic scattering can be observed using ac fields in the conduction regime. The formation of Williams domains has been related[9,10] to the dielectric anisotropies. This work suggests a maximum value for the ratio of the dielectric constants $\epsilon'_{\parallel}/\epsilon'_{\perp}$, above which Williams domains are not observed.

In the work reported here, we have attempted to relate the formation of Williams domains to the torque which is associated with the conductivity and dielectric anisotropies. Since the torque per unit volume is proportional to E^2 and the torques add for materials exhibiting positive conductivity and dielectric anisotropies, we can compare the torques in the dielectric and conduction regime.

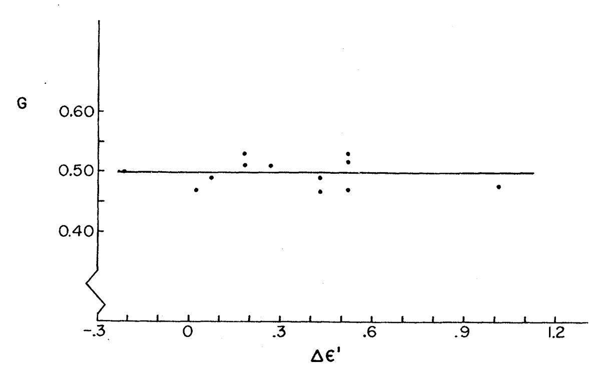

FIG. 3. G factor from Eq. (2) vs $\epsilon'_{\parallel} - \epsilon'_{\perp}$. $T = 120\,°C$.

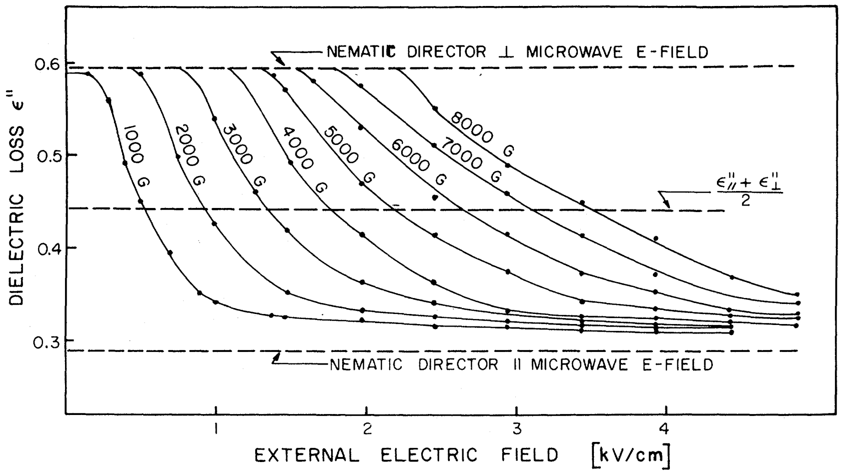

FIG. 4. Dielectric loss in PAA containing a small amount of PMBAB at a microwave frequency of 24.5 GHz as a function of a dc electric field. The individual curves are for various values of a magnetic field applied perpendicular to the external electric field. $T = 120\,°C$, $\sigma_{\parallel}/\sigma_{\perp} = 1.3$ and $\epsilon'_{\parallel} - \epsilon'_{\perp} = 0.14$.

If a value of E_0 (electric field intensity) in the dielectric regime is necessary to produce a loss $\epsilon'' = \frac{1}{2}(\epsilon''_{\parallel} + \epsilon''_{\perp})$, and $E_0/\sqrt{2}$ produces this value in the conduction regime, we can say that in the conduction regime, the torque due to the conductivity anisotropy is approximately equal to that due to the dielectric anisotropy. The curves in Fig. 1(b) nearly represent this situation, whereas Fig. 1(a) shows the case where the torque due to the conductivity anisotropy is much greater than that due to the dielectric anisotropy; Fig. 1(c) illustrates the case where the dielectric part is larger. The sample which was used for the results shown in Fig. 1(a) showed stable Williams domains, but the sample corresponding to Fig. 1(c) did not show stable Williams domains. The sample that was used for the results shown in Fig. 1(b) showed Williams domains but the stability was questionable. After investigating many samples, stable Williams domains appear to be likely if the torque due to the conductivity anisotropy is greater than that of the dielectric anisotropy. If the torque due to the conductivity anisotropy is less than that of the dielectric anisotropy stable Williams domains are not likely to occur. It should be remembered that the torques are compared for values of the dielectric loss $\epsilon'' = \frac{1}{2}(\epsilon''_{\parallel} + \epsilon''_{\perp})$.

In the upper frequency range of the conduction regime the effect of the electric field on the molecular alignment is frequency dependent as can easily be seen from Fig. 1(a). For the sample used in obtaining the results in Fig. 1(a), stable Williams domains were observed at 5000 Hz but not at 10 000 Hz. This suggests that for frequencies such that the torque due to the conductivity anisotropy is greater than that of the dielectric anisotropy, stable Williams domains are likely to be observed. Some preliminary measurements with the p-alkoxybenzoic acids also appeared to be in agreement with this observation.

CONCLUSION

Although a considerable amount of work has been carried out on electrohydrodynamic phenomena in liquid crystals, it has been mostly concerned with thin samples and small deviations of the director. Equation (1) has been in the literature for many years and there does not appear to have been any references to it by other investigators, so the opinion of others concerning any model which involves an average angle of rotation of the director of approximately 45° is unknown. Much of this effort should probably be regarded as an empirical approach, but a model similar to that suggested by Helfrich,[2] and verified by other investigators,[11,12] to explain Williams domains could be suggested

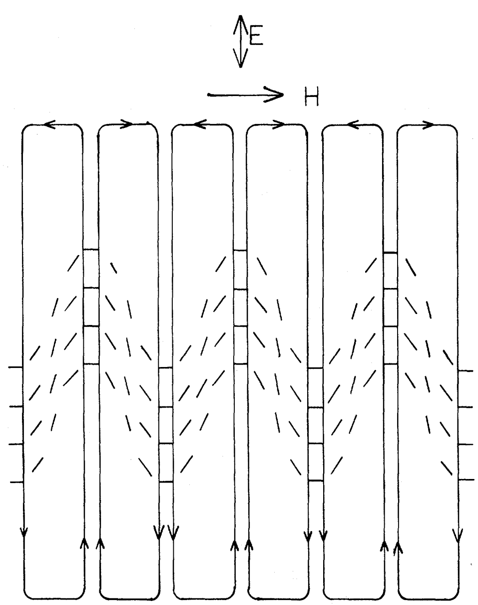

FIG. 5. Molecular alignment in presence of magnetic and electric (conduction regime) fields.

here.

A model that shows flow patterns and a possible ordering of the molecules is shown in Fig. 5. Earlier work[13,14] has shown similar flow patterns in the presence of high electric field intensities. The average angle that the director makes with magnetic field is considerably larger than that proposed by Helfrich to explain Williams domains. Although the diagram may appear to illustrate a cosine function we do not intend to imply that the arrangement of the molecules can be represented by a cosine function.

Flow patterns were observed using a cell identical to the microwave absorption cell but open at the top so that observations could be made perpendicular to both fields. The movement of small particles of dust indicated a movement of particles that was consistent with the flow cells shown in Fig. 5. MBBA was used for this observation. The movement of the particles did indicate that the flow cells were probably being constantly created and destroyed and that there was some turbulence. For a given value of the magnetic field, motion was not observed until a certain value of the electric field intensity was reached. This value of the threshold (not voltage threshold) appears to correspond to the threshold electric field intensity for molecular alignment using microwave techniques.

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