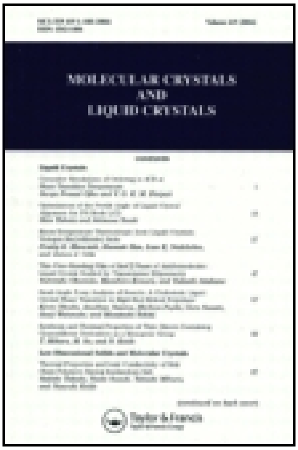

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E. F. Carr [a]

[a] Physics Department, University of Maine Orono, Maine, 04473

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Influence of Electric Fields on the Molecular Alignment in the Liquid Crystal *p*-(Anisalamino)-phenyl Acetate‡

E. F. CARR

Physics Department
University of Maine
Orono, Maine 04473

Abstract—The effects of electric fields on the molecular alignment in the liquid crystal *p*-(anisalamino)-phenyl acetate are discussed. The behavior of this material is similar to that of *p*-azoxyanisole in that the ordering which is normally observed shows an alignment with the molecular axis preferring a direction parallel to the field at low audio frequencies, and perpendicular to the field for frequencies of a few hundred kHz. Results comparing the effectiveness of electric and magnetic fields for producing molecular alignment are presented which support a theory presented earlier to explain the ordering in *p*-azoxyanisole at audio frequencies. This theory involves the anisotropy associated with the electrical conductivity. Results are also presented which show that the effectiveness of dc electric fields is comparable to that for low audio frequencies. A few comments are made concerning recent work employing electric fields to produce ordering in liquid crystals for NMR studies.

Introduction

Electric fields used to produce molecular alignment in liquid crystals have recently generated much interest. While most contemporary research employing electric fields involved only very thin samples, the work reported in this paper and in previous articles by the author involves samples of a thickness greater than 1 mm.

The first experiments[1] employing microwave techniques to

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study the effects of electric fields on the molecular alignment involved the nematic material anisaldazine and the smectic material ethyl *p*-azoxybenzoate. Ethyl-*p*-azoxybenzoate exhibited an ordering with the long axes of the molecules preferring a direction perpendicular to the field as expected, whereas in anisaldazine the long axes preferred a direction parallel to the field which was not expected. Results[2] on *p*-azoxyanisole, which has a behavior comparable to anisaldazine, showed that the ordering was very dependent on frequency in the audio frequency region. This work emphasized the importance of ionic impurity in producing an ordering with the molecular axes parallel to the field at very low frequencies. Very pure samples did not always exhibit an ordering with the molecular axes parallel to a dc electric field immediately after melting the sample. To be sure, however, it is not known whether this was due to the lack of impurity or to the structure in the anisotropic liquid phase immediately after melting.

A model has been proposed[3,4] to explain the ordering in *p*-azoxyanisole owing to electric fields. This model involves interfacial polarization owing to the conductivity anisotropy. Williams[5] investigated the effect of electric fields on nematic liquids employing optical techniques and suggested that the nematic liquid may have a spontaneous electrical polarization similar to that in ferroelectrics. Heilmeier, Zanoni, and Barton[6] have recently reported some very interesting results on electric field effects in nematic liquids. They proposed a model based on the alignment of swarms due to the shear induced in the liquid crystal by ions in transit. Earlier workers had considered the problem involving nematic liquids in electric fields and a review of their work has been given by Gray[7] and Chistyakov.[8]

This investigation involves the liquid crystal *p*-(anisalamino)-phenyl acetate. The behavior of this material in electric fields is similar to *p*-azoxyanisole in that it normally exhibits an ordering with the long axes of the molecules preferring a direction parallel to the electric field at low audio frequencies and perpendicular to the field at a frequency of a few hundred kHz.

Experimental

The experimental techniques employed in this work were similar to those reported earlier.[9] The function of the microwave dielectric techniques was to provide a measure of the degree of ordering of the molecules. A microwave frequency of 24.5 GHz was chosen because of the availability of the microwave components and the size of the equipment at this frequency. Since the microwave beam was polarized with its electric field perpendicular to the wide side of the waveguide containing the sample, the amount of power transmitted through the sample depended on the orientation of the long axes of the molecules. If the amount of power transmitted through the sample depends on the orientation, measurements of the transmitted power should provide information about the molecular alignment.

The dielectric loss is a maximum in *p*-(anisalamino)-phenyl acetate when the long axes prefer a direction perpendicular to the microwave electric field, and a minimum when the long axes are parallel to the microwave electric field. The field intensity of the microwave field was not sufficient to have any effect on the orientation of the molecules.

The experimental setup with a center conductor in the cell requires that the externally applied electric field be applied parallel to the microwave electric field. The static magnetic field was applied externally and could be applied either parallel or perpendicular to the electric field. All measurements were made at a temperature of 90 °C.

Results and Discussion

A. MOLECULAR ALIGNMENT IN A 300 kHz ELECTRIC FIELD

The results shown in Fig. 1 can be used to compare the relative effectiveness of electric and magnetic fields for producing molecular alignment in *p*-(anisalamino)-phenyl acetate. These results show that in the absence of a magnetic field the molecules prefer an ordering with their long axes perpendicular to the electric field.

A change in the dielectric loss from $\epsilon'' = 0.24$ (lower dotted line) to $\epsilon'' = 0.60$ (upper dotted line) corresponds to a 90° rotation of the molecular axes. The effectiveness of the electric field is equal to that of the magnetic field for $\epsilon'' = 0.42$. This comparison is shown in Table 1 for the six curves in Fig. 1. Since the ratio of

Table 1 Ratios of Electric Field to Magnetic Field Corresponding to a Random Orientation of the Molecules Employing a 300 kHz Electric Field

$H \parallel E$	$f = 300$ kHz
H (Oersteds)	$\frac{E}{H}\left[\frac{\text{Volts}}{\text{Cm Oersteds}}\right]$
1000	0.34
2000	0.34
3000	0.35
4000	0.35
5000	0.35
6000	0.35

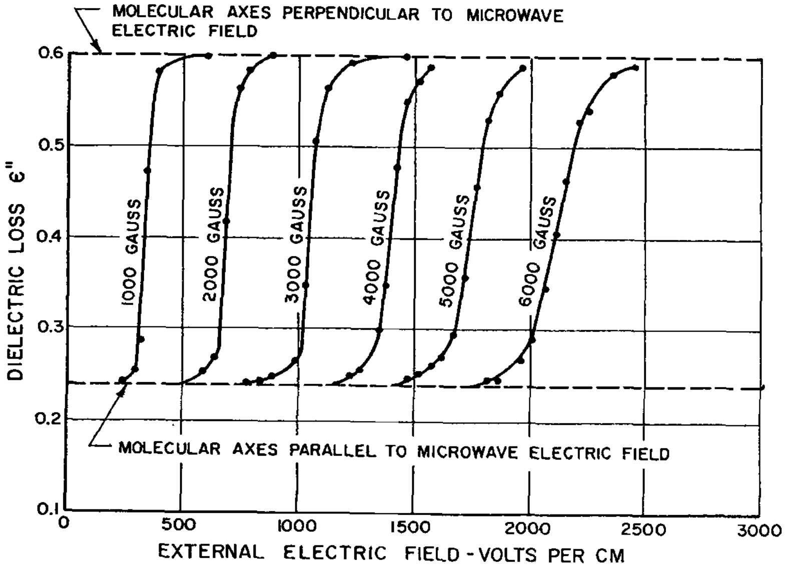

Figure 1. Dielectric loss in *p*-(anisalamino)-phenyl acetate at a microwave frequency of 24 GHz as a function of an externally applied 300 kHz electric field. Individual curves are for various values of a static magnetic field applied parallel to the external electric field. The temperature was 90 °C.

E/H (the electric field to the magnetic field) is constant within the limits of experimental error, and the results appear to be independent of frequency in the neighborhood of 300 kHz, the following theoretical relation is probably satisfied:

$$\frac{E}{H} = \left(\frac{\mu_{\parallel}' - \mu_{\perp}}{\epsilon_{\perp}' - \epsilon_{\parallel}}\right)^{1/2}$$

$\epsilon_{\perp}'$ and $\epsilon_{\parallel}'$ are the values of the dielectric constant measured perpendicular and parallel to the long axes of the molecules respectively. $\mu_{\perp}$ and $\mu_{\parallel}$ are the values of the permeability corresponding to the directions perpendicular and parallel to the molecular axes. Since the values of $\epsilon_{\perp}' - \epsilon_{\parallel}'$ and $\mu_{\parallel} - \mu_{\perp}$ are not available, this relation could not be further checked.

Figure 1 shows that the changes in orientation are more gradual for higher values of the field intensities. One might attribute this to disturbances in the liquid crystal, but observers[10] have reported that at these frequencies motion in the anisotropic phase does not appear to be appreciable.

B. MOLECULAR ALIGNMENT IN 500 Hz AND DC ELECTRIC FIELDS

Figure 2 shows that the molecules are ordered with their long axes preferring a direction parallel to a 500 Hz electric field rather than perpendicular to the electric field as shown in Figure 1 for a 300 kHz field. The dielectric loss does not drop to $\epsilon'' = 0.24$ (lower dotted line) for high electric fields even if the magnetic field is removed. This indicates that the degree of ordering is less in a high 500 Hz electric field than in a high magnetic field.

Table 2 shows the ratios of E/H corresponding to a value of the dielectric loss $\epsilon'' = 0.42$. For the higher values of the field this ratio approaches a constant. This implies that ordering is not due to a permanent electric dipole moment associated with a cluster of molecules. If this ordering is to be associated with an electric dipole moment, the ratios of E/H suggest that the dipole moment is proportional to the electric field intensity.

The results for *p*-(anisalamino)-phenyl acetate are similar to those of *p*-azoxyanisole[4] in that the following conditions must be

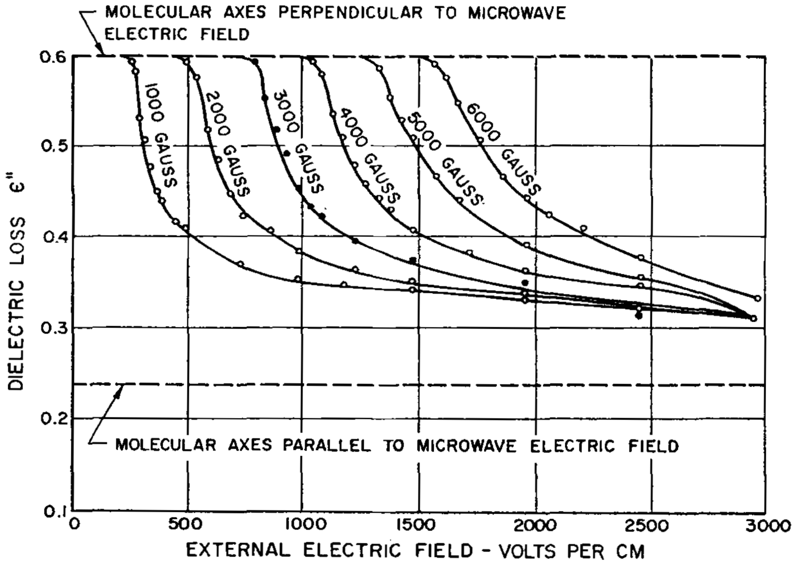

Figure 2. Dielectric loss in *p*-'anisalamino)-phenyl acetate at a microwave frequency of 24 GHz as a function of an externally applied 500 Hz electric field. The individual curves are for various values of a static magnetic field applied perpendicular to the external electric field. The temperature was 90 °C.

Table 2 Ratios of Electric Field to Magnetic Field Corresponding to a Random Orientation of the Molecules Employing a 500 Hz Electric Field

$H \perp E$	$f = 500$ Hz
H (Oersteds)	$\frac{E}{H}\left[\frac{\text{Volts}}{\text{Cm Oersteds}}\right]$
1000	0.44
2000	0.38
3000	0.37
4000	0.35
5000	0.35
6000	0.35

satisfied by the process primarily responsible for the alignment of the molecular axes parallel to the 500 Hz electric field.

1. If the interaction is associated with an electric dipole moment, it must behave like an induced moment.
2. This process must compete with the dielectric anisotropy.
3. The ordering in a high electric field is less complete than in a high magnetic field.
4. This process must be capable of showing a frequency dependence in the audio frequency region.
5. The effect of the electric field should be affected by the age of the sample.

A possible explanation compatible with the above conditions is illustrated in Fig. 3. Svedberg[11] showed that the conductivity in the anisotropic liquid phase of some liquid crystals is greatest parallel to the long axes of the molecules. This was found to be the case for *p*-(anisalamino)-phenyl acetate.

If clusters of molecules are arranged as shown in Fig. 3a, interfacial polarization will exist owing to the conductivity anisotropy. The magnitude of the polarization due to charge accumulation at the boundaries should be proportioned to the electric field intensity if Ohm's law holds. This could satisfy the first condition.

If clusters of molecules could be arranged as shown in the oversimplified diagram of Fig. 3b, charge could accumulate at the boundaries owing to the components of the electric field parallel and perpendicular to the molecular axes. The dipole moment associated with the cluster could interact with the electric field giving a torque proportional to the square of the electric field intensity. Since the results in Fig. 1 indicate that the low frequency dielectric constant is greatest in a direction perpendicular to the molecular axes, Fig. 3c illustrates the polarization owing to the dielectric anisotropy. Figures 3b and 3c show that it is possible for a process associated with the conductivity anisotropy to compete with the dielectric anisotropy which satisfies the second condition. The direction preferred by the molecules in an electric field should depend on the relative effectiveness of the processes illustrated in Figs. 3b and 3c.

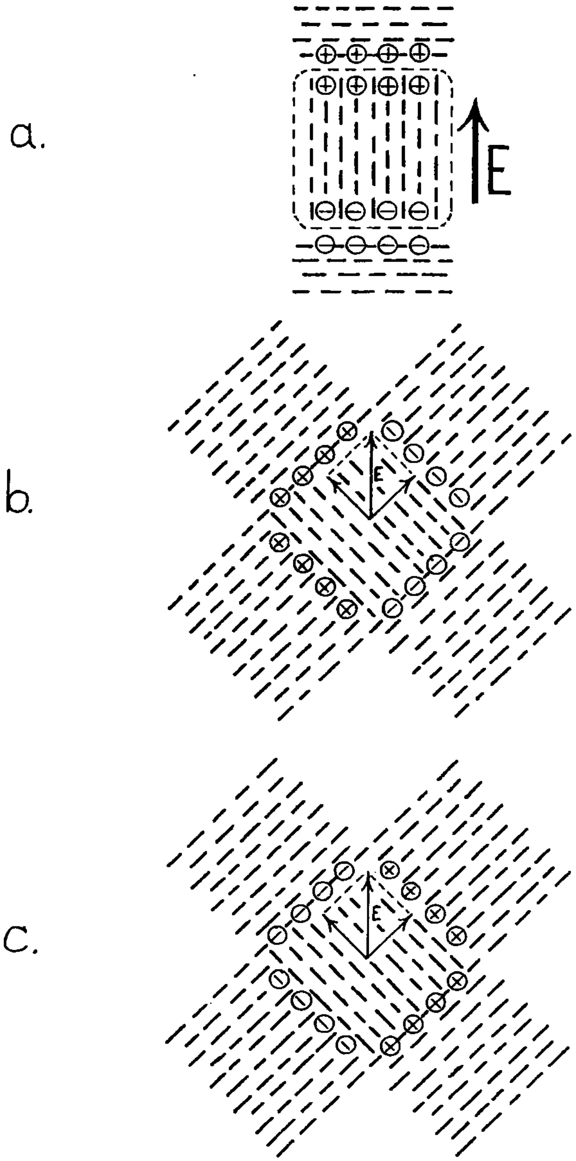

Figure 3. Model to illustrate interfacial polarization in nematic liquids exhibiting a negative dielectric anisotropy. (a) and (b) conductivity anisotropy, (c) dielectric anisotropy.

For an ordered sample the boundaries illustrated in Fig. 3b could vanish rendering the process associated with the conductivity anisotropy ineffective. Under these conditions the aligning process associated with the dielectric anisotropy would turn the molecular axes away from the field. The combined effect could favor an alignment with the molecular axes preferring a direction at a small angle with respect to the field which is consistent with the third condition.

Experiments with samples of *p*-azoxyanisole used in earlier work showed that the impedance of a condenser filled with *p*-azoxyanisole was primarily resistive at a frequency of 500 Hz and primarily reactive at 300 kHz. This indicates that the quantity of charge that passes through the circuit in a half-cycle due to the conductivity is very significant at low frequencies, but is relatively insignificant at 300 kHz compared to the current due

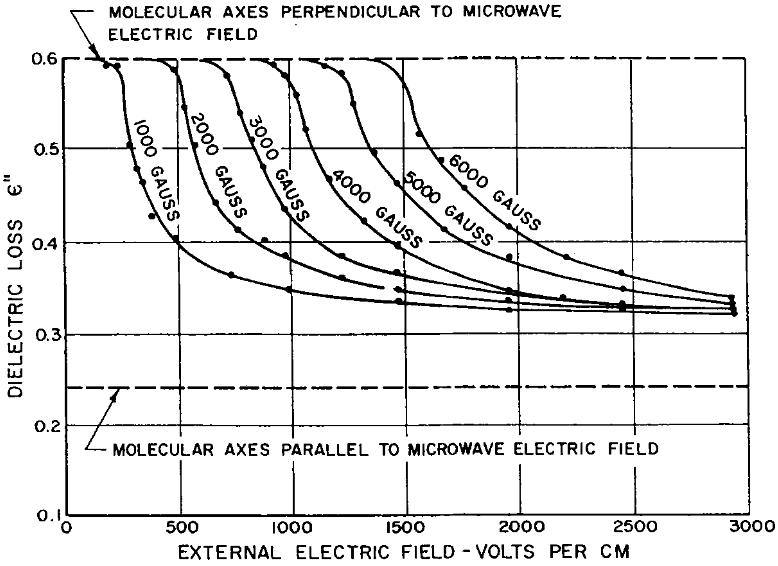

Figure 4. Dielectric loss in *p*-(anisalamino)-phenyl acetate at a microwave frequency of 24 GHz as a function of an externally applied dc electric field. The individual curves are for various values of a static magnetic field applied perpendicular to the electric field. The temperature was 90 °C.

to the dielectric polarization. It seems reasonable to assume that the conductivity of *p*-(anisalamino)-phenyl acetate is comparable to that of *p*-azoxyanisole and could satisfy the fourth condition.

Preliminary measurements on *p*-(anisalamino)-phenyl acetate showed that the relative effectiveness of electric and magnetic fields was different from that shown in Table 1. A process associated with the conductivity could be affected by impurity which would change with the age of the sample.

Results shown in Fig. 4 are similar to those shown in Fig. 2. The only change in the experimental procedure was that a dc electric field was used in place of the 500 Hz electric field. The ratios of E/H were slightly lower than those shown in Table 1, but this could be due to the age of the sample.

Figure 5 shows the results for a 500 Hz electric field applied parallel to a magnetic field. For a given value of the magnetic field a value for the electric field can be attained such that the

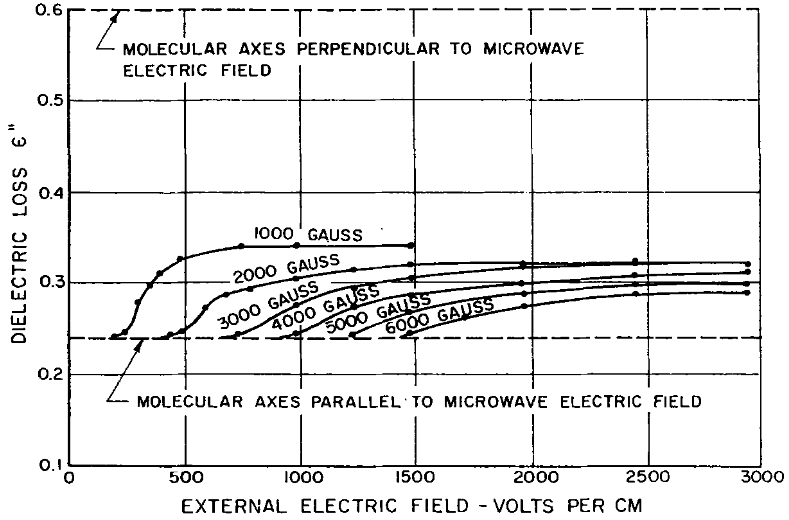

Fig. 5. Dielectric loss in *p*-(anisalamino)-phenyl acetate at a microwave frequency of 24 GHz as a function of an externally applied 500 Hz electric field. The individual curves are for various values of a static magnetic field applied parallel to the external electric field. The temperature was 90 °C.

ordering appears to become less complete. Preliminary results employing NMR techniques[12] have indicated that an appreciable portion of the molecules under these conditions prefer a direction which makes a small angle with the magnetic field and that this direction is not well defined.

C. Frequency Dependence of Molecular Alignment

The effect of the frequency on the molecular alignment with the electric field perpendicular to the magnetic field can be seen in Fig. 6. It is hoped that NMR techniques will aid in the interpretation of these results. Until results with NMR or other techniques are available it is felt that little can be said about the results in Fig. 6.

The effect of the frequency of the electric field on molecular

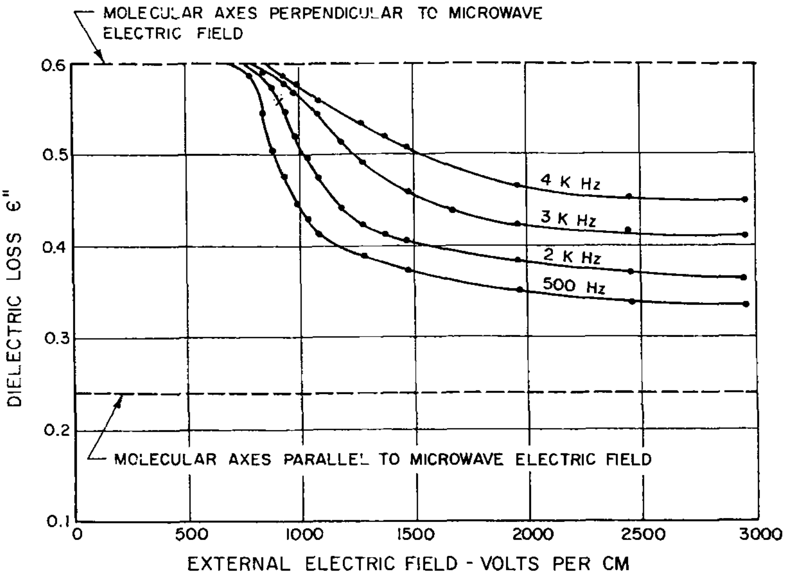

Figure 6. Dielectric loss in *p*-(anisalamino)-phenyl acetate at a microwave frequency of 24 GHz as a function of an externally applied electric field. The individual curves are for various frequencies of the electric field applied perpendicular to a 3,000 G magnetic field. The temperature was 90 °C.

alignment with the electric field parallel to the magnetic field is illustrated in Fig. 7. The changes in molecular alignment seem to occur at about the same value of the electric field intensity for all frequencies. This implies that the process primarily responsible for turning the molecular axes away from the magnetic field is associated with the dielectric anisotropy. The change in alignment is not only less at the lower frequencies, but it is also more gradual. This gradual change is probably due to disturbances in the material which are created by the electric field. The results in figures 6 and 7 appear to be consistent with the model suggested in Fig. 3.

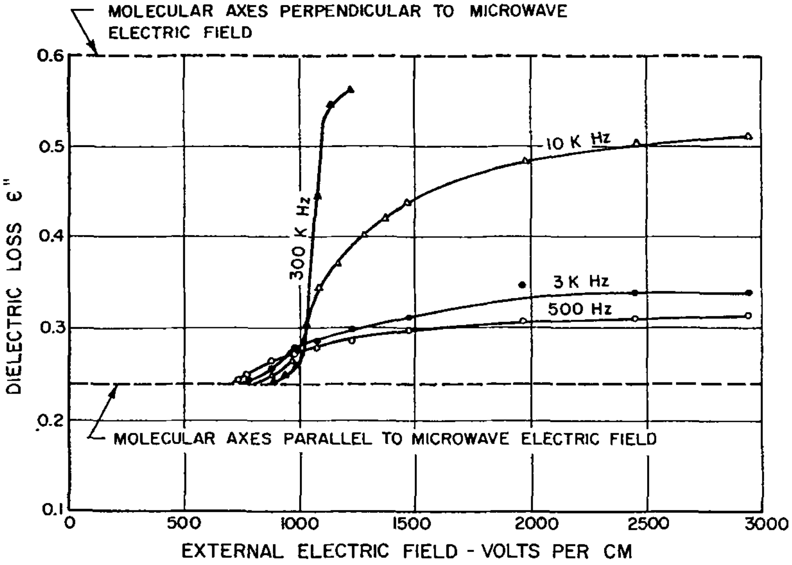

Figure 7. Dielectric loss in *p*-(anisalamino)-phenyl acetate at a microwave frequency of 24 GHz as a function of an externally applied electric field. The individual curves are for various frequencies of the electric field applied parallel to a 3,000 G magnetic field. The temperature was 90 °C.

Conclusions

Although the concept of clusters of molecules has been used to explain the results reported in this article, the author does not wish to imply that the results support the swarm theory. The length of time for molecules to respond to small changes in magnetic and electric field intensities may depend on the frequency of a previously applied electric field. Recent work by Flint and Carr[13] has indicated that butoxybenzoic acid responds much quicker to small changes in electric field intensity at 500 Hz than at a frequency of 300 kHz. It seems that if clusters exist as illustrated in Fig. 3, it may be the result of larger regions breaking up because of impurity, temperature gradients, wall effects and externally applied fields. The turbulence in the liquid crystal which has been reported by many observers in the presence of electric fields suggests the breaking up of ordered regions.

The results shown in Fig. 4 are similar to earlier results[4] on *p*-azoxyanisole in that the curves are reasonably well spaced and the ordering in a low audio frequency electric field is less complete than in a magnetic field. Vainshtein, Chistyakov, Kosterin and Chaikovskii[14] have done an X-ray analysis of the structure of nematic liquid crystals in electric and magnetic fields. They reported an ordering in *p*-azoxyanisole with the long axes of the molecules preferring a direction parallel to the field at low audio frequencies and they also reported that the degree of alignment was less complete than in a magnetic field. This was also found to be the case for electric field intensities comparable to those reported on this work by Slovac and Biscoe,[15] employing x-ray methods. The ratios of E/H shown in Table 2 are higher for lower values of the magnetic field, which suggests that the model illustrated in Fig. 3 does not completely explain the results at low field intensities. It was suggested earlier[4] that the higher ratios for *p*-azoxyanisole at low fields may be due to wall effects, but the lack of any appreciable wall effect at a frequency of 300 kHz indicates that this is not the explanation. Vainshtein, Chistyakov, Kosterin, and Chaikovskii[14] found that for very weak fields (below 50 volts/am for *p*-azoxyanisole at 123 °C) the long axes of the molecules preferred a direction perpendicular to the low audio frequency electric field. If an aligning process is associated with the conductivity anisotropy, which involves clusters of molecules resulting from the breaking up of larger regions, weak fields may not be sufficient to break up the larger regions. This might account for the larger ratios of E/H at low fields.

The work of Freedericksz and Zwetkoff[10] offers an opportunity to make some comparisons of results employing thin samples with those reported here. When a nematic liquid is placed between a plane and a curved surface, Freedericksz and Zwetkoff[10] showed that for every value of the electric or magnetic field there is a certain limiting layer thickness Z_0. For lesser thicknesses the optic axes maintain their original direction because of the surface effect. There are relationships between Z_0 and the fields:

$$Z_0 E = K_E$$

$$Z_0 H = K_H,$$

where K_E and K_H are constants. A comparison of the effectiveness of electric and magnetic fields indicated an ordering in *p*-azoxyanisole with the long axis perpendicular to the electric field for all frequencies, but the effectiveness of electric fields was greatest at a few hundred kHz. A very interesting aspect is that the effect is proportional to the square of the electric field intensity for all frequencies as it is in the work (except for the low fields) by the author. The aligning process which favors an ordering with the molecular axis parallel to the field appears to be proportional to the square of the electric field intensity but is less effective than the process associated with the dielectric anisotropy. A comparison of the effectiveness of electric and magnetic fields by Freedericksz and Zwetkoff[10] in *p*-azoxyanisole at a few hundred kHz varied by about 20% with results reported earlier[3] by the author. This difference could be due to their assumption that the dielectric constant of the glass and samples of liquid crystal were the same. Freedericksz and Zwetkoff discussed turbulence due to electric fields and suggested that the flow which was due to the field could be effective in aligning the molecules.

Motion in nematic liquids owing to electric fields might be aided by a force on the layers of sample near the walls because of the conductivity anisotropy. If one assumes that a layer next to the surface remains fixed, charge can accumulate on the side away from the wall because of the conductivity anisotropy. The sign of the charge in this region will depend on the direction of the field and the orientation of the molecules. The force on this region due to the accumulated charge should be toward the wall for molecules with their long axes parallel to the wall and away from the wall when molecules are perpendicular to the wall. The direction of the force will not depend on the direction of the field because when the direction of the field changes the sign of the charge will change so it should not matter whether one is using ac or dc electric fields. If the force in this region is not evenly distributed, it might give rise to motion in the nematic liquid.

Although the work discussed here only involves liquid crystals with a low frequency dielectric constant greatest in a direction perpendicular to the long axes, Flint and Carr[13] have found effects similar to those reported here in Butoxybenzoic acid which exhibits an ordering with the long axis parallel to an electric field for all frequencies. Most all comparisons of the effectiveness of electric and magnetic fields have been accomplished with the electric and magnetic fields parallel or perpendicular to each other. Carr[16] has shown that for an electric field applied at an angle which is not 90° with respect to a magnetic field, an ordering can be obtained in anisal *p*-amino-azobenzene with the molecular axis in a direction not parallel to either field. This work involved NMR techniques and the direction of the molecular axis relative to the fields was in agreement with calculations based on earlier results.[3]

Measurements similar to those reported here using higher and also lower field intensities are needed. Many ideas will probably have to be considered to explain the results such as motion in the liquid crystal which was mentioned by early investigators and dynamic scattering which has been discussed by Heilmeier, Zanoni, and Barton.[6]

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