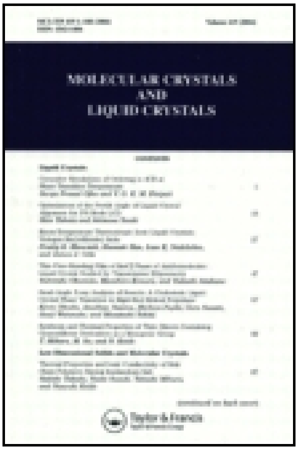

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Field and Frequency Effects in a Nematic Mixture of Negative and Positive Dielectric Anisotropy

P. R. Kishore [a] , N. V. S. Rao [a] , P. B. K. Sarma [a] , T. F. S. Raj [a] , M. N. Avadhanlu [b] & C. R. K. Murty [a]

[a] Physics Department, Nagarjuna University, Nagarjunanagar, 522 510, India

[b] Central Electronics Limited, Sahibabad, 201 005, India

Version of record first published: 18 Oct 2010.

To cite this article: P. R. Kishore , N. V. S. Rao , P. B. K. Sarma , T. F. S. Raj , M. N. Avadhanlu & C. R. K. Murty (1978): Field and Frequency Effects in a Nematic Mixture of Negative and Positive Dielectric Anisotropy, Molecular Crystals and Liquid Crystals, 45:3-4, 231-241

To link to this article: http://dx.doi.org/10.1080/00268947808085006

Mol. Cryst. Liq. Cryst., 1978, Vol. 45, pp. 231–241

Printed in Holland

Field and Frequency Effects in a Nematic Mixture of Negative and Positive Dielectric Anisotropy

P. R. KISHORE, N. V. S. RAO, P. B. K. SARMA, T. F. S. RAJ, M. N. AVADHANLU,† and C. R. K. MURTY,

Physics Department, Nagarjuna University, Nagarjunanagar, 522 510, India

(*Received October 18, 1976; in final form November 28, 1977*)

The molecular alignment in the nematic liquid crystal mixture of *p*-ethoxy benzylidene *p*'-*n*-butyl aniline (EBBA) and *p*-ethoxy benzylidene *p*'-cyano aniline (EBCA) has been investigated by measuring the dielectric constant at 1 MHz. Detailed investigation has been carried out for a composition of 2.74% of EBCA in EBBA for different electric and magnetic field strengths and at different frequencies of the applied electric field. Both parallel and perpendicular electric and magnetic field configurations have been employed. Temperature and frequency dependence of the dielectric anisotropy have been studied.

Two interesting features have been observed. 1) In the crossed field configuration complete molecular alignment could be observed by suitably changing the electric field strength. The range of electric field strength required to change the molecular ordering, is frequency dependent. This range shows a minimum in the neighbourhood of 2 kHz. 2) It has also been observed that in the parallel field configuration minimum dielectric constant change is observed apparently independent of frequency and electric field strength. Detailed results of the field and frequency effects and of optical studies in this mixture are reported.

INTRODUCTION

Considerable amount of work has been done on the electric field effects in nematic liquid crystals because of their useful applications in electro-optical devices.[1,2] Sufficient experimental investigation has been carried out to explain the instabilities[3,4] in nematic liquid crystals by Carr[5–7] and his associates,[8–11] the Orsay group[12] and de Jeu *et al.*[13–16] Adequate theoretical justification has also been obtained by Helfrich,[17] Dubois-Violette *et al.*[18] to explain the experimental results.

† Central Electronics Limited, Sahibabad 201 005, India.

As a result of these investigations, it has become clear that the dielectric and conductivity anisotropies in nematic liquid crystals play a very important role on the alignment of the molecules in external electric and magnetic fields. It is also clear that the ionic conductivity plays an important role in dc and low audio frequency electric fields while the dielectric anisotropy is responsible for alignment at higher frequencies. The nematic liquid crystal systems with different signs of dielectric and conductivity anisotropies which have been investigated so far are classified as (+ +), (+ −), (− +) and (− −) systems. It is conventional to relate the first sign in the bracket to the dielectric anisotropy and the second to the conductivity anisotropy. In all these systems it has been found that the molecular axes align parallel to the electric field when the conductivity or dielectric anisotropy is positive and they align perpendicular to the electric field when the conductivity or dielectric anisotropy is negative.

The effects of electric and magnetic fields on the molecular alignment in pure EBBA have been reported in our earlier publication.[19] In this work, we have investigated the electric and magnetic field effects on molecular ordering and also optical behaviour in a mixture of 2.74% by weight of EBCA in EBBA.

EXPERIMENTAL:

Dielectric constant measurement at 1 MHz has been used to study changes in the molecular alignment. The dielectric cell and the experimental technique were similar as reported earlier.[19] In this experimental arrangement, the external electric field is always parallel to the r.f. measuring field and the magnetic field is either parallel or perpendicular to the r.f. field.

The EBBA and EBCA samples have been prepared in our laboratory by condensation of appropriate p-substituted benzaldehydes with p-substituted anilines. EBBA has been subjected to fractional distillation under reduced pressure and EBCA has been recrystallised twice before use. The dielectric anisotropy of EBBA is −0.75 at 1 MHz and 32°C and has a nematic range 32°C–76°C (35.5°C–79°C[20]). EBCA, which has a cyano group along the para axis, exhibits a large positive dielectric anisotropy $\Delta\varepsilon = +21$ at 1 MHz and 107°C and has a nematic range 105°C–128°C (107°C–128°C[21]). The dielectric anisotropy of the mixture is −0.36 at 1 MHz and 32°C and has a nematic range 28°C–77°C. The conductivity ratio $(\sigma_{\parallel}/\sigma_{\perp})$ is 1.3 measured at 80 Hz. A.C. conductivity is of the order of 10^{-10} Ohm^{-1} cm^{-1}.

The temperature during the experiment has been maintained with an accuracy of ±0.5°C. Frequency dependence of the dielectric constant is investigated in the frequency range 100 kHz–1 MHz using crystal controlled oscillators. Susceptibility anisotropy is usually positive in nematic liquid crystals and not determined in this work. Moderately thick samples (280 μm) have been employed in the present experimental investigations, so the wall effects are unavoidable. However these wall effects do not influence the general experimental observations and their validity.

RESULTS AND DISCUSSION

A Frequency and temperature dependence of the dielectric anisotropy

In nematic liquid crystals, $\varepsilon_{\parallel}$ (dielectric constant parallel to the molecular axes) and $\varepsilon_{\perp}$ (dielectric constant perpendicular to the molecular axes) have different frequency dependence.[22–25] $\varepsilon_{\parallel}$ shows high frequency relaxation (Microwave region) as well as the low frequency relaxation while $\varepsilon_{\perp}$ exhibits high frequency relaxation only. In nematic liquid crystals with positive dielectric anisotropy, relaxation of $\varepsilon_{\parallel}$ at low frequencies leads to a change of sign of the dielectric anisotropy $\Delta\varepsilon$.[15,26]

Figure 1 illustrates the dielectric dispersion of $\varepsilon_{\parallel}$ in the low r.f. region for 2.74% by weight of EBCA in EBBA at 32°C, and the frequency independence

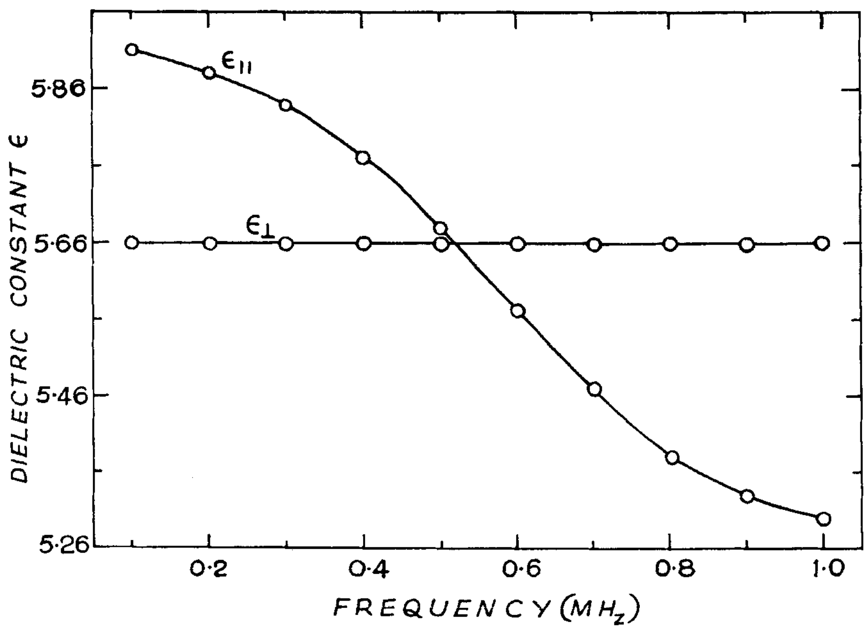

FIGURE 1 Dielectric constant $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ of EBBA-EBCA mixture as a function of frequency. Temperature = 32°C.

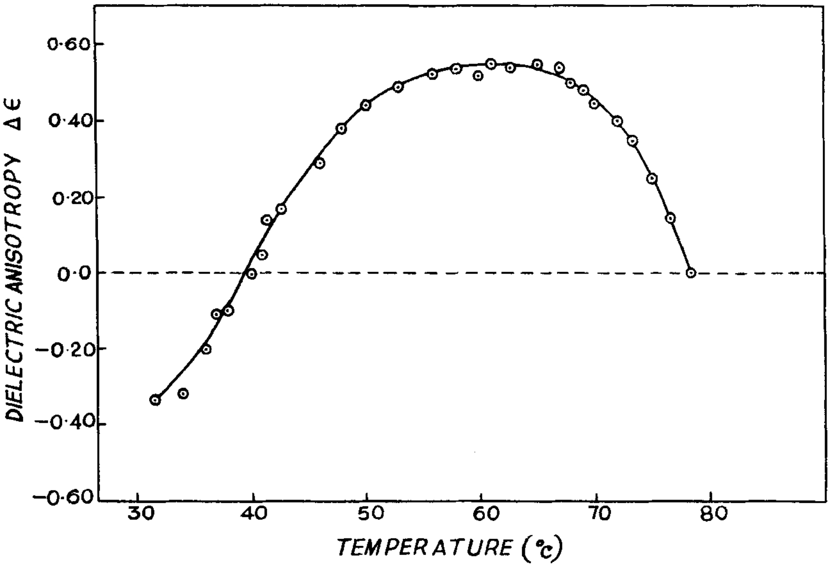

FIGURE 2 Dielectric anisotropy, $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$ of EBBA–EBCA mixture at 1 MHz as a function of temperature.

of $\varepsilon_{\perp}$, in the frequency range 100 kHz–1 MHz. The dielectric anisotropy changes sign from positive to negative due to a relaxation of $\varepsilon_{\parallel}$ at a crossover frequency $f_0 = 520$ kHz. At the crossover frequency, the mixture is dielectrically isotropic, i.e., $\varepsilon_{\parallel} = \varepsilon_{\perp}$.

Figure 2 shows the temperature dependence of the dielectric anisotropy $\Delta\varepsilon$ at 1 MHz. Dielectric dispersion of $\varepsilon_{\parallel}$ leads to a change of sign of $\Delta\varepsilon$ at 40°C, i.e., the crossover frequency is 1 MHz at 40°C in this mixture.

B Frequency dependence of the molecular alignment

Figure 3 shows the frequency dependence of the molecular alignment in the presence of 5.3 KG magnetic field applied perpendicular to the external electric field of different frequencies. As the strength of the electric field increases, the molecular axes approach parallel alignment with the electric field independent of the frequency of the electric field. As the frequency of the electric field increases, the threshold field for causing a change in the molecular alignment increases up to a certain frequency (about 1 kHz) and remains constant above that.

These results indicate that the low frequency electric fields (conduction regime) are more effective in changing the orientation of the molecular axes than a 2 kHz electric field which is in the dielectric regime. In the conduction

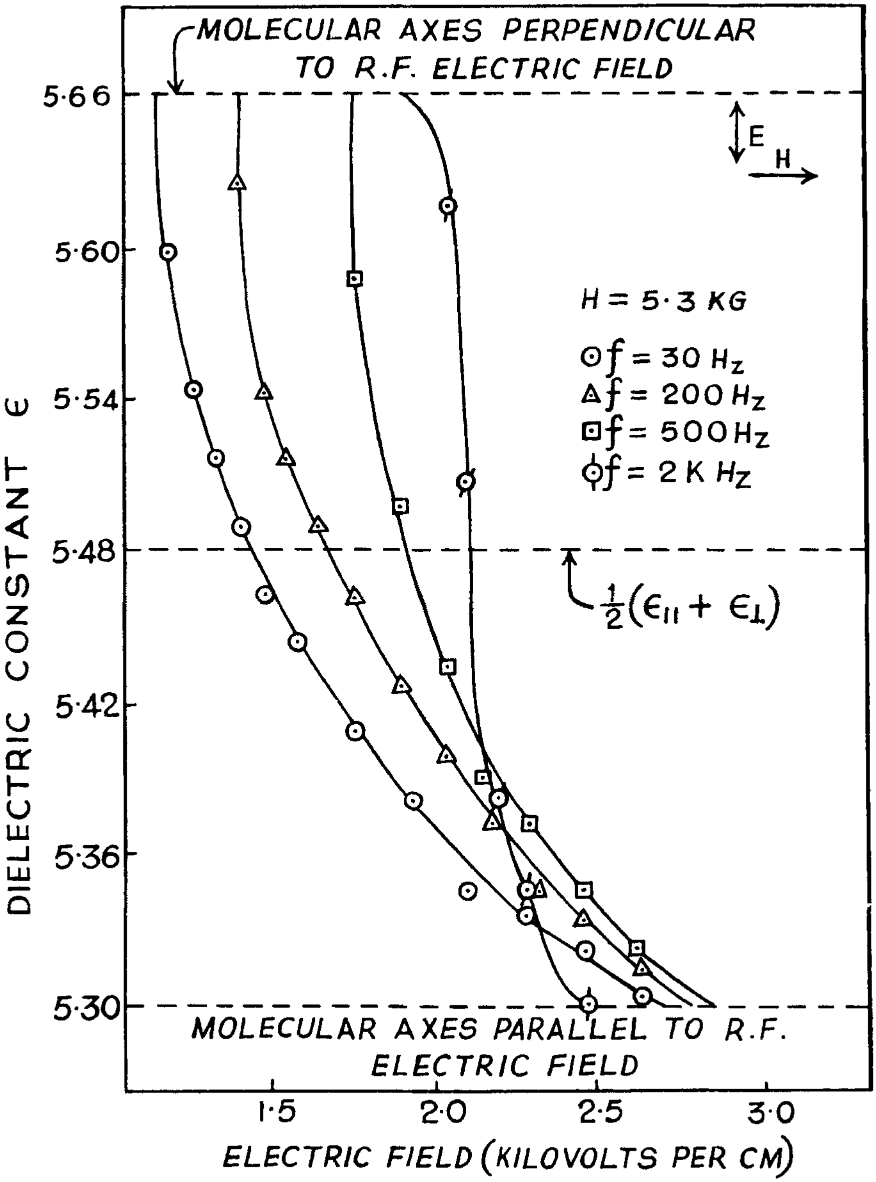

FIGURE 3 Dielectric constant, ε, of EBBA–EBCA mixture at 1 MHz as a function of externally applied electric field of various frequencies. A static magnetic field of 5300 G was applied perpendicular to the external electric field, which was parallel to the rf electric field. Temperature = 32°C.

regime the torques due to the conductivity and dielectric anisotropies aid each other in causing parallel molecular alignment, but in the dielectric regime sudden switching over of molecular axes through 90° involves the torque due to dielectric anisotropy only (Fredericksz effect).[27] The parallel molecular alignment with the electric field at all frequencies indicate positive dielectric anisotropic nature. But in pure EBBA[19] the complete parallel molecular alignment with the electric field is not achieved in the conduction regime due to the opposing nature of dielectric and conduction torques. The range of electric field strengths necessary to produce a rotation of the molecular axes for the parallel alignment in the low frequency region are larger than in the high frequency region. This behaviour is similar to that of nematics with negative dielectric anisotropy.[6,19]

Electric and magnetic fields, when applied in parallel configuration, do not produce any appreciable change in the dielectric constant value of $\varepsilon_{\parallel} = 5.30$. This behaviour is independent of frequency and applied electric field strength, indicating the positive dielectric anisotropic nature of the mixture. But in pure EBBA, parallel configuration of E and H fields produce a considerable change in the molecular ordering in the conduction regime and exhibit a switching over of the molecular axes from parallel to the perpendicular alignment in the dielectric regime (see Figure 4 of Ref. 19).

Due to a change of sign of the dielectric anisotropy the mixture shows negative dielectric anisotropy at the probing frequency and behaves like a positive dielectric anisotropic material for the low frequency reorientation field. This mixture may retain negative dielectric anisotropic nature if the frequency of the reorientation field is above the crossover frequency (520 kHz). So, in this type of materials, molecular alignment parallel or perpendicular to the electric field may be obtained by properly choosing the frequency of the applied electric field.[26]

C The relative effectiveness of *E* and *H* fields on molecular ordering:

Figure 4 shows the relative effectiveness of the electric and magnetic fields in producing molecular alignment in 3 kHz electric field for various values of the static magnetic field strengths. In the crossed field configuration, change in the dielectric constant from perpendicular to parallel alignment, i.e., $\varepsilon_{\perp} = 5.66$ to $\varepsilon_{\parallel} = 5.30$ corresponds to a 90° rotation of the molecular axes. The competing influence of E and H fields on the molecular ordering can be compared for a value of the dielectric constant $\varepsilon_{\text{random}} = \frac{1}{2}(\varepsilon_{\parallel} + \varepsilon_{\perp}) = 5.48$, which represents the random orientation of the molecules in the plane of E and H. Then the following equation used by Carr,[5] Carr and Murty[28] should hold good

$$(E/H) = C(\Delta\mu/\Delta\varepsilon)^{1/2}$$

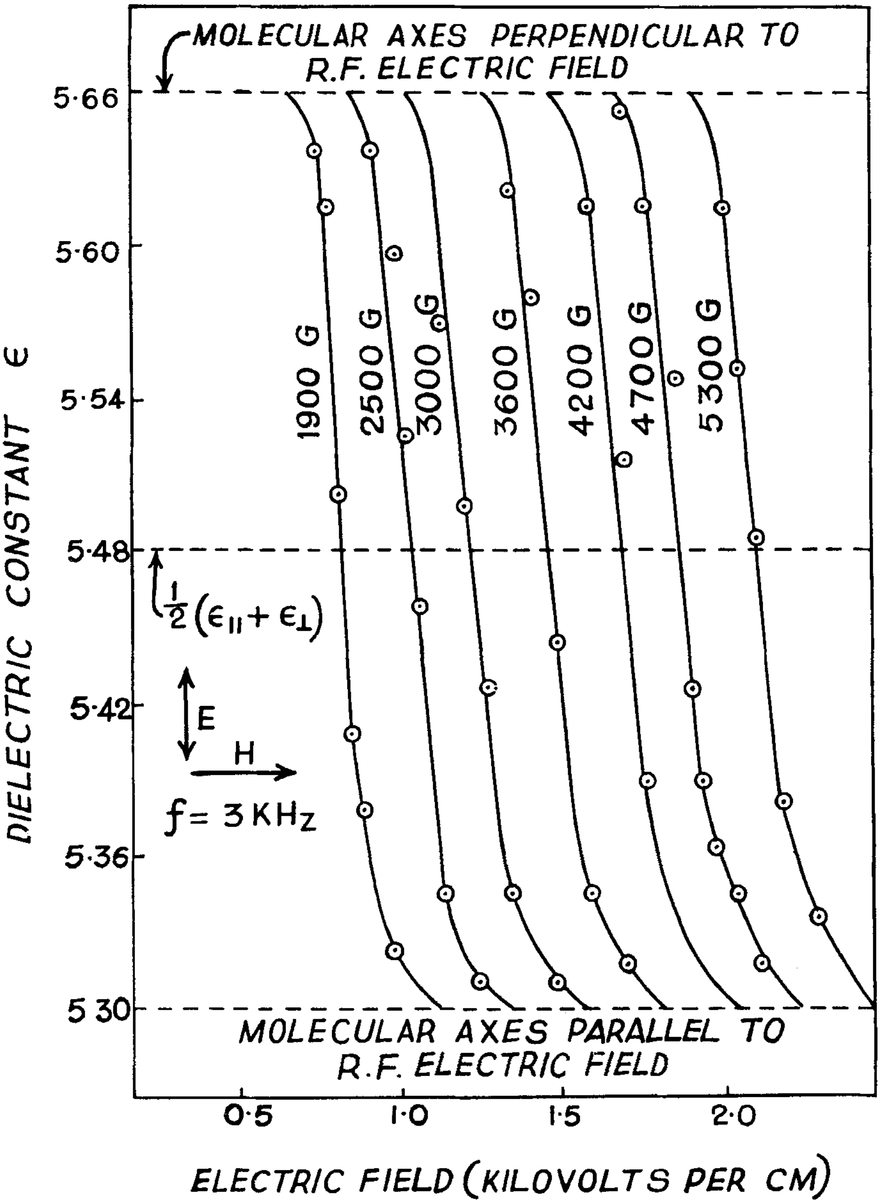

FIGURE 4 Dielectric constant, ε, of EBBA–EBCA mixture at 1 MHz as a function of an externally applied 3 KHz electric field. The individual curves are for various values of the static magnetic field applied perpendicular to the external electric field and rf measuring field. Temperature = 32°C.

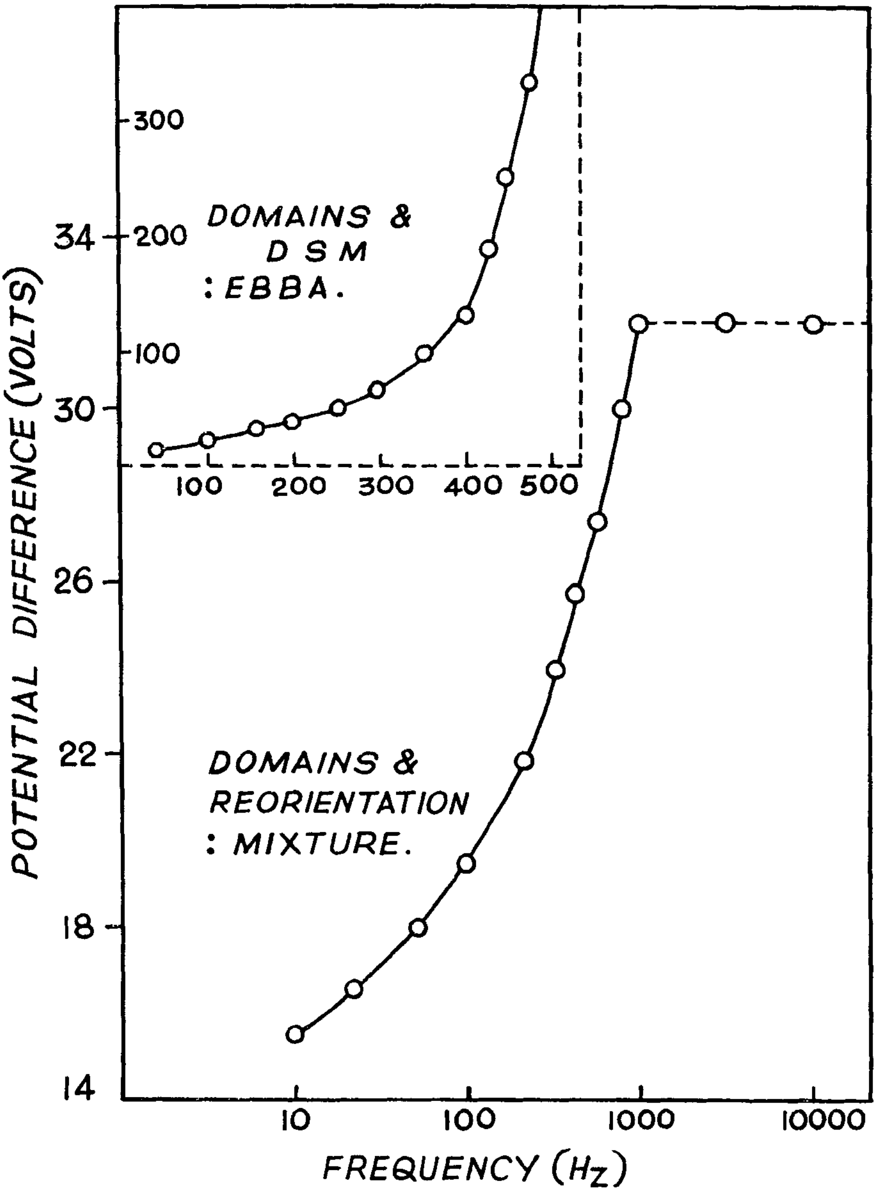

FIGURE 5 Threshold voltage for domain formation in EBBA and EBBA–EBCA mixture as a function of the frequency of the electric field. Outerscale corresponds to EBBA–EBCA mixture. Innerscale corresponds to EBBA. Thickness = 280 μm, H = 3000 G, Temperature = 32°C.

where $\Delta\mu$ and $\Delta\varepsilon$ are the anisotropies associated with the magnetic permeability and the low frequency dielectric constant, C is a constant associated with the units of the above equation.

Figure 4 indicates that the ratio of $(E/H) = 0.40$ Volts/cm-Gauss is fairly constant within the limits of experimental error at different magnetic field strengths, confirming the dielectric regime. The value of (E/H) in this mixture is slightly less than the value of pure EBBA.[19]

D Molecular alignment and Optical observations

In nematic liquid crystals with positive dielectric anisotropy, domains[29] and dynamic scattering[30] have been reported in dc fields[31] as well as in ac fields.[8,16,32–34] The instabilities observed in the positive dielectric anisotropic nematics are domains and dynamic scattering, domains and reorientation and pure reorientation depending on the magnitude of the dielectric anisotropy. A maximum value of $(\varepsilon_{\parallel}/\varepsilon_{\perp}) = 1.05$ has been suggested[16] above which domains are not likely to occur.

Recently Carr[33] correlated the domain formation in the positive dielectric anisotropic materials to the relative effectiveness of the torques due to the conductivity and dielectric anisotropies. Figure 3 nearly represents the situation of the torque due to the conductivity anisotropy is approximately equal to the torque due to the dielectric anisotropy in the conduction regime. So unstable domains and reorientation are likely to occur as observed in this mixture.

Figure 5 shows the frequency dependence of the threshold voltages for the domain formation in pure EBBA and for the domain formation and dielectric alignment in the mixture. The threshold voltages are considerably larger in EBBA as compared to the mixture. The nature of instability changes from domains and dynamic scattering in EBBA to unstable domains and reorientation in the mixture. At low frequencies, as the voltage increases domains change into loop domains[14] followed by reorientation. But at higher frequencies loop domains are observed as a transient effect in the reorientation process. These optical observations are similar with the observations reported earlier[14,34] on nematics with small positive dielectric anisotropy.

CONCLUSIONS

Molecular alignment changes and instabilities in this mixture are similar to nematics with small positive dielectric anisotropy. Results reported in this mixture suggest that the type of instability depends on the relative effectiveness of the torques associated with the dielectric and conductivity anisotropies.

The mixing of EBBA with EBCA extends the nematic range of EBBA, suggesting that EBCA strengthens the nematic ordering of EBBA.[35]

The property of frequency dependent sign change in this mixture is very useful to study molecular alignment and different type of instabilities in the same sample under the varied conditions of the dielectric anisotropy.

Acknowledgements

The authors are grateful to Prof. E. F. Carr for his kind interest and encouragement. They wish to express their appreciations to Dr. K. V. J. Rao, Department of Chemistry, for his help in synthesis and purification of the samples. They also thank CSIR, DAE, Defence and US National Science Foundation for financial assistance (NSF Grant No. GF 36748).

References

1. R. Steinstraesser and L. Pohl, *Angew. Chem. Int. Ed. Engl.*, **12**, 617 (1973).
2. L. A. Goodman, *R.C.A. Review*, **35** (4), 613 (1974).
3. G. Durand and J. D. Litster, *Ann. Rev. Mater. Sci.*, **3**, 269 (1973).
4. P. G. De Gennes, *The Physics of Liquid Crystals*, Oxford Press (1974).
5. E. F. Carr, *Advan. Chem. Ser.*, 63, 76 (1965).
6. E. F. Carr, *Mol. Cryst. Liq. Cryst.*, **7**, 253 (1969).
7. E. F. Carr, *J. Chem. Phys.*, **39** (8), 1979 (1963).
8. W. T. Flint and E. F. Carr, *Mol. Cryst. Liq. Cryst.*, **22**, 1 (1973).
9. L. S. Chou and E. F. Carr, *Phys. Rev. A.*, **7**, 1639 (1973).
10. R. P. Twitchell and E. F. Carr, *J. Chem. Phys.*, **46**, 2765 (1967).
11. D. P. Mclemore and E. F. Carr, *J. Chem. Phys.*, **57**, 3245 (1972).
12. Orsay Liquid Crystal Group, *Mol. Cryst. Liq. Cryst.*, **12**, 251 (1971).
13. W. H. De Jeu and C. J. Gerritsma, *J. Chem. Phys.*, **56**, 4752 (1972).
14. W. H. de Jeu, C. J. Gerritsma, and Th. W. Lathouwers, *Chem. Phys. Lett.*, **14**, 5031 (1972).
15. W. H. de Jeu, C. J. Gerritsma, P. Van Zanten, and W. J. A. Goossens, *Phys. Lett.*, **39A**, 355 (1972).
16. W. H. de Jeu and Th. W. Lathouwers, *Mol. Cryst. Liq. Cryst.*, **26**, 235 (1974).
17. W. Helfrich, *J. Chem. Phys.*, **51**, 4092 (1969).
18. E. Duvois-Violette, P. G. de Gennes, and O. Parodi, *J. Phys.*, **32**, 305 (1971).
19. N. V. S. Rao, P. R. Kishore, T. F. S. Raj, M. N. Avadhanlu, and C. R. K. Murty, *Mol. Cryst. Liq. Cryst.*, **36**, 65 (1976).
20. P. R. Patel, *J. Ind. Chem. Soc.*, L, 514 (1973).
21. G. Elliott, *Chem. in Br.*, **9**, 213 (1973).
22. G. Meier and A. Saupe, *Mol. Cryst. Liq. Cryst.*, **1**, 515 (1966).
23. L. Bata and G. Molnar, *Chem. Phys. Lett.*, **33**, 535 (1975).
24. M. Schadt, *J. Chem. Phys.*, **56**, 1494 (1972).
25. F. Rondelez, D. Diguet, and G. Durand, *Mol. Cryst. Liq. Cryst.*, **15**, 183 (1971).
26. H. K. Bucher, R. T. Klingbiel, and J. P. Van Meter, *Appl. Phys. Lett.*, **25**, 186 (1974).
27. V. Freedericksz and V. Zolina, *Trans. Faraday Soc.*, **29**, 919 (1933).
28. E. F. Carr and C. R. K. Murty, *Mol. Cryst. Liq. Cryst.*, **18**, 369 (1972).
29. R. J. Williams, *J. Chem. Phys.*, **39**, 384 (1963).

30. G. H. Heilmeier, L. A. Zanoni, and L. A. Barton, *Proc. Inst. Elect. Electronics Engrs.*, **56**, 1161 (1968).
31. G. Elliott and J. G. Gibson, *Nature*, **205**, 995 (1965).
32. P. A. Penz, *Mol. Cryst. Liq. Cryst.*, **23**, 1 (1973).
33. E. F. Carr, W. T. Flint, and J. H. Parker, *Phys. Rev., A*, **11**, 1732 (1975).
34. H. Gruler and G. Meier, *Mol. Cryst. Liq. Cryst.*, **12**, 289 (1971); *Mol. Cryst. Liq. Cryst.*, **16**, 299 (1972).
35. S. Yano, Y. Hayashi, M. Kuwa Hara, and K. Aoki, *Jap. J. Appl. Phys.*, **16**, 649 (1977).