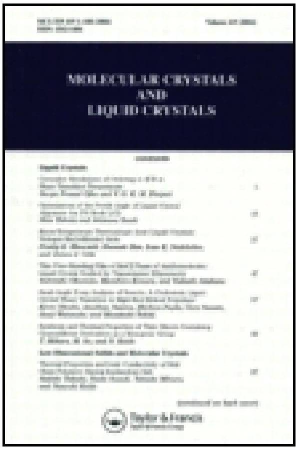

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# Dielectric Studies in Solid Phase EBBA

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# Dielectric Studies in Solid Phase EBBA

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Dielectric measurements have been made in the stable and metastable solid phases of EBBA in the frequency range 0.1 KHz to 100 KHz and in the temperature range −170 to −10°C. The dielectric dispersion was absent in the stable phase while in the metastable phase, obtained by rapid cooling, a clear dielectric dispersion was seen. In addition to the primary dispersion extending above about −125°C there also appears a clear secondary dispersion region below −125°C. The strength of the second dispersion is lower by one order of magnitude than the primary dispersion. The primary dispersion is of the Debye type with a symmetric distribution of relaxation times. The Cole–Cole distribution parameter varies with temperature and shows a maximum at about −64°C. The results in the primary dispersion region can be qualitatively explained by assuming the free rotation of dipoles above −64°C and a restricted rotation of dipoles at low temperatures.

## 1 INTRODUCTION

Measurements of specific heat,[1] infrared and farinfrared absorption,[2] and dielectric behaviour[3,4] at low frequencies have revealed the existence of two monotropic modifications of the solid MBBA: a stable and a metastable one, which are obtained depending on the thermal history of the sample. In the metastable phase of MBBA dielectric dispersion[3,4] has been observed which is absent in the stable phase. Dielectric[4] as well as specific heat[2] measurements indicate a phase transition in the metastable phase of MBBA at about −60°C. However, very little work has been reported on the properties of solid phase EBBA.

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The dielectric dispersion in the solid phase MBBA is considered to be due to rotation of methoxy group.[4] A conclusive evidence about the rotating group in the metastable state of these liquid crystals can be obtained by replacing the methoxy group of MBBA by ethoxy group. The present study has been carried out to characterise the dielectric behaviour of solid phase EBBA and to establish the nature of the group responsible for the dielectric dispersion in the metastable phase of these nematic liquid crystals. Measurements have been made in the temperature range −170 to −10°C and in the frequency range 0.1 KHz to 100 KHz and the results are reported in this paper. It has been observed that on slow cooling of the sample a stable phase characterised by the absence of dielectric dispersion is obtained while rapid cooling gives a metastable solid phase of EBBA which shows a dielectric dispersion.

## 2 EXPERIMENTAL

The dielectric permittivity ($\varepsilon'$) and the dielectric loss factor ($\tan \delta$) of solid phase EBBA (both stable and metastable modifications) have been measured in the temperature range −170 to −10°C and in the frequency range 0.1 KHz to 100 KHz using a General Radio Schering Bridge type GR 716 CS. The experimental set up and the measuring technique have been described earlier.[4] The EBBA sample which had a nematic range 37 to 79°C and a resistivity of $7 \times 10^{10}$ ohm-cm at 23°C was procured from M/s Eastman Kodak Ltd., and was used without further purification.

The sample cell was placed inside a thick aluminium block, and the aluminium block was placed inside a copper container of large diameter and insulating material was filled between the aluminium block and the copper container. The whole assembly was placed in a thermocole flask. Liquid nitrogen was poured in the flask and the assembly was allowed to cool slowly. The cooling rate was less than 0.5°C/minute. This slow rate of cooling gave the stable phase. Once the sample cell attained the liquid nitrogen temperature, it was kept there for about 90 minutes. The dielectric measurements were made during the heating run. The heating rate could be adjusted by the level of liquid nitrogen in the flask and the heater wound around the aluminium block.

For obtaining the metastable phase, the assembly of sample cell and container were kept the same as described earlier. But, in addition to keeping liquid nitrogen in the flask, liquid nitrogen was also poured directly on the aluminium block at a fast rate, producing a cooling rate of more than 5°C/minute. This resulted in the metastable modification of the sample.

Once the sample cell achieved the liquid nitrogen temperature this temperature was maintained for more than 30 minutes. The dielectric measurements were made in the heating run as described earlier. Measurements were made after about every 5°C and the temperature of the cell could be controlled to within 0.3°C during the time (about 10 minutes) required for measurements at five different frequencies in the range 0.1 KHz to 100 KHz. The measurements from −170 to −10°C took about 10 hours and in this time there was no evidence of transition from metastable to the stable phase.

The agreement in the measured values of dielectric permittivity $\varepsilon'$ and dielectric loss $\varepsilon''$ in different runs on stable phase was within 1% and 2% respectively, which was close to the accuracy of measurements. However, in metastable phase different runs showed a random variation of ±5% in $\varepsilon'$ and ±10% in $\varepsilon''$, though there was no change in the overall behaviour in different runs. In the metastable phase at low frequencies and temperatures above about −40°C, there was a significant increase in the dielectric loss, probably caused by the ionic conductivity of the impurities, and this was taken into account in deriving the values of $\varepsilon''$.

## 3 RESULTS AND DISCUSSION

The loss tangent (tan $\delta$) and dielectric permittivity ($\varepsilon'$) are plotted as a function of temperature at two fixed frequencies 1 KHz and 100 KHz. These are shown in Figure 1 for stable solid phase and in Figure 2 for the metastable

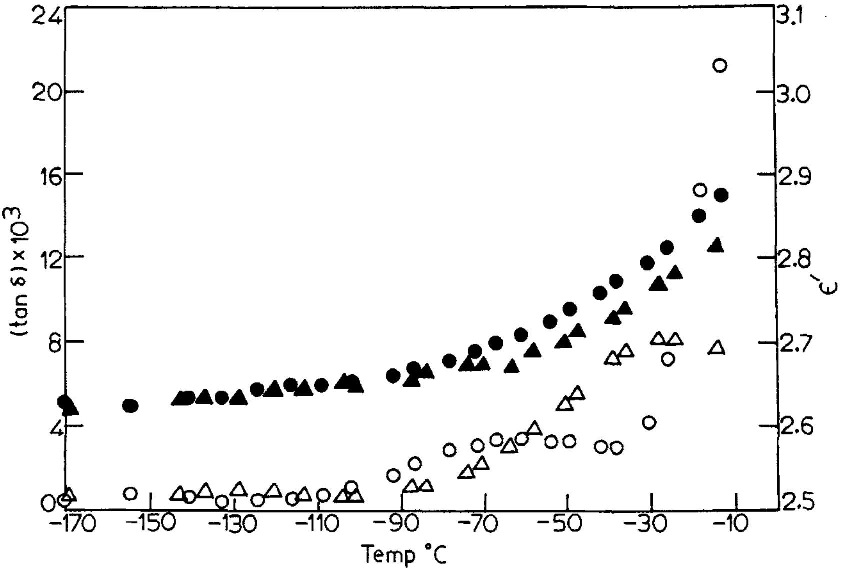

FIGURE 1 Temperature dependence of dielectric loss factor (tan $\delta$) and dielectric permittivity ($\varepsilon'$) at 1 KHz ○, ● and at 100 KHz △, ▲ for the stable solid phase of EBBA.

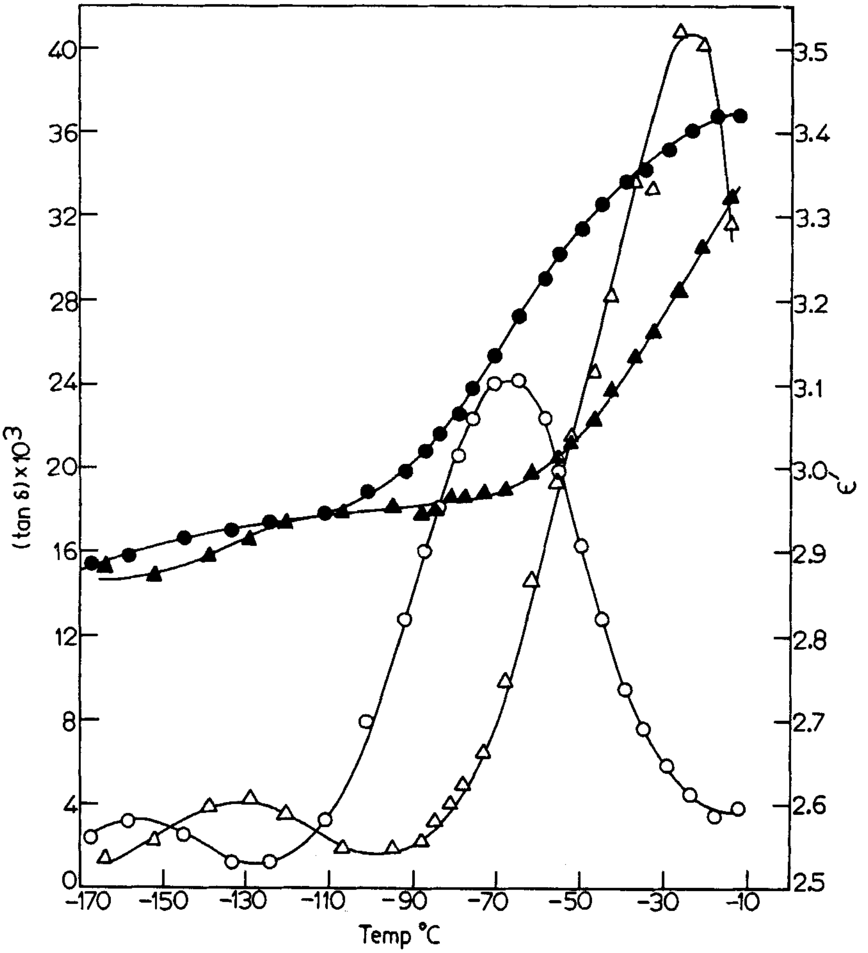

FIGURE 2 Temperature dependence of dielectric loss factor (tan δ) and dielectric permittivity (ε′) at 1 KHz ○, ● and at 100 KHz △, ▲ for the metastable solid phase of EBBA.

solid phase of EBBA, respectively. The substantial difference between the dielectric properties of both phases is evident. In the metastable form the dipolar dispersion and absorption were observed which do not appear in the stable modification. A similar difference in the stable and metastable solid phase of MBBA has also been reported.[3] However, there is some significant difference between the dispersion behaviour of the metastable phase of MBBA and EBBA. In the metastable phase of EBBA two clear dispersion regions, indicated by the peaks in tan δ, are observed at a fixed frequency of measurements while a single peak in tan δ has been reported in MBBA.[3,4]

The two dispersion regions can be separated by a characteristic temperature of about −125°C where a dip in tan $\delta$ is obtained at the lowest frequency of measurement. This temperature may be indicative of a glass transition temperature Tg, as has been suggested by Johari and Goldstein.[5] The secondary peak appears about 20 to 50°C below the glass transition temperature Tg as shown in Figure 2. For a given frequency of measurements the ratio of temperatures, (Tp °K/Ts °K), at which maxima in tan $\delta$ are obtained in the primary and secondary dispersion regions, is found to be about 0.6. The strength of the secondary relaxation process is about one order of magnitude less than that of primary relaxation. Similar features of the two

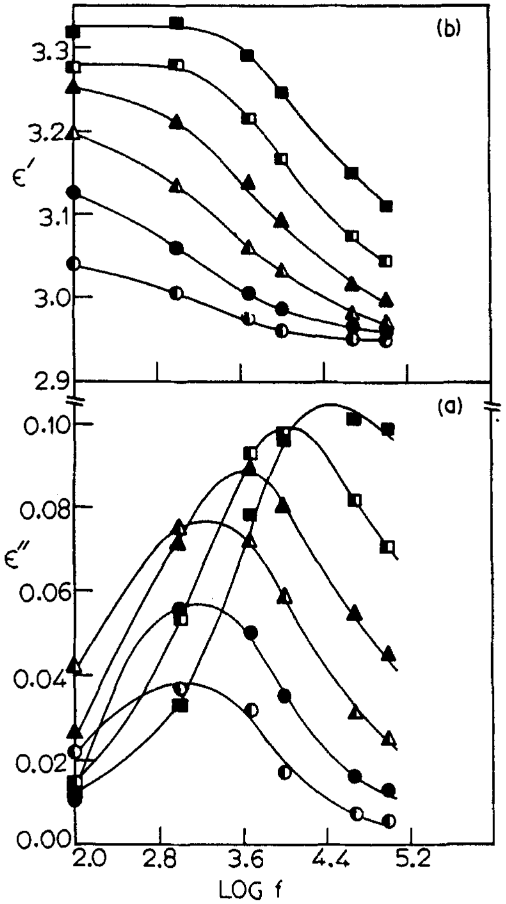

FIGURE 3 Frequency dependence of the dielectric loss $\varepsilon''$ (a) and dielectric permittivity $\varepsilon'$ (b) in the primary relaxation at −90°C ◐; −80°C ●; −70°C △; −60°C ▲; −50°C ◧ and −40°C ■.

relaxation regions have been observed in the glassy state of many rigid molecules, in pure state, in mixtures, or in solutions with nonpolar solvents,[6,7] long chain alcohols, aromatic and aliphatic esters,[5,6] hydrocarbons, inorganic salts, organic polymers,[8] silicate glasses[9] and molecular glasses.[10] In spite of the fact that this secondary relaxation region has been observed in so many systems its origin is not yet clearly understood. Goldstein[11] has suggested that the secondary relaxation is a necessary feature of the glassy state and associated it with the local arrangements involving the lower barriers that may exist even at lower temperatures. However, the primary dispersion region which is similar to the dispersion in MBBA (to be discussed later) requires both free and hindered rotation to explain completely all its features. The presence of secondary dispersion region in EBBA and its absence in MBBA is not surprising. Johari and Goldstein[5] have also noted the presence of a secondary dispersion region in some alcohols and its absence in others. However, the origin of secondary dispersion region in EBBA is not obvious and requires further investigations on more nematic liquid crystals to ascertain its origin. The strength of the secondary relaxation is so small that the data are obtained almost at the limit of experimental accuracy and hence no attempt has been made for detailed analysis of the relaxation behaviour.

For the primary dispersion region graphs of $\varepsilon'$ and $\varepsilon''$ as functions of frequency and at different temperatures are shown in Figure 3. The present data can be represented by a symmetrical distribution of relaxation times, which is indicated by the Cole–Cole[12] arc plots. Representative curves at three temperatures are shown in Figure 4. The values of limiting dielectric

TABLE I

Dielectric relaxation parameter ($\alpha$), limiting permittivity at low frequencies ($\varepsilon_0$), the extrapolated permittivity on high frequency side ($\varepsilon_\infty$), the relaxation frequency ($f_c$) derived from Cole–Cole plots and the frequency of maximum dielectric loss ($f_{max}$) at several temperatures in the primary relaxation of metastable solid phase EBBA.

| Temp. °C | $\varepsilon_0$ | $\varepsilon_\infty$ | $\alpha$ | $f_c$ KHz | $f_{max}$ KHz |
|---|---|---|---|---|---|
| −100 | 3.00 | 2.95 | 0.26 | 1.0 | 1.0 |
| −90 | 3.06 | 2.95 | 0.31 | 1.3 | 1.3 |
| −80 | 3.14 | 2.95 | 0.38 | 1.5 | 1.8 |
| −70 | 3.25 | 2.95 | 0.42 | 2.2 | 2.3 |
| −60 | 3.30 | 2.96 | 0.46 | 5.0 | 4.8 |
| −50 | 3.33 | 2.98 | 0.43 | 13.2 | 12.6 |
| −40 | 3.36 | 3.01 | 0.39 | 29.0 | 28.9 |
| −30 | 3.39 | 3.03 | 0.37 | 69.5 | — |

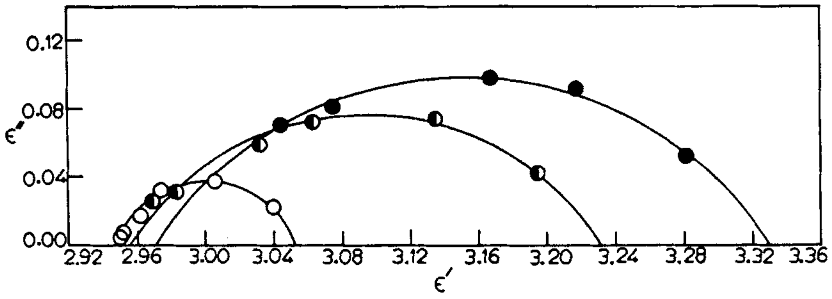

FIGURE 4 Cole–Cole plots in the primary relaxation at −90°C ○ ; −70°C ◐ ; and −50°C ●.

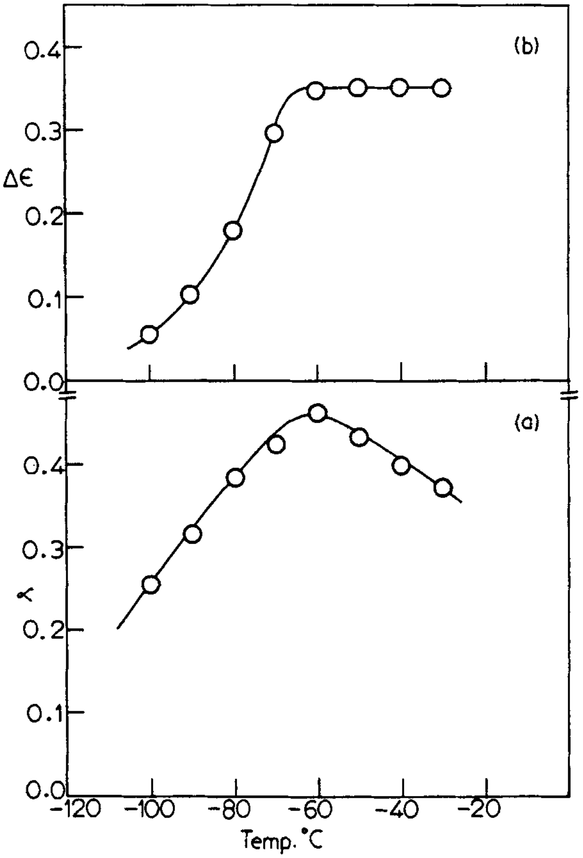

FIGURE 5 Temperature dependence of distribution parameter α (a) and dielectric relaxation strength Δε (b) in the primary relaxation.

permittivity at low frequencies ($\varepsilon_0$), the extrapolated permittivity on high frequency side ($\varepsilon_\infty$), the relaxation frequency ($f_c$), the distribution parameter ($\alpha$) derived from Cole–Cole arc plots and the frequency of maximum dielectric loss ($f_{\max}$) at different temperatures are given in Table I. The value of $\alpha$ increases with temperature up to about −64°C and then decreases with increase in temperature (Figure 5a). The dielectric relaxation strength ($\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$) becomes constant at −64°C (Figure 5b). The plot of log $\tau$ vs. $1/T$ is shown in Figure 6. As is evident, the slope is different below and above the transition temperature −64°C. The activation energies are respectively 9.89 and 2.04 K.Cal/mole above and below the transition temperature. These results are similar to those reported by us in the metastable phase of MBBA.[4] The transition temperature in EBBA is slightly lower than that reported for MBBA (−60°C). The numerical value of the distribution

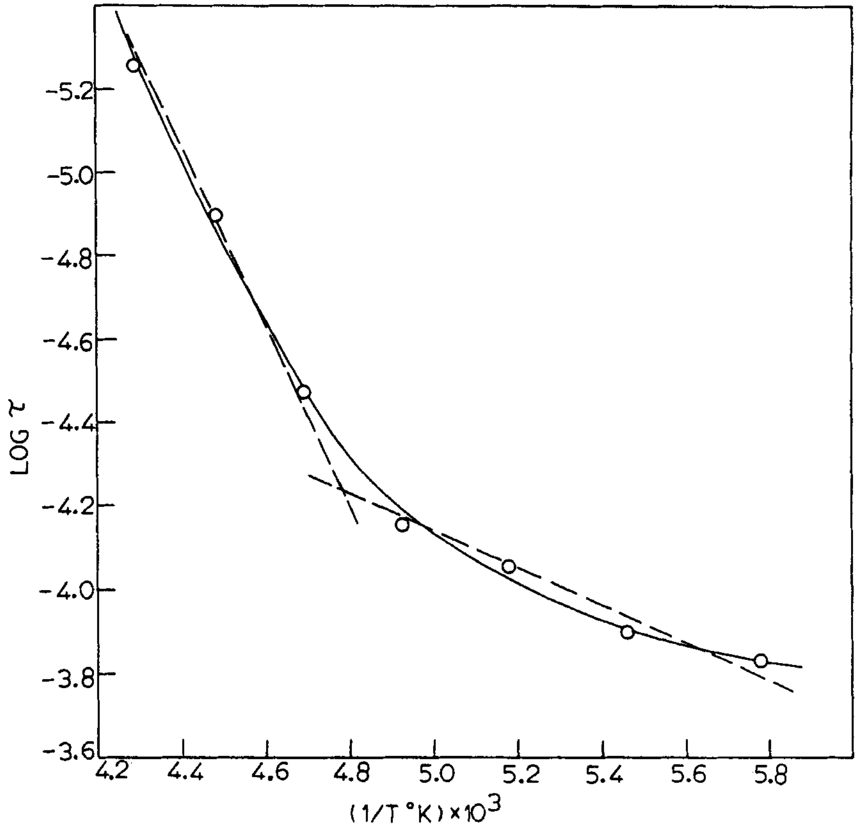

FIGURE 6 Temperature dependence of the dielectric relaxation time in the primary relaxation.

parameter ($\alpha$) at a given temperature is higher in EBBA. The most significant difference is in the relaxation times at different temperatures. These values in MBBA and EBBA at a temperature of $-80°C$ are $62.4 \times 10^{-6}$ sec and $106 \times 10^{-6}$ sec respectively and at $-50°C$ $3.0 \times 10^{-6}$ sec and $12.1 \times 10^{-6}$ sec respectively. A substantial increase in the relaxation time by changing methoxy group in MBBA by ethoxy group in EBBA indicates that the rotation of the end group is responsible for the dispersion in the metastable solid phase of these substances. A nominal increase in relaxation times would have been expected for the overall rotation of the molecule in changing the end group as has been noted in the solution studies of these molecules.[13]

## 4 CONCLUSION

The dielectric studies indicate the existence of two modifications of the solid EBBA: stable and metastable. The dielectric dispersion is observed in metastable phase which is absent in the stable phase. The end group is responsible for the dispersion in the metastable solid phase. A secondary region which is absent in MBBA has been observed in EBBA.

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