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Dielectric Relaxation Studies in the Solid Phase Nematic Crystal

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Dielectric measurements have been made in the stable and metastable solid modifications of *p*-(*p*-Ethoxyphenylazo)phenyl Hexanoate (EPPH) in the frequency range 0.5 to 100 KHz and in the temperature range 103 to 273° K. The dielectric dispersion was absent in the stable modification while in the metastable modification, obtained by rapid cooling, a clear Debye-type dispersion with symmetric distribution of relaxation times was obtained at temperatures above about 198° K. The plots of dielectric relaxation strength $\Delta\varepsilon$ $(=\varepsilon_0-\varepsilon_\infty)$ and distribution parameter α vs. reduced temperature $(T/T_{\text{dipole-freezing}})$ exhibit the similar behaviour as for EBBA [*Mol. Cryst. Liq. Cryst.*, **45**, 117 (1978)] which indicates that the dielectric dispersion observed in the present study is due to the hindered rotation of ethoxy groups which remain active (with an activation energy of 7 K. cal/mole) in the low temperature region.

1 INTRODUCTION

Dielectric studies in the solid phase of a few Schiffs' base nematic liquid crystals[1–4] has indicated the absence of dielectric dispersion in the stable solid modifications while in the metastable solid phases a clear dielectric dis-

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persion arising from the partial reorientation of active dipoles has been observed. In our earlier study on metastable solid phase EBBA,[2] the dielectric dispersion was suggested due to the reorientation of end group (ethoxy group) which remains active even though the mobility of the molecule is seized. In order to ascertain the origin of mechanism of dielectric dispersion in metastable solid phase EBBA we have studied dielectric properties of solid phase *p*-(*p*-Ethoxyphenylazo) phenyl Hexanoate (EPPH) which also has ethoxy group at the identical position of the benzene ring as in EBBA. This study is expected to help in understanding the dielectric relaxation mechanism in metastable solid phase of nematic liquid crystals.

2 EXPERIMENTAL

The electric permittivity (ε') and the loss factor ($\tan \delta$) of the solid phase EPPH have been measured in the temperature range 103 to 273° K and frequency range 0.5 to 100 KHz using a General Radio Schering bridge type GR716 CS. The experimental set up and the measuring techniques were the same as described earlier.[2] The EPPH sample was procured from M/s Eastman Kodak Ltd. and was used as such without further purification.

The cooling, heating and temperature measuring techniques were the same as described earlier.[2] The slow cooling at the rate of about 0.5 °K/min. using liquid nitrogen yielded stable solid form of the sample. When 103° K temperature was reached, the cell was kept at this same temperature for more than 40 minutes. The metastable solid phase of the sample was obtained by rapidly cooling the cell at the rate of about 8° K/min. and the cell was then maintained at this same temperature for about 30 minutes. The measurements for both the stable as well as metastable solid forms were taken during heating cycle only. It took about 7 hours to complete each run.

The error in the measurement of the electric permittivity (ε') and dielectric loss (ε'') was about $\pm 1\%$ and $\pm 2\%$ respectively. In deriving the values of ε'' due account was taken for the ionic conductivity which had a significant effect above about 240° K.

3 RESULTS AND DISCUSSION

The variation of electric permittivity (ε') and loss tangent ($\tan \delta$) with temperature for both stable and metastable forms are shown in Figure 1 at a typical frequency 50 KHz. The curves indicate the absence of dielectric dispersion in

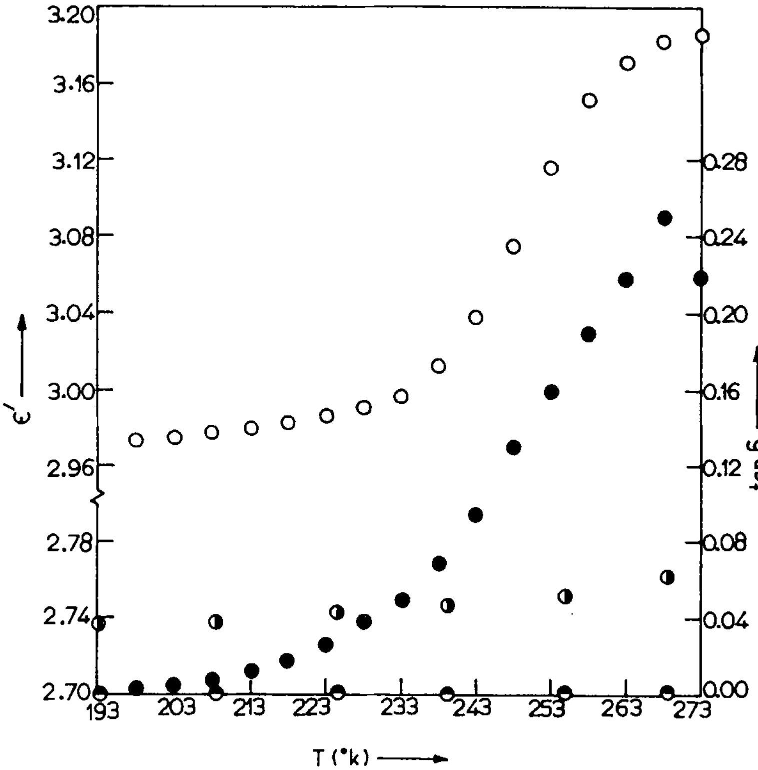

FIGURE 1 Temperature dependence of electric permittivity (ε′) and dielectric loss factor (tan δ) at 50 KHz for stable (◑ and ◒ respectively) and metastable (○ and ● respectively) solid phases of EPPH.

the stable solid form while metastable form exhibits pronounced dispersion above about 198° K. This behaviour is similar to those observed for other metastable solid phase liquid crystals.[2–4] For the metastable form the variation of electric permittivity (ε') and loss (ε'') with frequency at different temperatures is indicated in Figure 2. The present data can be fitted on the empirical equation developed by Cole and Cole.[5]

$$\varepsilon^* = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (jw\tau_0)^{1-\alpha}}$$

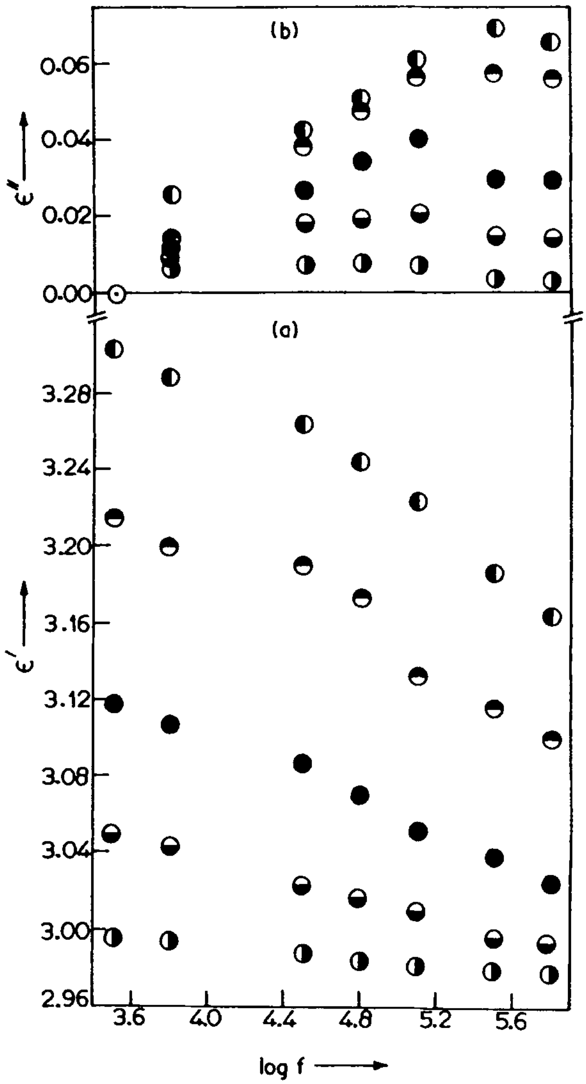

FIGURE 2 Frequency dependence of (a) electric permittivity (ε′) and (b) dielectric loss (ε″) for the metastable solid phase EPPH at 213°K (◑), 233°K (◒), 243°K (●), 253°K (◓) and 273°K (◐). (⊙) in (b) is a common point at all temperatures.

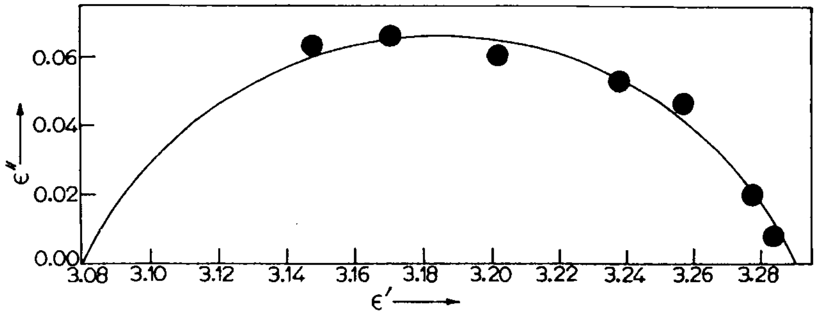

FIGURE 3 Cole–Cole plot at 263°K.

where $\varepsilon^*(=\varepsilon' - j\varepsilon'')$ is the complex permittivity at any frequency $f(=w/2\pi)$, ε_0, ε_∞ are respectively the limiting permittivity at low frequencies and the extrapolated permittivity on high frequency side of Cole–Cole arc plot, τ_0 is the relaxation time, and α is the distribution parameter, having values between 0 and 1.

A representative Cole–Cole arc plot of our data at 263° K is shown in Figure 3. The values of ε_0, ε_∞, the relaxation frequency f_0 $(=1/2\pi\tau_0)$ and the distribution parameter (α) derived from Cole–Cole arc plots at different temperatures are given in Table I. Thus in the metastable solid phase of nematic liquid crystals there is a distribution of relaxation times in contrast to that observed in their mesomorphic phase[6–8] for which α is zero.

The results of the present study indicate that the values of relaxation frequency (f_0) are in close agreement with the values of maximum dielectric loss

TABLE I

Dielectric relaxation parameter (α), limiting permittivity at low frequencies (ε_0), the extrapolated permittivity on high-frequency side (ε_∞) the relaxation frequency (f_0) derived from Cole-Cole plots at several temperatures in the solid phase EPPH.

Temperature (°K)	ε_0	ε_∞	α	f_0 (Khz)
213	3.00	2.98	0.32	8.3
223	3.02	2.98	0.33	8.3
233	3.05	2.98	0.35	12.9
243	3.11	3.00	0.38	19.1
253	3.21	3.05	0.42	33.2
263	3.29	3.08	0.44	40.0
273	3.30	3.07	0.50	63.4

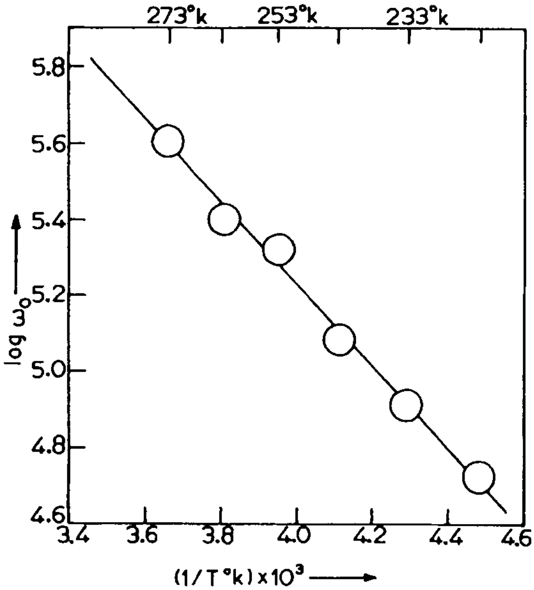

FIGURE 4 Temperature dependence of the dielectric relaxation frequency in the metastable solid phase EPPH.

frequency (f_{max}). The dielectric relaxation strength $\Delta\varepsilon (= \varepsilon_0 - \varepsilon_\infty)$ and the distribution parameter (α) both increase with temperature. The plot of log w_0 vs. $1/T$ is shown in Figure 4 from which an activation energy of 4.97 K.cal/mole was obtained for the metastable solid phase EPPH. These results are similar to those reported by us in the metastable solid phase EBBA,[3] indicating only the hindered rotation of ethoxy groups in the metastable solid phase EPPH. The dipole-freezing temperature $T_{\text{dipole-freezing}}$, defined as the temperature at which all the dipoles get frozen in their sites so that $\Delta\varepsilon$ becomes zero, is 198° K for EPPH as compared to 148° K for EBBA.[3] Figure 5 shows the variation of dielectric relaxation strength $\Delta\varepsilon$ ($= \varepsilon_0 - \varepsilon_\infty$) and Cole–Cole distribution parameter with reduced temperature $T/T_{\text{dipole-freezing}}$ for EBBA and EPPH. So far there is no direct experimental evidence to the reorientation of the ethoxy group in metastable solid phase systems, but this figure clearly confirms our earlier prediction that dielectric dispersion is due to the reorientation of ethoxy group, since the relaxation strength at a given reduced temperature is almost the same for both samples. However, the local environment for dipolar reorientation in the two cases are different, as indicated by the unequal value of distribution parameter at any reduced temperature.

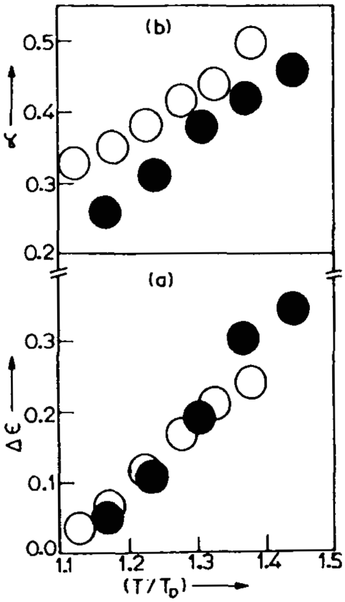

FIGURE 5 Dependence of (a) dielectric relaxation strength $\Delta\varepsilon(=\varepsilon_0 - \varepsilon_\infty)$ and (b) distribution parameter α on reduced temperature T/T_D (T_D = Dipole-freezing temperature) for the metastable solid phases of EPPH (○) and EBBA (●).

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