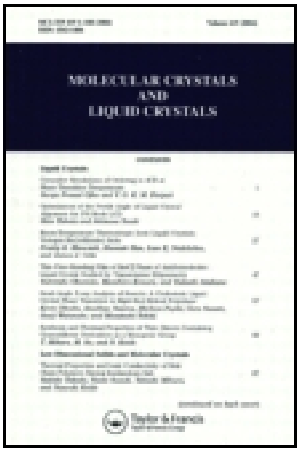

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Dielectric Relaxation and Nematic Potential of Some Nematogenic Compounds

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DIELECTRIC RELAXATION AND NEMATIC POTENTIAL OF SOME NEMATOGENIC COMPOUNDS

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Abstract: Component of $\epsilon_{\parallel}$ of dielectric tensor has been studied in the nematic phase of three nematogenic compounds namely, 6 OCB, 7 OCB and IPBOC. Using the relaxation data the nematic potential associated with the above molecules has been estimated based on Maier and Saupe mean field theory.

INTRODUCTION

It is well known that the dielectric constants $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ are frequency dependent. The perpendicular component $\epsilon_{\perp}$ exhibits relaxation only in the microwave region. The parallel component $\epsilon_{\parallel}$ shows relaxation even in the lower frequency region also. This low frequency relaxation of $\epsilon_{\parallel}$ was first observed by Maier and Meier [1,2] in several members of the p-azoxyanisole series. The low frequency relaxation mechanism can be attributed to the reorientation motion of the molecules around an axis perpendicular to their longitudinal axis[2]. Mircea-Roussel and Rondelez [3] from their studies on the low frequency dispersion of $\epsilon_{\parallel}$ have estimated the activation energy in different members of the homologous series of 4,4'-di-n-alkoxy azoxybenzenes. Later, the study of low frequency dielectric dispersion of $\epsilon_{\parallel}$ in the nematic phase of liquid crystals exhibiting large and low positive dielectric anisotropy has been the subject matter of several investigators[4–11]. In the following we discuss the low frequency dielectric dispersion of $\epsilon_{\parallel}$ and nematic potentials of the three nematogenic compounds, namely, (i) 4'-(hexyloxy)-4- biphenylcarbonitrile (6 OCB) ,(ii) 4'-(heptyloxy)-4- biphenylcarbonitrile (7 OCB), (iii)4-isothiocyanatophenyl-4-pentylbicyclo (2,2,2) octane-1-carboxylate (IPBOC). The dielectric relaxation of 7OCB is reported over a frequency range upto 18GHz and over a temperature well into the isotropic phase[12]. However, the type of dielectric studies and the temperature range reported in this study do not overlap with the earlier work.

EXPERIMENTAL

The low frequency dielectric relaxation of $\epsilon_{\parallel}$ was carried out at Liquid Crystal Laboratory, Raman Research Institute, Bangalore, using an experimental set up described in our earlier paper[13]. For each of the nematic compounds the dispersion of dielectric constants was measured at different fixed temperatures (maintained constant in each case to within ± 25mK) in the nematic phase, in the range of frequencies 5 Hz to 13 MHz using Hewlett packard impedance analyser (model HP 4192A).

RESULTS AND DISCUSSION

The frequency dependence of the dielectric loss, $\epsilon''_{\|}$ is plotted for different temperatures and is shown in Figures 1(a,b,c) for all the three nematic compounds. As expected, the maximum of $\epsilon''_{\|}$ decreases slowly with increasing temperature, while the frequency at which the maximum of $\epsilon''_{\|}$ occurs increases with temperature. This may be due to the fact that the orientation polarization which determines the magnitude of $\epsilon''_{\|}$ decreases at higher temperature due to the decrease of orientational order parameter. The Cole-Cole plot [14] of $\epsilon''_{\|}$ against $\epsilon'_{\|}$ is also given in Figures 2(a,b,c) for different temperatures. For all the three compounds, the experimental points lie on a semi circle with centre on $\epsilon'_{\|}$ axis indicating that the relaxation process can be characterized by a single relaxation frequency f_R. With the increase in temperature, the radius of the semi circle decreases and the centre shifts to a lower value of $\epsilon'_{\|}$. Here we have determined the radius by fitting a least squares circle and hence estimated the corresponding value of the relaxation frequency f_R.

From the relaxation frequencies estimated from the above figures we have calculated the relaxation time τ_R corresponding to the reorientation of the longitudinal component of the dipole moment (μ_l) in the nematic phase, using the relation $\tau_R = 1/2\pi f_R = Aexp(W/k_BT)$. Here, W represents the activation energy for dielectric relaxation in the nematic phase and k_B is the Boltzmann constant. The value of τ_R decreases with increase of temperature. Using Arrhenius plot [8-10] we find that τ_R do obey $exp(W/k_BT)$ law in the nematic phase for all the compounds. Thus it was possible to calculate the activation energy for the dielectric relaxation in the nematic phase, from the slope of straight line graph of $ln(\tau_R)$ versus $1/T$. Table 1 gives the activation energies estimated for different nematic

Table 1: The activation energies(W) and the values of k_o in the case of some nematogenic compounds.

Compound	W(in eV)	k_o (in kJ mol^{-1})
6 OCB	0.76	7.25
7 OCB	0.75	7.60
IPBOC	0.72	5.57
6 CB	-	7.5

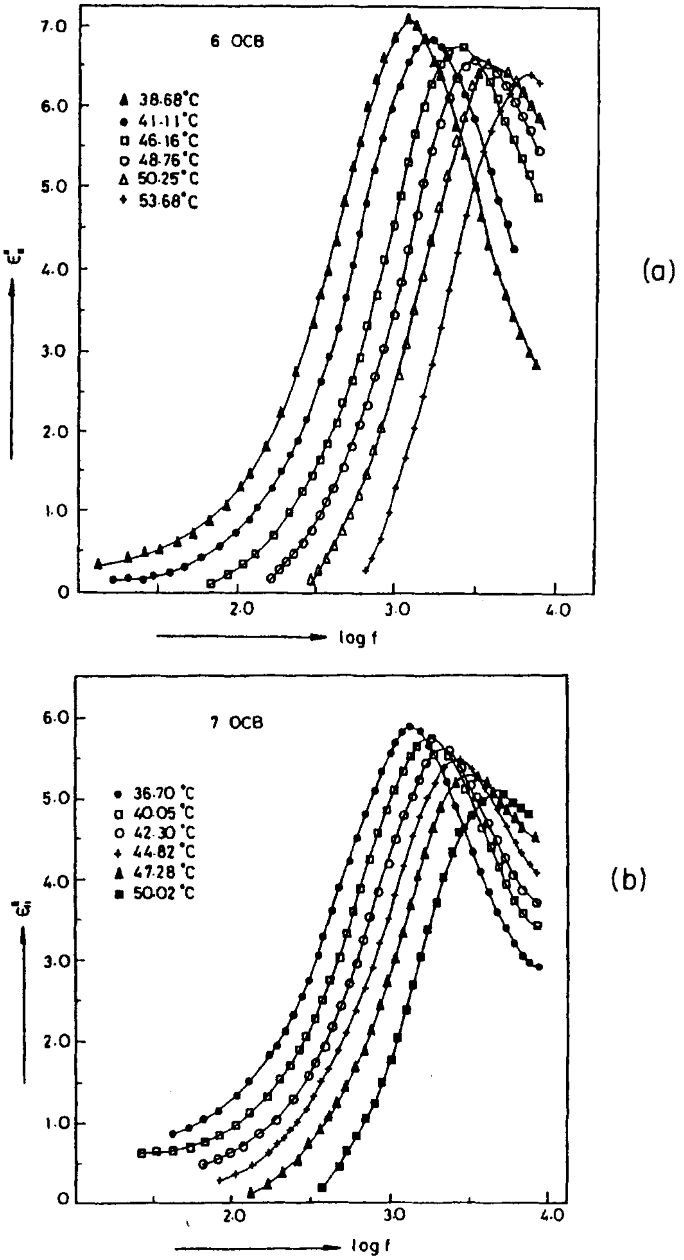

Figure 1(a,b). The representative loss curves at different temperatures in the nematic phases of (a) 6 OCB and (b) 7 OCB .

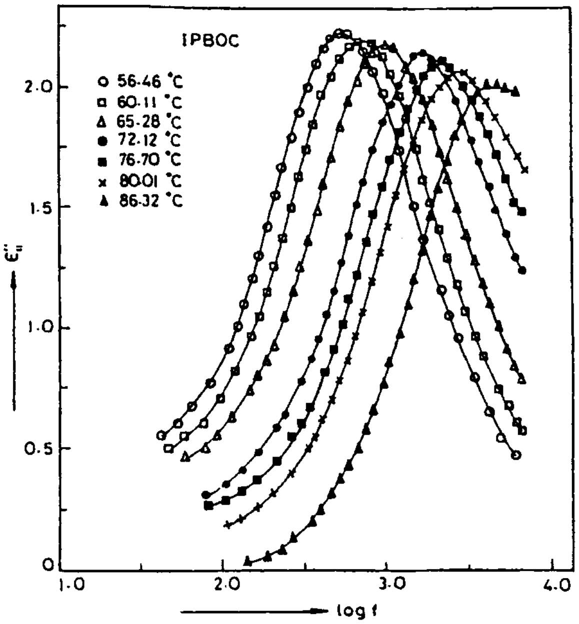

Figure 1(c) The representative loss curves at different temperatures in the nematic phase of IPBOC.

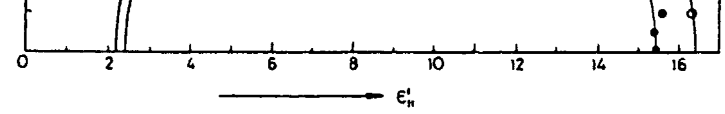

Figure 2(a) Cole-Cole plots in the nematic phase of 6 OCB.

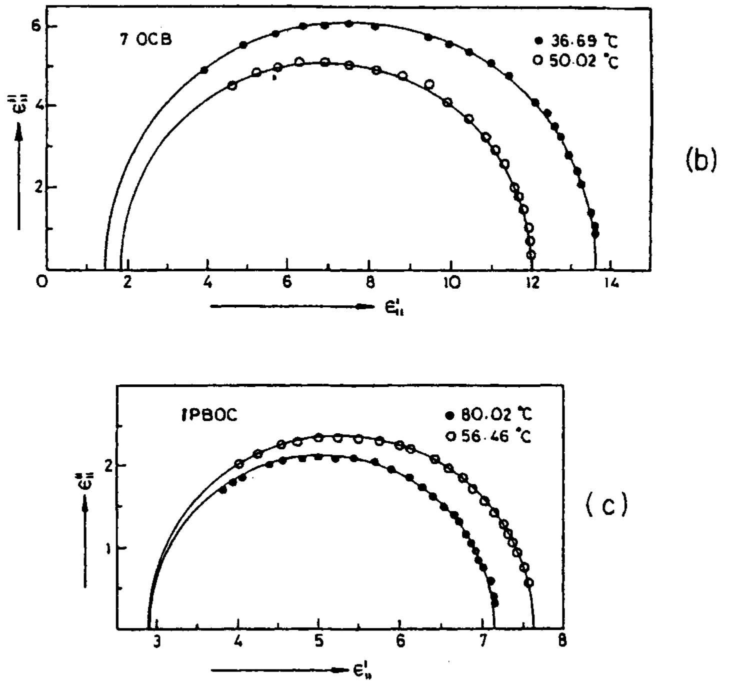

Figure 2(b,c) Cole-Cole plots in the nematic phase of (b) 7 OCB and (c) IPBOC.

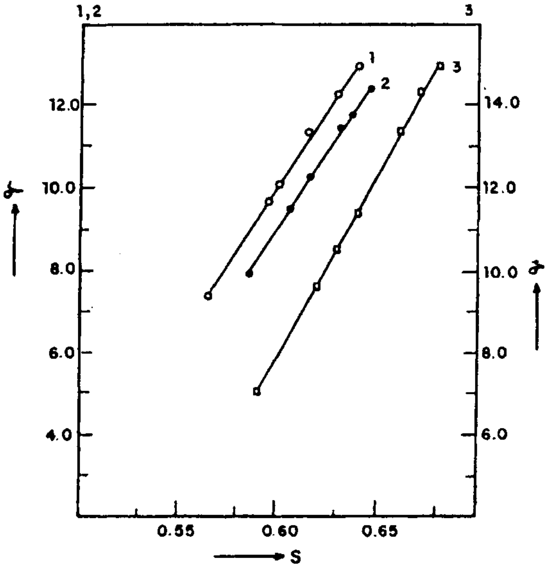

Figure 3. Plot of nematic potential q(in kJmol^{-1}) versus orientational order parameter S in the cases of (i) 6 OCB , (ii) 7 OCB and (iii) IPBOC.

compounds. It may be noted from Table 1 that the activation energy is more in all the compounds. This is due to fact that the effective parallel component of corresponding dipole moment along the length of the molecule is larger.

Using the f_R data estimated from Figures 1 and 2 and the formula derived by Meier and Saupe [15] for retardation factor g ie.,

$$g = \frac{\tau_R}{\tau_0} = \frac{k_B T}{q}[exp(\frac{q}{k_B T}) - 1] \qquad (1).$$

we have also calculated the nematic potential[16] q using a minimization programme as a function of temperature at atmospheric pressure. The normal Debye relaxation time τ_0 has been estimated by extrapolation of τ_R to the lowest nematic phase. It is found that the variation of nematic potential q with temperature follows a trend which is similar to the orientational order parameter S. It has also been noticed by earlier investigators [17] that $q = k_o S$, where k_o is a proportionality constant. According to this relation a plot of q versus S should exhibit a straight line with a slope equal to k_o. This result has been verified (see Figure 3) in all the three compounds using the estimated values of nematic potential q and the orientational order parameter [18]. Table 1 gives the values of k_o estimated for all the compounds from the slopes of the straight lines shown in Figure 3 . The value of k_o reported for 6 CB[16] is also shown in Table 1 for comparison. These studies clearly indicate that the dipole-dipole correlations in the nematic phase essentially determine the behaviour of dielectric constant with frequency and temperature. Only pressure can affect such types of interactions [19].

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