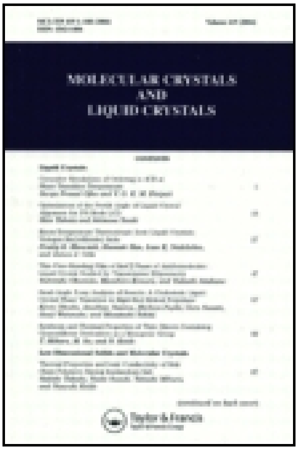

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Study of Dielectric Anisotropy of an Ester/Biphenyl Mixture Exhibiting an Induced Smectic Phase

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In this paper we present dielectric investigations of the binary mixtures of 4-n-pentyl 4′cyanobiphenyl (5CB) and 4-n-pentyl 4-n′ hexyloxy benzoate (ME6O.5) at different compositions which show an induced smectic phase. Physical properties from different experimental observations have been reported earlier. We have undertaken this study to have information relating the macroscopic anisotropy and the molecular properties. Mixtures with different mole fractions of ME6O.5 were prepared and their transition temperatures were observed under polarising microscope. $\Delta\varepsilon$ was measured using a digital LCR bridge at 10 kHz. A cell was constituted by means of two plane parallel tin oxide coated conducting glass plates separated by thin glass spacer. Sample was aligned by external magnetic field. $\Delta\varepsilon$ for smectic phase is found to be less than nematic phase. Results in detail will be discussed.

Keywords: binary mixture; induced smectic phase; dielectric anisotropy

INTRODUCTION

In many binary systems consisting of nematic compounds smectic phase induction is observed although the components do not possess smectic properties[1-6]. The specific solute-solvent interactions are responsible for the formation of induced smectic phases.

In this paper we present the dielectric permittivity investigation of the binary mixtures of 4-n-pentyl 4′cyanobiphenyl (5CB) and 4-n-pentyl 4-n′ hexyloxy benzoate (ME6O.5) at different compositions. The mixture shows smectic A_d phase in certain composition range. To understand the formation of the induced smectic phases and their influence on the adjacent nematic phase, study of the physical properties of this mixture had been undertaken by different workers in our laboratory. Small angle x-ray diffraction study, measurement of density and optical birefringence have been performed by Das and Paul[5,6]. The ratio of bend and splay elastic constants had been determine by Adhikari and Paul[7], magnetic susceptibility anisotropy by Pradhan and Paul[8]. The dielectric method is a powerful tool for studying the properties of mesophases. Static field measurements give information about the dielectric anisotropy which strongly depend on dipole organisation and dipole-dipole interactions in this phase.

Experimental

Both the components 5CB and ME6O.5 were gifted by E. Merck, U.K. The transition temperatures of the pure compounds are

5CB .... Cr 22.5 N 35.3 I
ME6O.5........ Cr 49.5 N 62.2 I.

Eight mixtures (1–8) with mole fractions of ME6O.5 equal to 0.2925, 0.3573, 0.4403, 0.5014, 0.5992, 0.6975, 0.7512 and 0.8155 were prepared by weighing the components and mixing thoroughly in their isotropic state. Phase transition of the components as well as their mixtures were studied by observing textures under crossed polarisers. Phase diagram is presented in Figure 1.

Dielectric permittivity and $\Delta\varepsilon$ was measured by a digital LCR bridge at 10 kHz. A cell was constructed by means of two plane parallel tin oxide coated conducting glass plates (thickness 7000 Å, conductivity 10.5-11.1Ω/□) separated by glass spacer. These conducting glass plates were given to us as gifts by Dr Murray Bennet, Solarix Thin Film Division, USA. The cell was put in a thermostated block fabricated by us whose temperature was controlled to ± 0.2 K. The complete assembly was placed between the pole pieces of an electromagnet. Sample capacitance parallel and perpendicular to the magnetic field was measured at different temperatures both during heating and cooling. The cell was pre calibrated by measuring the capacitance of standard dielectric liquids. The principal dielectric permittivity $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ were also measured for 7CB at different temperatures as shown in Figure 2 for the standardisation of the apparatus. These values agreed within 4% of the values given in references[9-11].

Results and Discussions:

The principal dielectric permittivities for the pure compounds 5CB and ME6O.5 are determined as a function of temperature. These are presented in Figure 3a and 3b. Our values of $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ for 5CB are consistent with

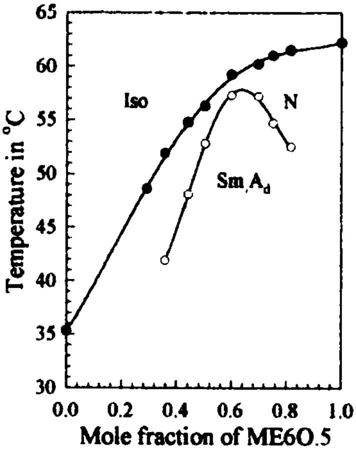


FIGURE 1 Phase diagram of binary Mixtures (ME6O.5 + 5CB)

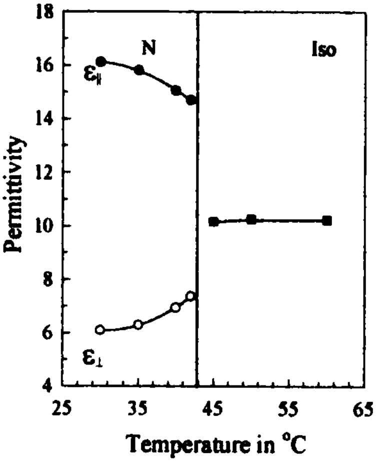
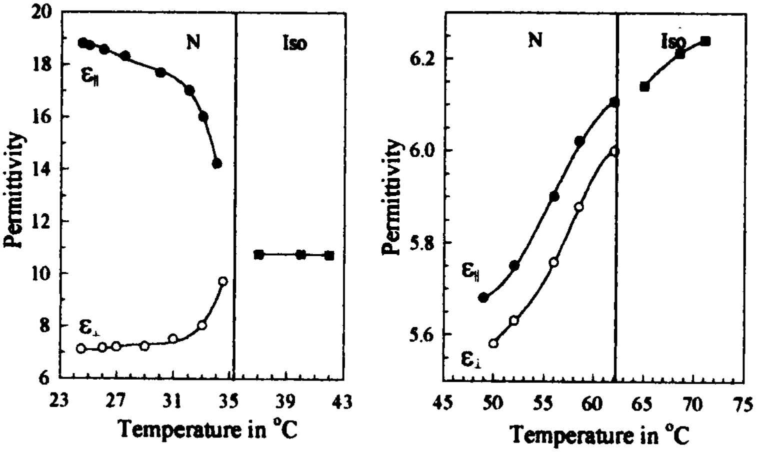


FIGURE 2 Variation of permittivity with temperature of 7CB



(a) (b)

FIGURE 3 Variation of permittivity with temperature (a) 5CB and (b) ME6O.5

other published results[4,9,11]. For ME6O.5 density and refractive indices have been determined by Ibrahim[12], Adamski[13] and Das[5], magnetic susceptibility, elastic constants by Pradhan[8], but dielectric permittivity has not been determined so far.

For the polar compound 5CB the dielectric anisotropy ($\Delta\varepsilon$) is large due to the highly polar end group which lies along the director axis. For the non-polar compound ME6O.5 $\Delta\varepsilon$ is very small. ε_{iso} and $\bar{\varepsilon}$ almost coincide at T_{NI}. These facts are in conformity with the predictions by Madhusudana and Chandrasekhar[14]. Of the eight mixtures only the Mixtures-1 has nematic phase, all others have both nematic and induced smectic A_d phase. The measured permittivity components $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are plotted against temperature for different molar concentration of ME6O.5. These are presented in Figure 4 and 5. In the Mixture-1 $\Delta\varepsilon$ is very large as expected from the simple rule of mixtures. In all other mixtures we find a significant jump in the parallel permittivity components at the smectic-nematic (Sm-N) transitions. This is due to the increased antiparallel dipole-dipole correlation in the layered structure that does not effect $\varepsilon_{\perp}$ significantly. Similar effects have been observed[4] in mixtures of 5CB and ME5O.5. The change of $\varepsilon_{\perp}$ at the Sm-N transition is continuous at the lower and higher concentrations and is discontinuous in between. However opposite behaviour was observed[5,6] in case of order parameters. This is due to the fact that packing[6] in the nearly equimolar mixtures consisting of monomers and dimers is rather loose and thereby decreasing the dimeric effect. Monomeric effect is now more prominent and hence the increase in $\varepsilon_{\perp}$.

We have plotted $\Delta\varepsilon$ as a function of concentration corresponding to a reduced temperature $T_R = (T/\ T_{NI}) = 0.99$ in Figure 6. Since $T_R = 0.99$ for Mixtures-4, 5 and 6 is in the Sm A_d phase we have also shown data for $T_R = 0.995$ for these mixtures.

We have calculated the anisotropy $\Delta\varepsilon$ for the mixtures using the additive rule

$$\Delta\varepsilon_{12} = y_1(\Delta\varepsilon_1)\left(\frac{S_{expt}}{S_{cal}}\right)_1 + y_2(\Delta\varepsilon_2)\left(\frac{S_{expt}}{S_{cal}}\right)_2$$

where $\Delta\varepsilon_{12}$ is the dielectric anisotropy of the mixture, y_1, y_2 are the volume-fractions of the components, S_1 and S_2 are the order parameters of the pure components at the same reduced temperature. The calculated result for the dielectric anisotropy is in fair agreement with the experiment in the nematic phase. In the induced smectic region there are additional contributions to $\Delta\varepsilon$ which are not considered in the theoretical calculations.

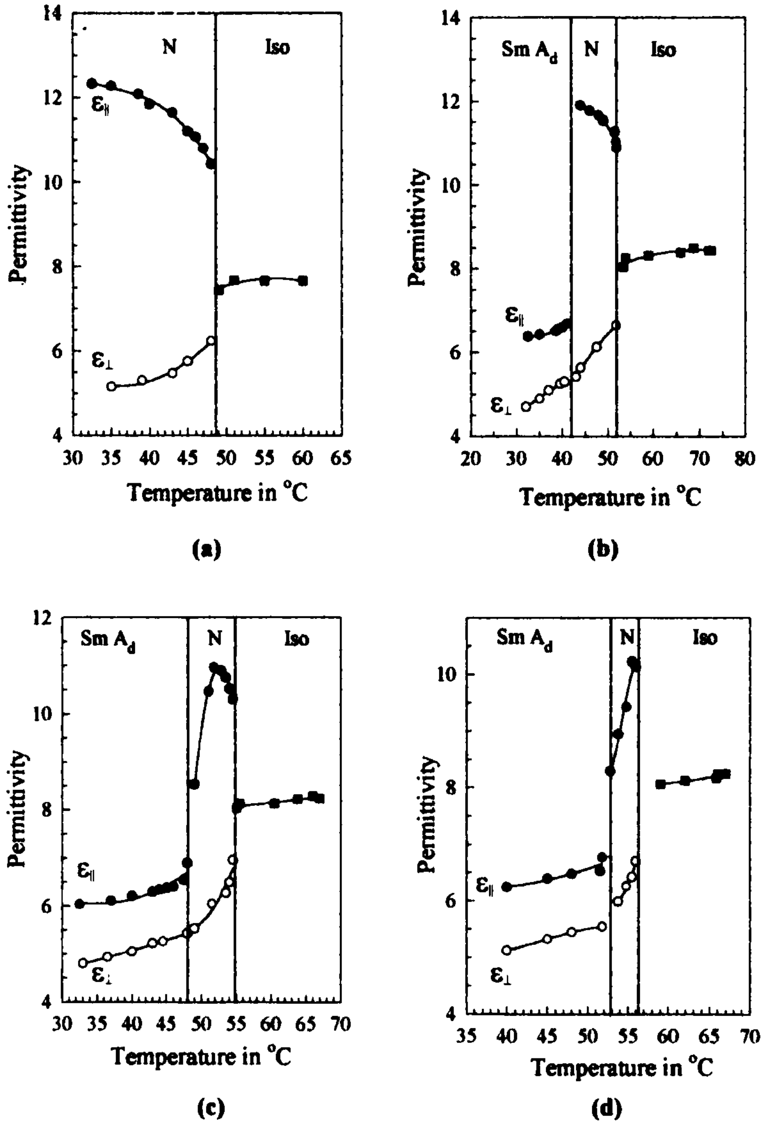
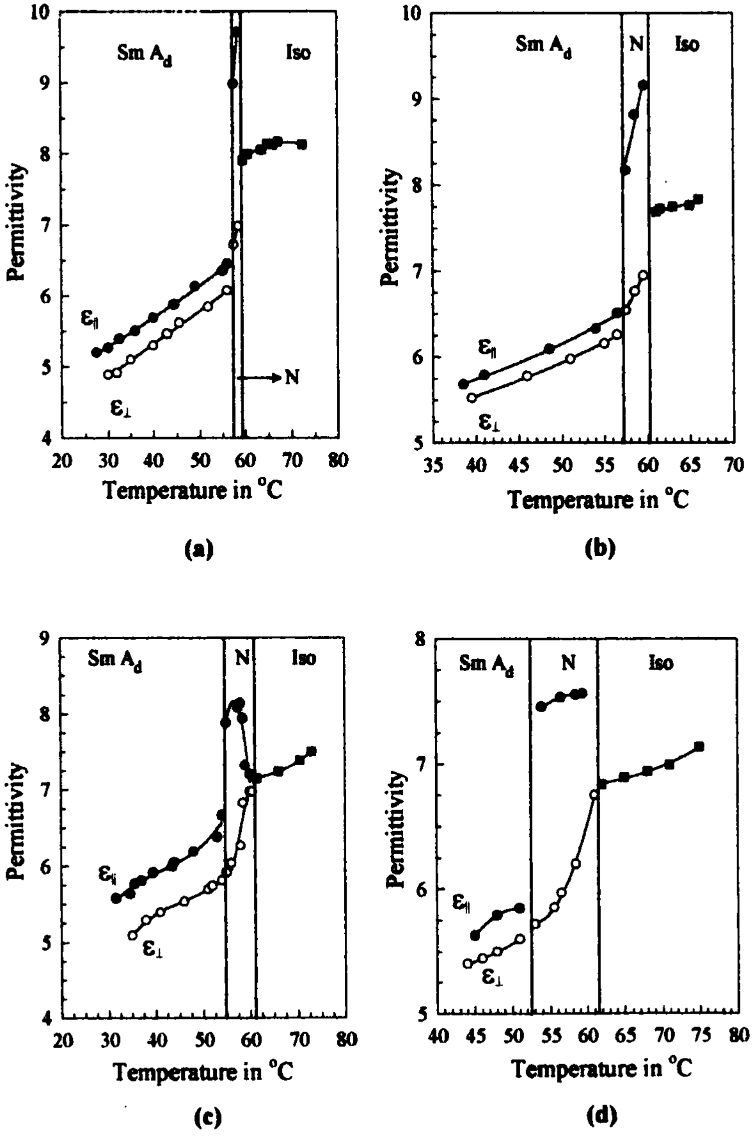


FIGURE 4 Variation of permittivity with temperature (a) Mixture-1, (b) Mixture-2, (c) Mixture-3 and (d) Mixture-4



(a) (b) (c) (d)

FIGURE 5 Variation of permittivity with temperature (a) Mixture-5, (b) Mixture-6, (c) Mixture-7 and (d) Mixture-8

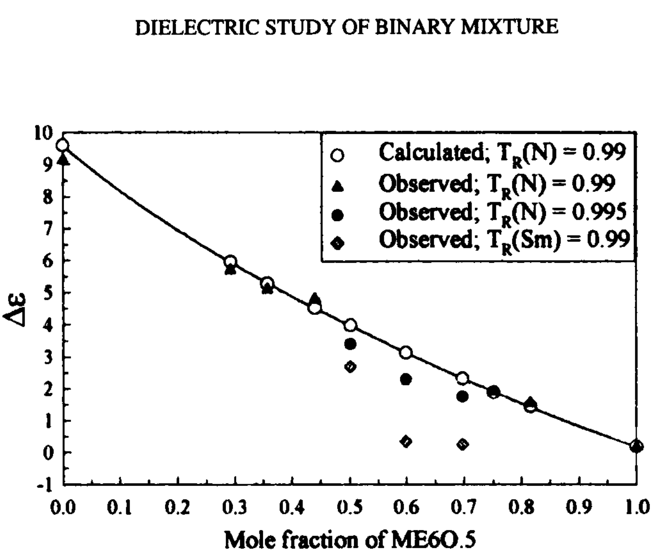


FIGURE 6 Variation of permittivity anisotropy with mole fraction of ME6O.5

$\Delta\varepsilon$ shows a minimum around $x = 0.6$. Similar results have been reported earlier[4]. This minimum has been observed for packing fractions, layer spacings, $\langle P_2 \rangle$ from x-ray study and susceptibility measurements. At this composition stability of the Sm A_d phase is maximum. In our study of other binary mixtures having induced Sm A_d phase, layer spacings show maxima rather than a minima[15] at the composition of maximum stability.

We thus find that the degree of stabilisation of Sm A_d phase plays a major role in determining the physical properties of the binary mixtures. The minimum values are observed probably for those concentration for which monomer concentration is large, maximum occurs when dimer concentration exceeds monomer.

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