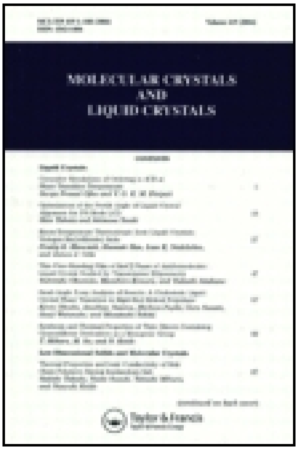

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Dielectric Studies of Highly Polar Nematic Liquid Crystals and Their Mixtures

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Dielectric Studies of Highly Polar Nematic Liquid Crystals and Their Mixtures

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The dielectric properties of the nematic liquid crystal, 4-4′-*n*-pentylcyanobiphenyl (K15), and three binary mixtures of K15 with 4-[4′-alkylcyclohexyl]cyanophenyl homologs have been studied. The parallel, perpendicular and isotropic dielectric constants are given as a function of temperature. All measurements were made at 1 KHz. Values of $\epsilon_\perp$ and $\epsilon_\parallel$ are typically in the range of 7 ± 1 and 17 ± 2, respectively. Temperature ranges from 10°C to T_{NI} + 5°C were explored. The dielectric anisotropy versus $T-T_{NI}$ is also given. $14 > \Delta\epsilon > 7$ for pure K15 and all three mixtures when $T-T_{NI} < -1°C$. This large dielectric anisotropy is due to the highly polar cyano end group, which has a dipole moment of 4.05 D, and lies along the nematic director for each of these compounds.

INTRODUCTION

The use of nematic liquid crystals in flat-panel displays is common-place.[1] The speed at which such display panels can be addressed depends on specific material and design parameters. The single most important parameter governing the electro-optic effect of the nematic fluid is its dielectric anisotropy. The magnitude of this value influences the speed of the optical transition, whereas, the sign governs the cell geometry needed to achieve the desired effect. Thus, previous researchers have sought to measure and understand the dielectric properties of nematic phases.[2–4]

The elastic constants are also of fundamental importance in understanding electro-optical effects of liquid crystals. These constants help determine the decay time for a given display cell.[5] The decay time is defined as the time it takes for the contrast of an addressed element to fall off to 10% of its initial value, after the driving voltage is turned off. Along with the elastic constants, the cell dimensions, e.g. the thickness, also play a role in determining the decay time.[5]

Recently, we have demonstrated[6] an interesting optical effect for a pure, room-temperature nematic, 4-4′-*n*-pentylcyanobiphenyl (K15). This study revealed a reproducible, wavelike interface could be generated when certain external conditions of temperature, frequency and voltage were met. To understand the importance of the material properties of the nematic on this phenomenon, the physical properties of K15 were systematically modified by mixing it with a second nematic compound.

The phase studies of the three binary mixtures used here have been given elsewhere.[7] In this paper, we focus our attention on the dielectric properties of these mixtures.

EXPERIMENTAL

Three nematic homologs were chosen for study on the basis of their near room-temperature clearing points and their range of dielectric anisotropy. The homologs are the *n*-ethyl (S1236), *n*-butyl (S1188) and *n*-heptyl (S1115) members of the 4-[4-alkylcyclohexyl]cyanophenyl series. Binary mixtures of these compounds with 4-4′-*n*-pentylcyanobiphenyl (K15) have been prepared elsewhere and their phase diagrams are published.[7] Based on that work, the eutectic mixture of each system was selected for further characterization. Table I gives the eutectic composition of each mixture. Both experimental and theoretical values are tabulated. The Schröder van-Laar (S-vL) theory was used. Thermal transition data for these mixtures and for pure K15 are also given in this Table.

The dielectric properties were calculated from capacitance measurements taken at 1 KHz with a Gen Rad-1689 DigiBridge reading to an accuracy of 0.1%. This frequency was chosen because it obviates low-frequency conduction and is the conventional frequency used when reporting dielectric properties of nematics. The dielectric cells were constructed from two indium oxide coated glass plates spaced between 12 and 70 microns by Mylar or Teflon windows. Freshly distilled toluene and standard LC mixtures were used for calibration. The values obtained agreed within 4% of the standard values. The active window area measured 380 mm^2 and was surrounded by a guard ring to eliminate fringe fields. Measurements were made in an inert nitrogen atmosphere. Electrical resistivities were of the order of

TABLE I

Composition and thermal properties of the eutectic mixture for 3 binary systems as compared to pure K15.

	Eutectic Composition		Property of Eutectic Mixture		
	(Mole % K15)				
Binary System	EXPT	S-vL	T_{KN} (°C)	T_{NI} (°C)	Range (°C)
K15	--	--	22.3	35.1	12.8
K15/S1236	62	66	5.8	21.6	15.8
K15/S1188	60	66	5.8	32.5	26.7
K15/S1115	40<x<80	63	---	41.5	>41.5

10^9–10^{10} ohm-cm. Uniaxial rubbing generated uniform, planar alignment[8] of the nematic. This is deduced by observing four-fold extinction of the sample when it is rotated through 360° in polarized-light microscopy.

The perpendicular component, $\epsilon_\perp$, of the dielectric constant was calculated from capacitance measurements made using a 500 mV driving voltage. This was below the threshold voltage, V_c, of all the mixtures. Thus, molecular orientation is controlled solely by the substrate surfaces. Voltage controlled orientation was produced by increasing the test voltage above V_c. The maximum 1.275 driving voltage of the bridge was increased to 12.75V by a 10:1 operational amplifier inserted on the high side of the signal. Consequently, a voltage divider was inserted between the test cell and the bridge on the low side of the loop. The temperature was regulated to within 1°C by a Neslab circulating water bath. Thermocouples mounted above and below the test cell were used to monitor thermal equilibrium.

The relative variation of $C_\parallel$ and $C_\perp$ were measured within $\pm 0.5\%$. The absolute accuracy in capacitance measurements is believed to be $\pm 4\%$.

RESULTS AND DISCUSSION

The principal dielectric constants of (i) pure K15 and (ii) three binary mixtures of K15 with a second nematic are plotted as a function of temperature in Figures 1–4. The average value of the dielectric constant, $\bar{\epsilon} = ([\epsilon_\parallel + 2\epsilon_\perp]/3)$, is calculated from the measured values of $\epsilon_\parallel$ and $\epsilon_\perp$ in the nematic phase and is also shown in the Figures (solid line). For direct comparison, the dielectric constant of the isotropic phase, ϵ_{is}, has been extrapolated into the nematic phase (broken line).

Our values of $\epsilon_\parallel$ and $\epsilon_\perp$ for K15 are consistently 4 to 7% higher than those of Ratna and Shashidar.[9] This difference is likely due to some systematic experimental error between the two sets of measurement. From Figures 1–4 it can be seen that the dielectric constant along the nematic director ($\epsilon_\parallel$) is about twice that in the transverse direction ($\epsilon_\perp$). This large dielectric anisotropy is due to the highly polar cyano end-group which lies in the director axis. The dipole moment of this moiety, as given by Minkin *et al.*, [10] is 4.05 D. We also note that $\bar{\epsilon}$ in the nematic phase is always less than the extrapolated value of ϵ_{is} (with the single exception of the K15/S1188 mixture). Similar results have been observed by others in the case of highly polar compounds.[9,11] (This is in contrast to the behavior of non-polar molecules wherein it has been experimentally observed that $\bar{\epsilon}$ and ϵ_{is} coincide at T_{NI}[12]). Also, it is seen that $\bar{\epsilon}$ decreases with decrease of temperature. These facts are in conformity with the predictions of the statistical model of antiferroelectric short range order in nematic liquid crystals composed of polar molecules proposed by Madhusudana and Chandrasekhar.[13–14] According to this theory $\bar{\epsilon}$ should increase on going over from the nematic to the isotropic phase due to a decrease in the antiparallel correlation at the transition.

The dielectric anisotropy $\Delta\epsilon$ is plotted as a function of the sub-clearing temperature, defined as $T-T_{NI}$, for the four nematic systems in Figure 5. One pure component nematic and three binary nematic mixtures are represented. For all four fluids, the dielectric anisotropy decreases monotonically as $T-T_{NI}$ approaches

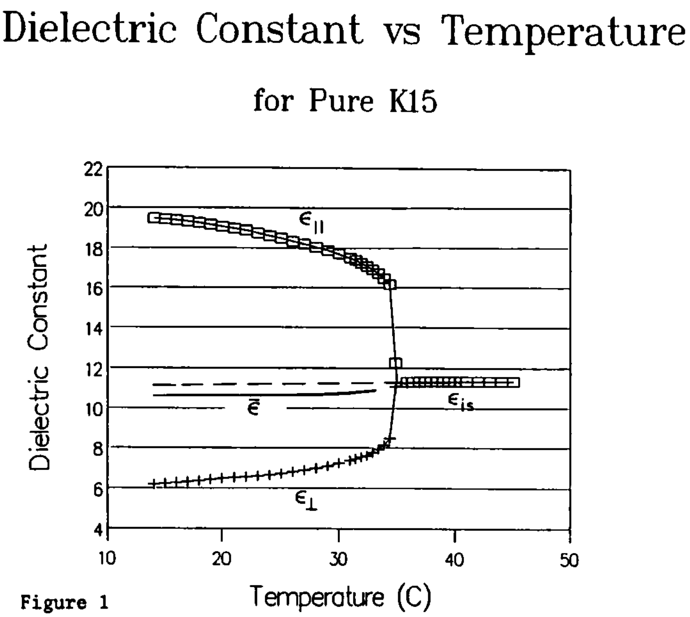


Figure 1

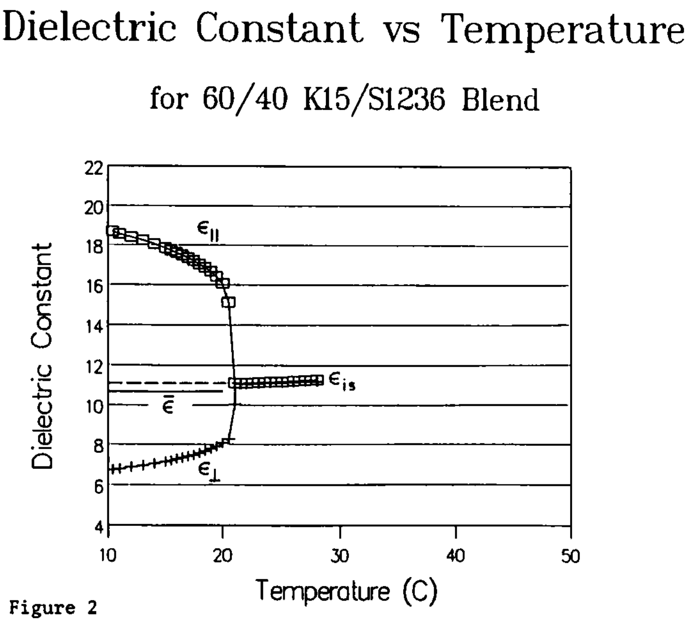
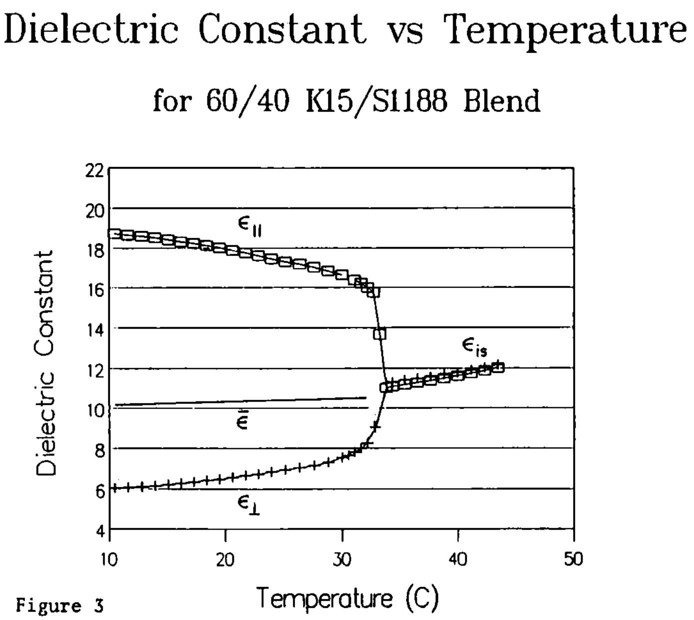


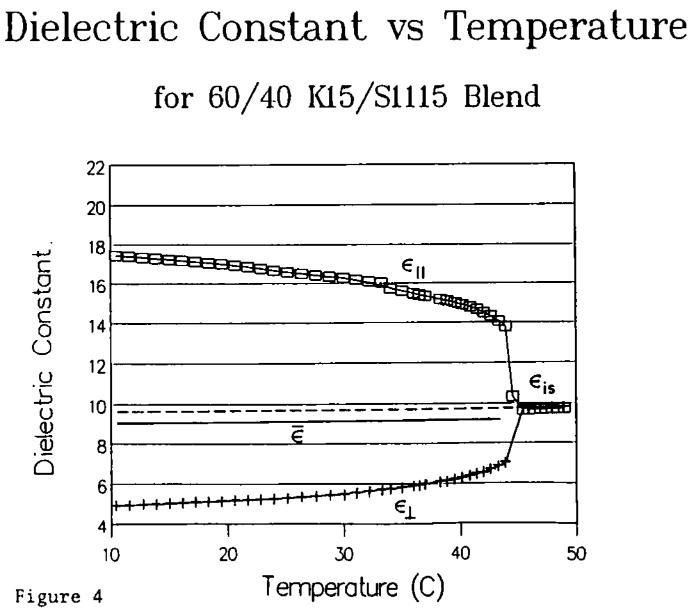
Figure 2



Dielectric Constant vs Temperature

for 60/40 K15/S1188 Blend

Figure 3



Dielectric Constant vs Temperature

for 60/40 K15/S1115 Blend

Figure 4

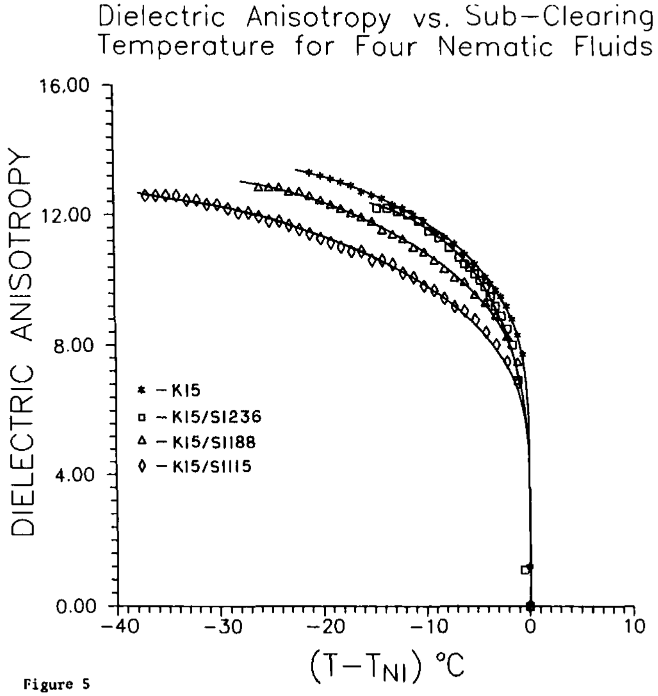


Figure 5

0. Pure K15 has the highest $\Delta\epsilon$ at all equivalent sub-clearing temperatures. This result was unexpected. A simple rule of mixtures states that $\Delta\epsilon$ of a binary mixture will equal the linear weighted average of the two pure components.[15] From Table II, we can see that $\Delta\epsilon$ of S1236 is higher than that of K15. Thus, the dielectric anisotropy of any K15/S1236 mixture would be expected to be higher than that of pure K15. However, as seen in Figure 5, the 60/40 mole percent mixture has a lower dielectric anisotropy at all equivalent temperatures.

TABLE II

Dielectric anisotropy for four pure nematic liquid crystals; [a]our measurements at 26°C, [b]EM Catalog value (temperature not specified).

Pure Nematic	Dielectric Anisotropy
K15	11.5[a]
S1236	13.7[b]
S1188	11.2[b]
S1115	8.2[b]

Table II also shows that the dielectric anisotropy of the 4-[4′-alkylcyclohexyl]-cyanophenyl homologs decreases as the length of the alkyl tail increases. Reconsidering Figure 5, we finally note that the mixtures of K15 with members of this homologous series also demonstrate a similar trend in dielectric anisotropy, i.e. $\Delta\epsilon$ of K15/S1236 > K15/S1188 > K15/S1115 for 60/40 mole percent blends.

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