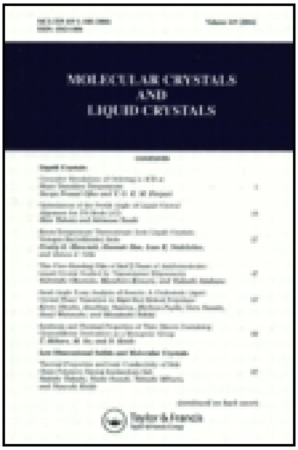

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Dielectric Properties of a Nematic Binary Mixture

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DIELECTRIC PROPERTIES OF A NEMATIC BINARY MIXTURE

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In this paper, a phase diagram is developed for the molar mixtures of nematic liquid crystals of 5CB and MBBA. In order to understand the interaction of the two systems, dielectric permittivities $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ were measured for mixtures of various concentrations. The usual assumption is that in the absence of chemical reactions the bulk physical properties add up as a weighted sum of the individual properties. Our dielectric permittivity data clearly show a correlation to the phase diagram and the existence of the induced phase. In order to understand the interactions from a fundamental level, we modeled the 5CB and MBBA molecules using a Silicon Graphics O2 workstation running the software Spartan 5.1. Different electrical surfaces were calculated for a geometrically optimized molecule. Our investigations support the idea of strong charge interactions between the nematic systems.

Keywords: binary nematic mixtures; dielectric permittivity; molar mixtures; molecular modeling; phase diagram

INTRODUCTION

Our aim was to study the dielectric properties of mixtures of nematic liquid crystals with dissimilar dielectric anisotropies but similar phase properties. Using light scattering and microscopy, we have established the phase boundaries and transition widths of mixtures of 4′-n-pentyl-4-cyanobiphenyl (5CB) and 4′-methoxybenzylidene-4-butylaniline (MBBA) [1]. In addition to the isotropic-nematic transition, there is a second induced phase for certain concentrations, which we concluded to be an induced smectic B phase. Recent theoretical works [2] provide a model for nematic to induced smectic A transition by combining Flory–Huggins and Maier–Saupe–McMillan theories. From our phase transition data and

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the application of the above theoretical framework, we concluded [1] that there is a possibility of strong interaction between the two mesogens that produces the smectic B phase.

Each of the two materials used in this project has been the subject of a large number of investigations. Their physical properties such as dielectric permittivities, elastic constants and birefringence have been well documented. Yet, there has been very little work reported on their mixtures prior to our work except for the brief report by Parks, Bak and Labes [3].

EXPERIMENT AND DATA

A. Phase Diagram

Binary mixtures of 5CB and MBBA were prepared in various molar ratios, as shown in Table 1. These were then filled in prefabricated cells purchased form EHC, Japan. The two types of cells used in our project had planar and homeotropic alignment layers respectively and the cells were manufactured at $50 \pm 5\,\mu m$ in thickness. The glass plates were coated with ITO so that when leads were attached electrical properties of the mixtures could be investigated. In order to reduce the uncertainty in the thickness of the cell, we measured it independently using an Ocean Optics CHEM2000 spectrometer. There were two parts to the experimental measurements. First the nematic-isotropic (NI) phase transition temperatures were determined for each mixture using video microscopy observations. The experimental details are similar to those described in Reference [1]. Video images

TABLE 1 Sample Concentrations of 5CB and MBBA. The Isotropic-Nematic Transition Temperatures (°C) Measured on the Planar Cells by Video Microscopy are Shown. T_1 is the onset and T_2 is the Completion of Transition

% 5CB (weight)	MBBA:Molar ratio	Transition (T_1)	Transition (T_2)	Smectic B
0	–	32.66	28.96	NA
18.91	4:1	41.944	40.894	NA
23.72	3:1	45.39	44.39	25.965
31.8	2:1	50.95	50.425	35.7
38.34	3:2	51.026	51.551	38.301
48.54	1:1	51.268	50.643	36.293
58.31	2:3	47.803	47.178	27.003
65.1	1:2	43.834	43.334	NA
73.67	1:3	39.302	37.977	NA
78.86	1:4	40.192	39.467	NA
100	–	34.255	33.88	NA

collected by Javelin CCD camera mounted on the microscope were digitized using Miromotion DC30 digitizer board on a Macintosh G4. An INSTEC HS1-RTC1 temperature controlled stage was used for this part of the experiment. Our microscope data were collected on cooling the mixtures from the isotropic phase at a rate of 0.025°C/min and show the phase transitions as well as the width of transitions for all of the compositions. Temperatures T_1 were marked as those at which the nematic droplets appeared at the NI transition. A clear schlieren texture is visible as the isotropic material cools into the nematic phase and the droplets coalesce to form the bulk phase. The first appearance of droplets is indicated as the start of the isotropic-nematic mixed phase. The disappearance of the last of the isotropic phase indicates the onset of pure nematic phase and will be referred to as T_2. Similarly, the temperatures T_S corresponding to the start of the dendritic growth indicating the start of smectic B phase and

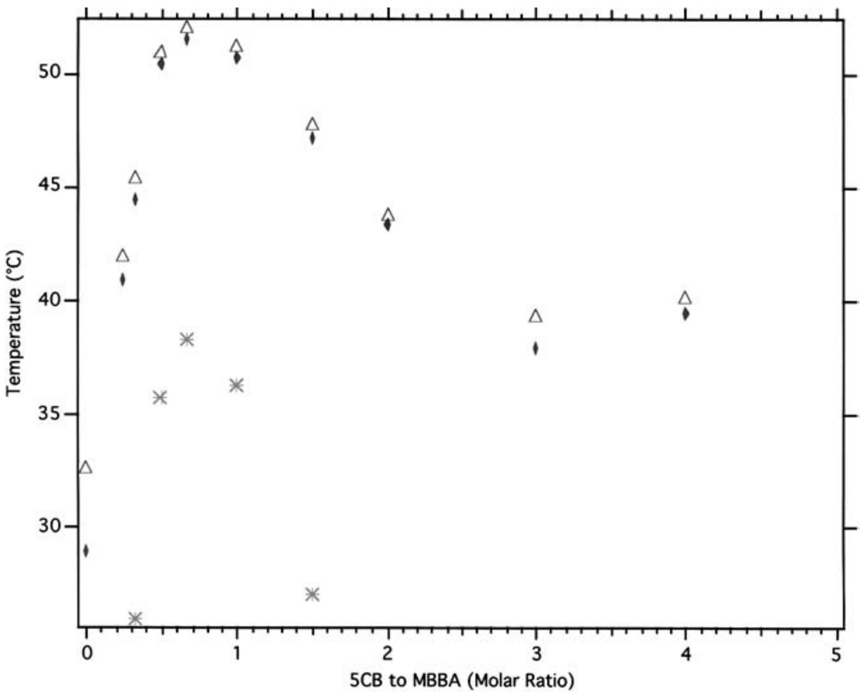

FIGURE 1 Phase transition data and coexistence regions as measured by microscopy. Open triangles are the onset of isotropic-nematic transition by appearance of nematic droplets; closed diamonds indicate the completion of the transition by the disappearance of isotropic phase. The stars indicate the start of smectic B phase due to the appearance of dendrites.

the disappearance of the nematic texture are monitored for the lower transition. Figure 1 show the phase diagram measured for our planar cells.

B. Dielectric Measurements

A simple inverting operational amplifier (TL 082) circuit was used to measure the dielectric properties of the mixtures. A function generator (Hewlett Packard model 33120 A) was set at 1000 Hz output and 1 Vpp for all the measurements. The waveform output of the generator was connected to the cell and the output was fed into the amplifier circuit as the input signal. The resulting output signal from the circuit was fed into channel 2 of the digitizing oscilloscope (Hewlett Packard 54510B) whereas channel 1 monitored the waveform generated by the function generator before it was fed into the cell. The block diagram of the apparatus is shown in Figure 2. Since the different mixtures had nematic phase at different temperatures, it was decided that the dielectric measurements will be made at a fixed temperature drop from the isotropic nematic transition of each

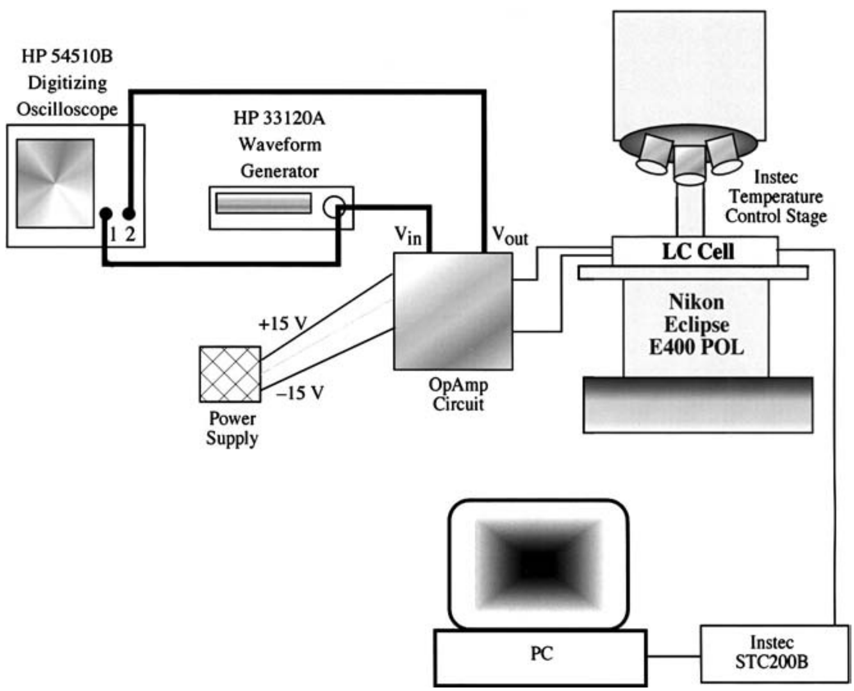

FIGURE 2 Experimental block diagram. The operational amplifier circuit is shown in Figure 3.

mixture. Since there is a width involved in these transitions, the cells were maintained at five degrees below T_2 while the measurements were made. For both sets of cells the phase transition temperatures were independently determined, as described earlier. The liquid crystal cell was modeled as a resistor and capacitor in parallel (see Fig. 3) which allowed us to determine the permittivity of a particular cell if C, the capacitance of the cell; h, cell thickness; and A, active area of the liquid crystal material (i.e. area of the ITO) were known. The area of the ITO was measured using a traveling microscope arrangement. The capacitance of each cell was determined by measuring the V_{in}, V_{out}, R_f (feed back resistor) and θ (the phase difference between V_{in}, and V_{out} signals).

$$C = \frac{V_{out} \tan\theta}{\sqrt{(1+\tan^2\theta)V_{in}R_f\omega}}$$

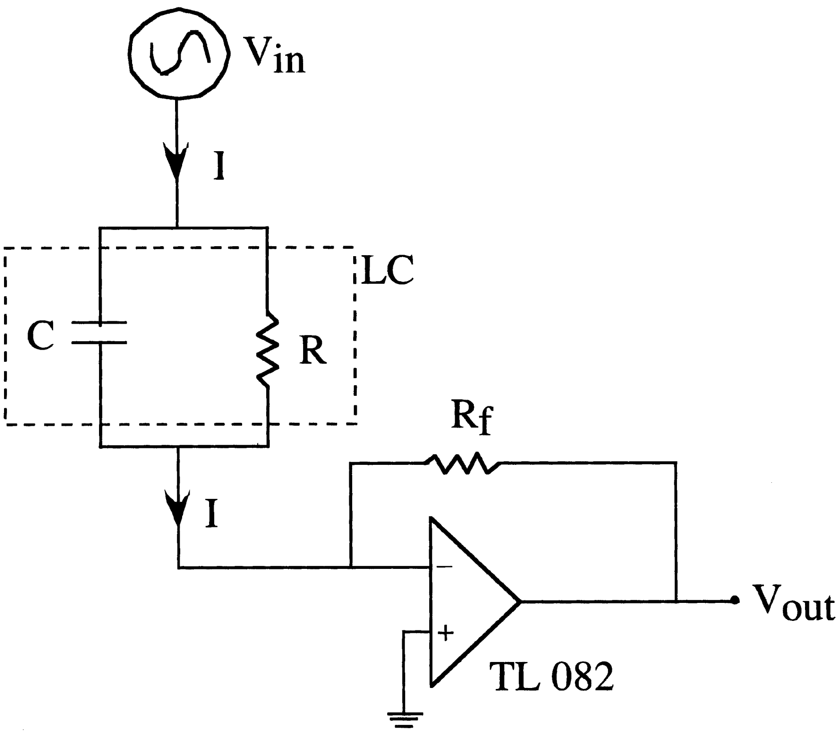

FIGURE 3 The operational amplifier circuit. LC: liquid crystal cell, modeled as a resistor and capacitor in parallel.

$$\varepsilon_{\parallel} = \frac{Ch}{\varepsilon_0 A}$$

where ω is the angular frequency of AC signal and ε_0 is permittivity of free space. If the cell was planar we were able to determine $\varepsilon_{\perp}$ and if the cell was homeotropic we were able to extract the $\varepsilon>_{\parallel}$. Our $\varepsilon_{\parallel}$ data will be reported in greater detail in a forthcoming publication [4]. Each cell was maintained at 5°C below its T_2 measured temperature while the electrical measurements were performed. Signal averaging was performed on the oscilloscope in order to optimize the signal to noise ratio. Typically, four sets of measurements were made on each cell and data collected were averaged in order to compute the mean electrical permittivity for the particular composition. The data for epsilon perpendicular are shown in Figure 4. We are in the process of completing the epsilon parallel measurements in order to compute the complete set of the anisotropy values (ε_a). While measuring ε care was taken not to apply high input voltages, since that would cause the cell to undergo Freedericksz transition. Due to the very high positive anisotropy of 5CB ($\varepsilon_a = 10.6$) [5] and comparatively small negative value of MBBA ($\varepsilon_a = -0.59$) [6], most of our mixtures had positive anisotropy of

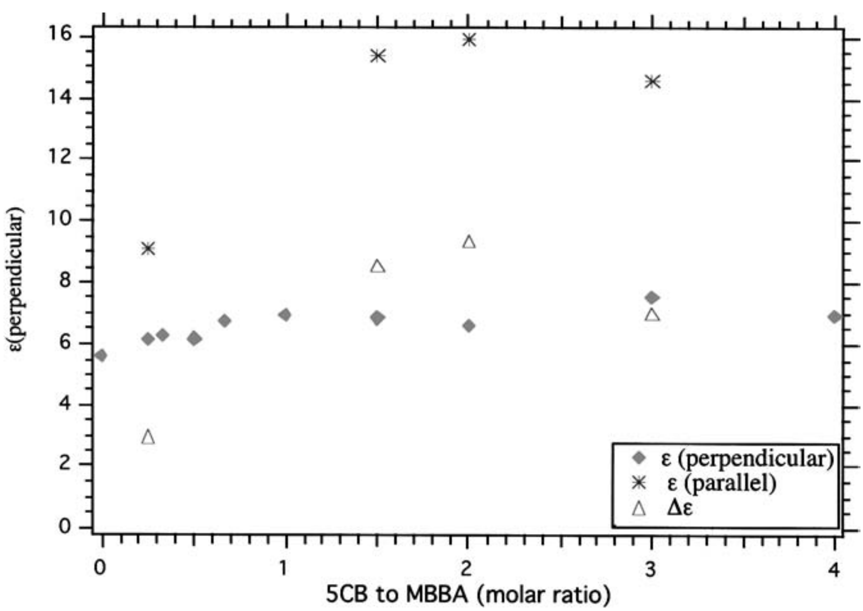

FIGURE 4 Epsilon values as a function of concentration of the mixtures by molar ratio.

dielectric permittivity until very high concentrations of MBBA were reached.

MOLECULAR MODELING

A Silicon Graphics O2 Workstation that ran Spartan 5.1 was used. The first runs consisted of modeling each of the molecules separately. MBBA and 5CB were built using Spartan's preprogrammed entry-level model kit. The theory used for the modeling was Hartree Fock, and a suitable calculation

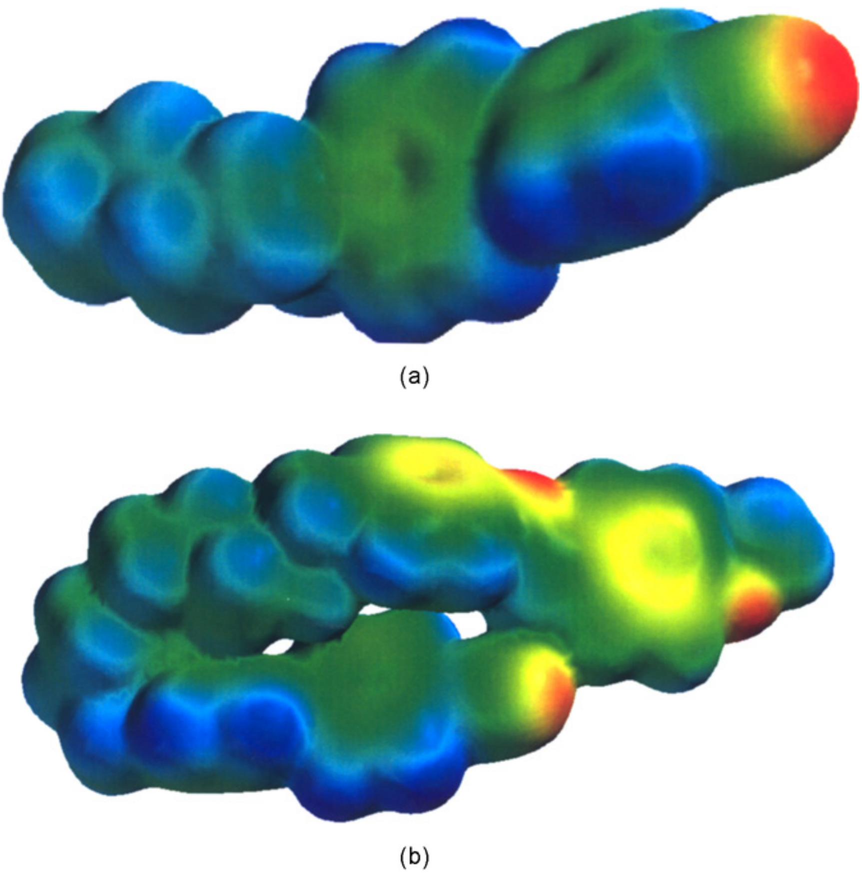

FIGURE 5 (a) The electricpotential surface of 5CB. Red indicates areas of higher negativity and the blue represents more positive areas. (b) The electricpotential surface of MBBA and 5CB tetherd together with a nine carbon chain forming a hybrid molecule. (See COLOR PLATE XIV)

set was chosen for looking at low energy conformations and the calculation of surfaces [7]. The electron density with the electric potential mapped on to the electron density was plotted. This gives a qualitative view of the charge density of the 5CB molecule so that the charge distribution can clearly be seen in Figure 5(a). The areas of red indicate areas of higher negativity and areas of blue indicate areas that are positive. The colors of the spectrum in-between show the charge density gradient. The current modeling did not permit the mixing of the two species to check how they associate. As a start, the two molecules were tethered with the carbon chains to see how the electric potential might distribute itself. This is shown in Figure 5(b).

CONCLUSIONS

From the coexistence diagram as well as the epsilon data, it is clear that there is interaction between 5CB and MBBA. The interaction is not strong enough to form an entirely new molecule, as is indicated by further modeling of the hybrid molecule using the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) surfaces. Interaction of the two species via the molecular orbitals will be reported in a future paper [4]. Earlier work by Park *et al.* [3] showed that for one to one molar mixtures of 5CB and MBBA the dielectric permittivity did not add up linearly. Our earlier work [1] showed that there was a strong cross interaction between the two species and the trend observed in our current measurements confirm these observations.

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