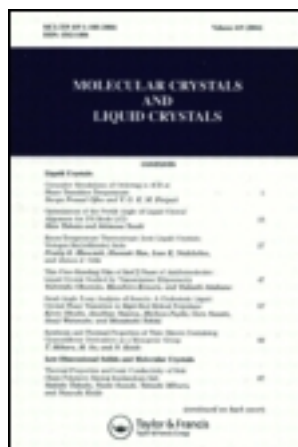


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A Direct Observation of the Switch-Over Transition in Mixed Liquid Crystals of Opposite Diamagnetic Anisotropies

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A DIRECT OBSERVATION OF THE SWITCH-OVER TRANSITION IN MIXED LIQUID CRYSTALS OF OPPOSITE DIAMAGNETIC ANISOTROPIES

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ABSTRACT. From deuteron NMR studies of pure mixed liquid crystals of opposite diamagnetic anisotropies, a direct observation of the switch-over transition is reported. At the critical concentration and temperature, two spectra corresponding to two different orientations are observed. No noticeable change in the optical properties was observed around the critical point. At the critical concentration, the higher temperature corresponds to the orientation similar to that for the system with positive diamagnetic anisotropy in all the cases investigated.

INTRODUCTION

A switch-over transition at a critical concentration and temperature in mixed liquid crystals of opposite diamagnetic anisotropies has been observed from the NMR spectra of probe molecules dissolved therein.^{1,2} At the critical point, the optic axis of the mixed liquid crystals rotates by 90° with respect to the applied magnetic field and the

spectra corresponding to both the orientations of the optic axis are observed. The results have been theoretically interpreted and are based upon the assumption that the dissolved molecules follow the orientation of the liquid crystal molecules.³⁻⁵ In the present communication, a direct observation of the switch-over transition is reported from the deutron NMR spectra of specifically deuterated liquid crystals without any probe molecule.

EXPERIMENTAL

Deutron NMR spectra of N-(p-methoxybenzylidene) p-n-butylaniline-d₂ (MBBA-d₂) (deuterated at positions meta with respect to the butyl group) studied with varying concentrations of ZLI-1167 (a ternary eutectic mixture of propyl, pentyl and heptyl bicyclohexyl carbonylnitrile) were recorded at a JEOL FX-100 spectrometer operating at 15.35 MHz for deuterons and using a conventional electromagnet. One hundred free induction decays were accumulated and Fourier transformed with the help of a 16K core memory computer. Both the proton coupled and proton decoupled spectra were recorded. Typical proton decoupled spectra of the solution with 0.3 : 1 weight ratio of MBBA-d₂ : ZLI-1167 at 23, 24 and 25°C are shown in figure 1. The spectra (Figure 1) were recorded without spinning the sample. Those (at 24°C with the sample spinning along the direction perpendicular to the magnetic field) are shown in Figure 2.

RESULTS AND DISCUSSION

In pure MBBA-d₂, the separation between the quadrupole split doublet at 22°C was 15.5 KHz. Each component of the doublet was essentially a broad doublet due to HD dipolar

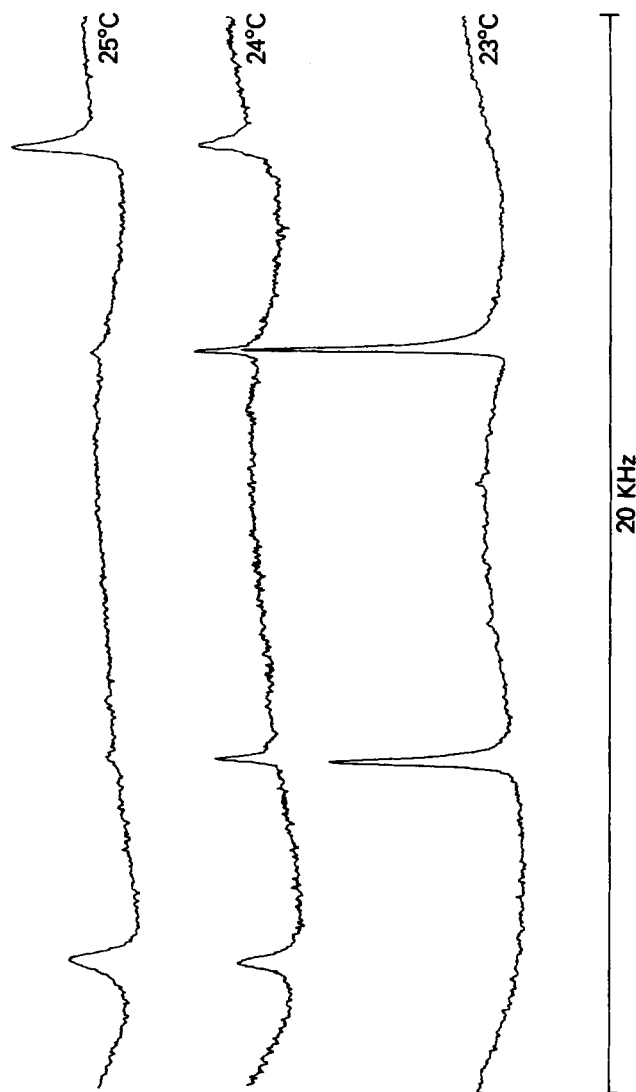


FIGURE 1. Proton decoupled deuterium NMR spectra of 0.3 : 1 weight ratio of MBBA- d_2 : ZLI-1167 at 23, 24 and 25°C.

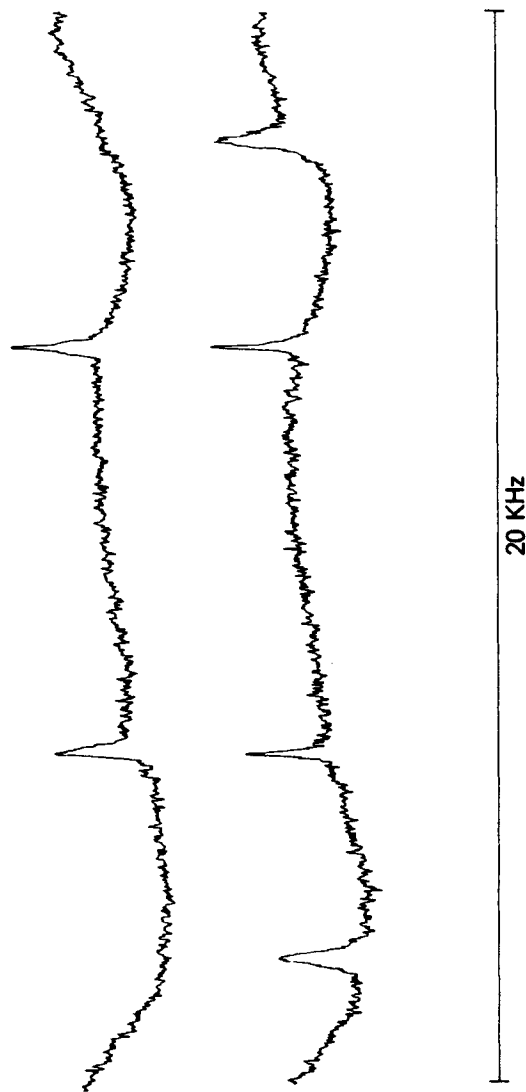


FIGURE 2: Proton decoupled deuteron NMR spectra of 0.3 : 1 weight ratio of MBBA-d₂ : ZLI-1167 at 24°C in a conventional electromagnet. Upper trace is with sample spinning and the lower one is without spinning of the sample.

coupling between the ortho deuterons and protons (separation = 1300 ± 100 Hz). Assuming the ortho HD distance as 2.48 \AA , this corresponds to the order parameter along the ortho HD axis as 0.54 ± 0.04 .

The splittings in the proton decoupled, deuteron spectra as a function of concentration of the opposite diamagnetic anisotropy material ZLI-1167 remained $\approx 15,500 \pm 300$ Hz until the critical point when the values changed to half with opposite sign. The critical concentration for MBBA-d₂ : ZLI-1167 mixture was 0.3 : 1 weight ratio. The spectra at 24°C show two quadrupole split doublets (Figure 1) corresponding to the orientations of the liquid crystal optic axis along and orthogonal to the magnetic field. The separation between the inner doublet is exactly half of that for the outer. At higher temperature ($\geq 25^\circ\text{C}$), the orientation of the optic axis was along the direction of the magnetic field whereas below 23°C , it was orthogonal. This is further confirmed by spinning the sample along the axis perpendicular to the magnetic field at normal speeds (≈ 20 Hz) in the conventional electromagnet (Figure 2) when the outer doublet disappears. It reappears when the spinning is stopped. It may be emphasized that the higher temperature corresponds to the orientation of the optic axis along the magnetic field direction, at the critical concentration. It was also found to be so in the following two other experiments performed with different ingredients.

- (1) A proton NMR study of acetonitrile dissolved in p-n-pentyl-p'-cyanophenyl cyclohexane (S-1114) ($\Delta\chi > 0$) and ZLI-1167 and
- (2) a deuteron NMR study of chloroform-d dissolved in a mixture of equimolar trans-4-n-butyl and hexyl-cyclohexane carboxylic acids (CCA, $\Delta\chi < 0$) and S-1114.

The critical concentration was 1 : 0.3 weight ratio of CCA : S-1114 at 28°C. Assuming a value of $4.3 \pm 0.2 \times 10^{-8}$ for the diamagnetic anisotropy of S-1114,⁶ the value for CCA is $-1.4 \pm 0.2 \times 10^{-8}$.

The fact that in all the mixtures studied, the higher temperature corresponds to the orientation for the positive diamagnetic anisotropy, shows that the relative temperature dependence of the molecular order is stronger for the aliphatic compounds which constitute the component with negative diamagnetic anisotropy. This is not affected by the presence of groups such as cyano with strong dipole moment. This has been demonstrated by the study of mixtures when both the components (with $\Delta\chi > 0$ and $\Delta\chi < 0$) have cyano groups (ZLI-1167 - S-1114 mixture) or when only one of the components has a cyano group either for the $\Delta\chi > 0$ component (CCA - S-1114 mixture) or for that with $\Delta\chi < 0$ (ZLI-1167 - MBBA mixture). Though it is not precisely understood why the aliphatic component has a higher temperature dependence of the order parameter, it may be attributed to the higher internal mobility in such systems because of the presence of the central C-C bonds.

It may be pointed out that the orientation in the CCA, S-1114 mixture is much slower (it takes a few minutes to observe the spectrum) than in the ZLI-1167, S-1114 or ZLI-1167, MBBA mixtures (the spectrum appears almost instantaneously) and it was difficult to achieve the critical point corresponding to the coexistence of the two spectra.

In absence of magnetic field, a study of the optical textures of the MBBA-d₂, ZLI-1167 mixture was also undertaken near the critical point as a function of temperature.

No detectable changes in the textures or birefringence were noticed.

CONCLUSIONS

1. At a critical concentration and temperature two spectra corresponding to the alignment of the optical axis along and perpendicular to the magnetic field are observed in pure liquid crystals also, as in solutes.

2. The solute molecules follow the orientation of the liquid crystal molecules.

3. No detectable change in the optical properties is observed at the critical point in absence of the magnetic field.

4. At the critical concentration, the higher temperature corresponds to orientation due to $\Delta\chi > 0$ and the lower to $\Delta\chi < 0$ for all the systems studied.

5. The orientation in the CCA - S-1114 mixture is much slower than in the ZLI-1167/S-1114 or ZLI-1167/MBBA mixtures. To our knowledge this is the slowest orientation observed in thermotropic liquid crystals.

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