Component Orientational Order Parameter in Binary Mixtures

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Component Orientational Order Parameter in Binary Mixtures

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We have used the IR dichroism technique to measure the component order parameters of two different cyanobiphenyl compounds in two binary mixtures. The measurements clearly show that smectic-like short range order considerably enhances the orientational order in the nematic phase. Further, the temperature variation of the orientational order is also increased by virtue of that of the smectic-like short range order.

Keywords: binary mixtures, component order parameter, smectic-like short range order

INTRODUCTION

Uniaxial nematic liquid crystals are characterized by an orientational order parameter $S = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle$ if the molecules can be considered to be cylindrically symmetric. The Maier-Saupe theory of uniaxial nematics has been extended to binary mixtures by several authors.[1-5] These models predict that the order parameter of the two components will not be equal to each other in general. Further, the order parameter of a component ($S_{A,B}$) at any given reduced temperature depends on its concentration in the mixture. However, if the chemical structure of the components are similar, it may be possible to describe the medium with a single order parameter.[6] In earlier investigations the NMR technique has been used[7,8] to measure the component order parameters in two different binary mixtures by an appropriate deuteration of the constituent molecules. The order parameter of dissolved non-mesomorphic dye molecules at very low concentration has been studied by the UV dichroism technique.[9-11]

In this paper we present measurements of one of the component order parameters in 2 binary systems using the IR dichroism technique. In particular, the influence of the smectic-like short range order on the orientational order parameter is investigated.

The infrared dichroism method is a simple technique for measuring the component order parameters in binary mixtures. This is possible if the components have different bonds which give rise to isolated and pronounced IR bands without any overlap. In the two systems studied by us the $C \equiv N$ stretching mode of the

nitrile group situated at one end of the cyanobiphenyl molecule has been exploited. It gives rise to a strong vibrational band which is distinct and free from overlap of other bands. Since the corresponding transition moment is parallel to the long axis of the molecule, the molecular biaxiality order parameter[12] D does not influence the measurement of S using this band.

We have made measurements on two systems. System I consists of mixtures of methoxyphenyl-*trans*-pentylcyclohexyl carboxylate (MPPC) and 4′-n-octyloxy-4-cyanobiphenyl (80CB). System II consists of mixtures of 4-(4′-ethoxyphenyl-azo)phenyl undecylenate (EPPD) and 4′-n-heptyl-4-cyanobiphenyl (7CB). The structural formulae and transition temperatures of the pure compounds used in the two systems are shown in Figures 1a and 1b respectively.

The phase diagrams were studied by making mixtures with specific compositions. The transition temperatures were noted on cooling, under a Leitz polarizing microscope (Model Ortholux II-Pol BK) in conjunction with a Mettler hot stage
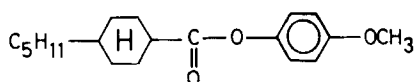
Methoxy phenyl trans pentyl cyclohexyl carboxylate (MPPC)

K 40°C N71°C I
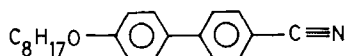
4′−n − Octyloxy − 4 − cyanobiphenyl (80 CB)

K 54·5°C S_A 67 °C N 80°C I

FIGURE 1a   Structural formulae and transition temperatures of the compounds MPPC and 80CB (System I).
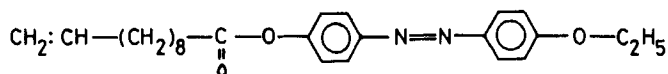
p−p′− Ethoxyphenyl azo) phenyl undecylenate (EPPD)

K 65.3°C N 108.1 °C I

4′− n −heptyl − 4 −cyanobiphenyl (7CB)

K 28.5 °C N 41.8°C I

FIGURE 1b   Structural formulae and transition temperatures of the compounds EPPD and 7CB (System II).

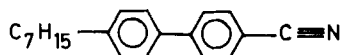(Model FP52). The complete phase diagrams involving the determination of the eutectic point, etc., were not investigated, as our main interest was in the liquid crystalline phases above the ambient temperature.

For recording the IR spectra, NaCl plates which could be mounted in a suitable heater were used as cell windows. Good homeotropic alignment could be obtained for most samples by rubbing the NaCl plates on chamois leather in a random manner or by coating a thin film of lecithin on the plates. 23 μm mylar spacers were used to control the sample thickness. The spectra were recorded in the isotropic phase (about 15° above T_{NI}) and at various temperatures in the liquid crystalline phases using an IR spectrophotometer (Shimadzu, Model IR-435). There is a clear reduction in the intensity of the $C \equiv N$ stretching band between the isotropic and the liquid crystalline phases, due to the orientational order. The order parameter in this geometry is given by

$$S = \frac{1 - R}{1 - \frac{3}{2}\sin^2 \alpha}$$

where R is the 'dichroic ratio,' equal to the ratio of the integrated absorption of the band in the liquid crystalline phase to that in the isotropic phase and α is the angle made by the transition moment with the long axis of the molecule.[13,14]

RESULTS AND DISCUSSION

System I: The phase diagram of system I is shown in Figure 2. The coexistence range of I and N phases in most of the compositions is relatively small, being ~0.5°. The nematic-isotropic transition temperatures of the mixtures exhibit a negative deviation from a linear interpolation between the values of the pure components. This trend is expected according to the theoretical model of Nakagawa and Aka-hane,[3] in which intermolecular repulsions are taken into account. The partial bilayer smectic A phase of pure 80CB is seen to be suppressed beyond ~13 mole% of MPPC. Usually when terminal polar compounds are mixed with non-polar or weakly polar compounds an induced smectic A phase can be expected to oc-cur.[15,16,17] However, in the present case, the induced phase could not be found down to the ambient temperature. The MPPC molecule consists of one cyclohexyl ring and one phenyl ring. Compared to compounds with two phenyl rings there is a decrease in the dipole-induced dipole interactions and charge transfer complexing. Indeed in other binary systems[18] a depression in the N-induced A transition temperature has been found when one of the benzene rings is substituted by a cy-clohexane ring.

We have in particular studied the IR dichroism of the mixtures with 20, 50 and 70 mole% of MPPC. The order parameter of 80CB as a function of temperature in the three mixtures and that of pure 80CB as measured by Prasad and Venugopalan[19] by the same technique are shown in Figure 3. Pure 80CB is seen to have the highest order parameter at any given relative temperature. The addition of 20 mole% of
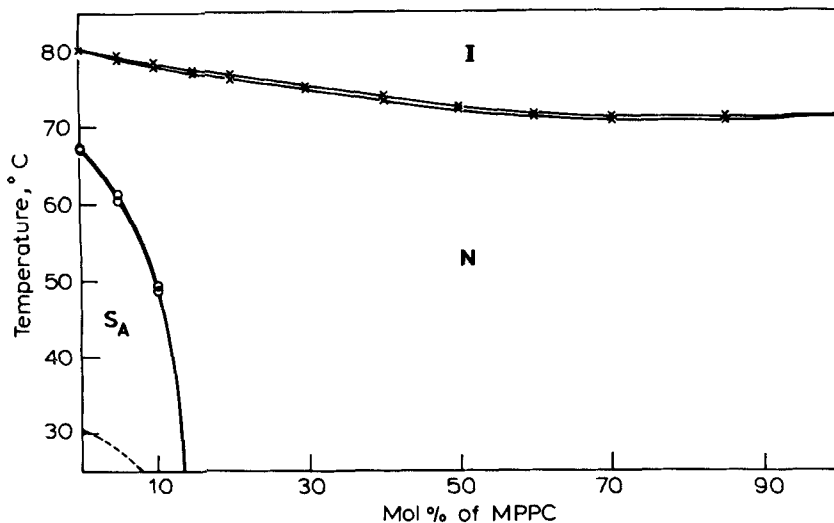
FIGURE 2   Phase diagram of mixtures of MPPC and 80CB (transition temperatures determined on cooling only). The dotted line indicates the temperatures at which the sample starts crystallizing.
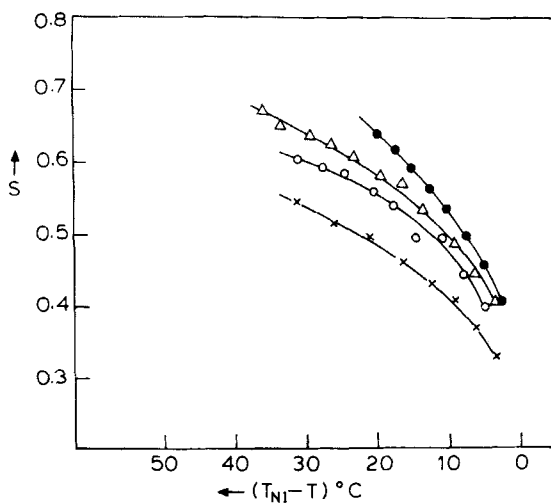
FIGURE 3   Variation of the order parameter S of 80CB as a function of the relative temperature in the pure compound and in three mixtures. ●, pure 80CB, ×, 20 mole% of MPPC, ○, 50 mole% of MPPC, △, 70 mole% of MPPC.

MPPC decreases the S-value of 80CB considerably. Further addition of MPPC is found to again increase the value of S. In Figure 4 we have plotted the variation of S with concentration of MPPC at three relative temperatures. The results can be interpreted as follows.

In a binary mixture, if the average diameters of both types of molecules are the same, the component order parameter of the longer molecules can be expected

FIGURE 4   Variation of the order parameter S as a function of the concentration of MPPC, at three relative temperatures.

to be higher than that of the shorter molecules purely for geometrical reasons, as has indeed been found in theoretical models.[4,20] The experimental studies on the order parameters of anisotropic dye molecules dissolved in various nematic hosts[21] have clearly confirmed this result. The molecular lengths 'l' of 8OCB and MPPC molecules calculated using Dreiding models are 20.9 Å and 19.5 Å respectively. T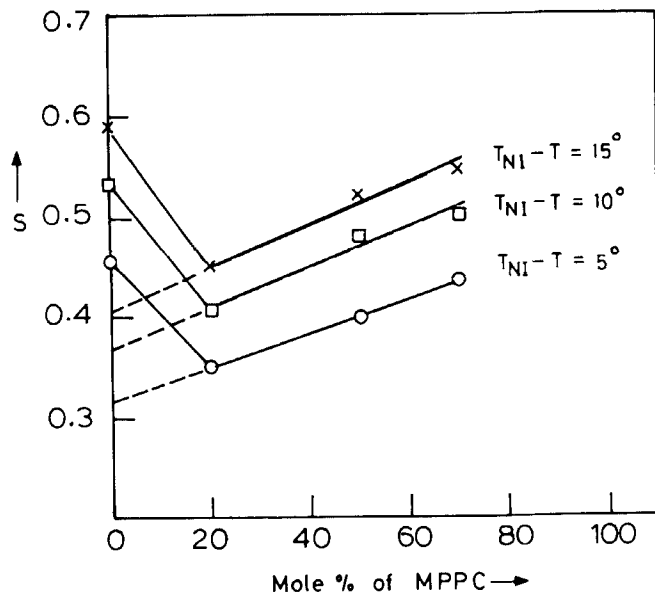herefore the component order parameter of 8OCB can be expected to be slightly higher than that of MPPC. Further, following the theoretical predictions of Palffy-Muhoray et al.[4] and Counsell & Warner[20] its value should increase as the concentration of 8OCB in the mixture decreases. In the three mixtures the S of 8OCB at any relative temperature increases linearly with the concentration of MPPC in agreement with this theoretically predicted trend. However, pure 8OCB exhibits a relatively high value of S compared to the value got by a linear extrapolation from the order parameters of the mixtures. In the mixtures, we can expect that 8OCB molecules no longer exist as antiparallel dimers but as individual molecules. If the order parameter curves are extrapolated to 0 mole% of MPPC (i.e., pure 8OCB) as indicated by the dashed lines in Figure 4 the values obtained are much lower than the measured ones.

Due to antiparallel correlations, 8OCB molecules are usually assumed to form dimers which exhibit a partial bilayer structure. The length of the dimer is about 1.4 times the molecular length.[22] However, the length to breadth ratio of a dimer is not very different from that of the monomer. Thus the origin of the increase in the order parameter of pure 8OCB is not likely to be a consequence of the formation of dimers. In the McMillan model of smectic liquid crystals, the orientational and translational orders are coupled in the smectic A phase. This results in an en-

hancement of the orientational order parameter in the A phase compared to the Maier-Saupe value for the nematic phase at the same relative temperature. In the Landau type phenomenological theory developed by de Gennes[23] a similar assumption is made about the enhancement of the S in the smectic phase. This enhancement has been confirmed experimentally.[24,25] But the above mean field theories do not predict any enhancement of the orientational order parameter in the nematic phase exhibited by smectogenic compounds.

Since none of the mixtures of 80CB and MPPC studied by us exhibits a smectic A phase at least down to room temperature, the value of S of pure 80CB extrapolated from those of the mixtures, corresponds to the orientational order parameter of a hypothetical 80CB which exhibits only a nematic phase. On the other hand, the experimental value is for real 80CB which exhibits both the nematic and smectic phases. The obvious conclusion is that the smectic A like short range order leads to a considerable enhancement of the orientational order. In fact as the temperature is lowered the difference between the measured and extrapolated values is seen to increase as the smectic like short range order becomes stronger. Also in Figure 3 it is clearly seen that the order parameter curve in the nematic phase of pure 80CB rises more steeply with decrease in temperature than the curves for the three mixtures. The origin of this will be discussed later.

System II: Both the compounds of this system exhibit only the nematic phase in the pure state. However, some of the mixtures exhibit an induced smectic A phase above room temperature. The phase diagram is shown in Figure 5. As the sample was cooled from the I phase a coexistence of the I & N phases extending over
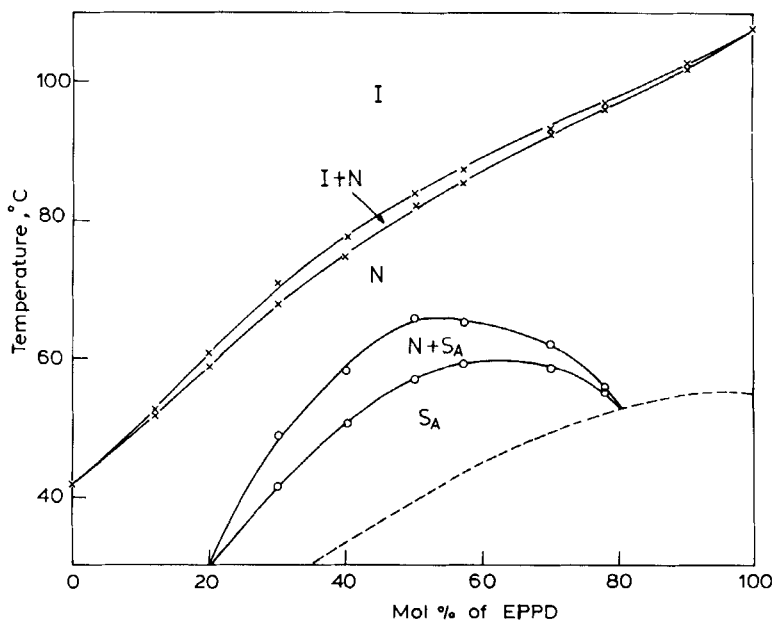

FIGURE 5   Phase diagram of mixtures of EPPD and 7CB (transition temperatures determined on cooling only). The dotted line indicates the temperatures at which the crystallization begins.

1–2° was observed before the entire sample was transformed to the nematic phase. In compositions exhibiting the induced smectic A phase a wide range of coexistence of nematic and smectic A phases is seen. The maximum range of this coexistence is about 8–9° for a concentration with ~50 mole% of EPPD.

In contrast to system I the I-N coexistence curve has a slight positive deviation from a linear interpolation between the T_{NI} of the two pure compounds. This curve reflects the induced A-N coexistence boundary which characteristically peaks around 50 mole% of EPPD. The short range smectic like order in the nematic phase of compositions exhibiting the induced A phase enhances the orientational order, thus sustaining the N phase up to higher temperatures.

We have studied the IR dichroism of mixtures with 20, 50 and 70 mole% of EPPD. The variation with temperature of the order parameter S of 7CB in the three mixtures along with the values of S obtained by the same technique for pure 7CB by Prasad and Venugopalan[19] have been shown in Figure 6. A considerable jump in the values of S between the nematic and smectic A phase is observed for
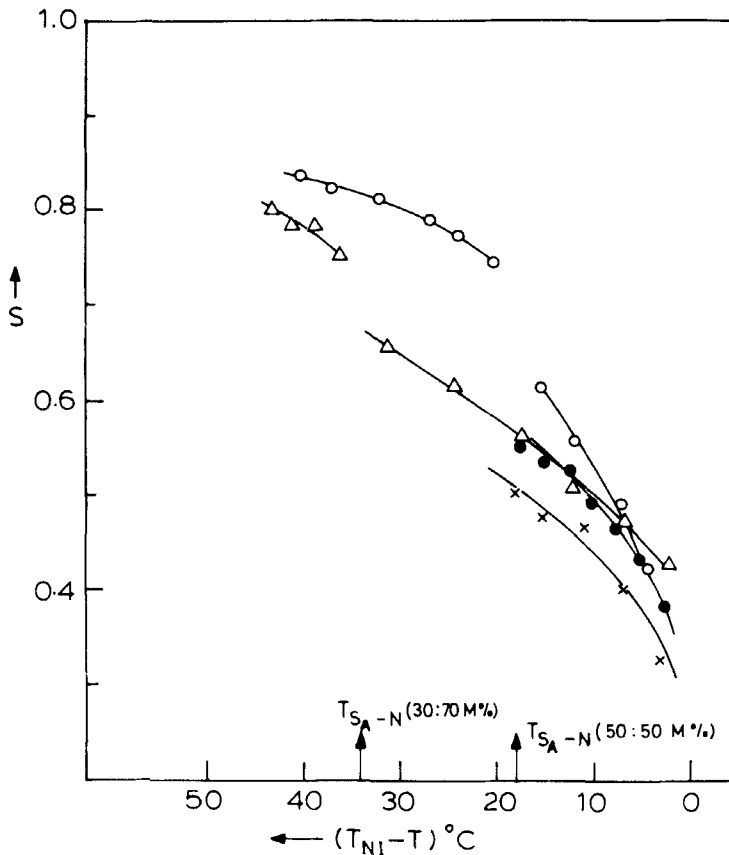

FIGURE 6 Variation of the order parameter S of 7CB as a function of the relative temperature in the pure compound and in three mixtures. ●, pure 7CB, ×, 20 mole% of EPPD, ○, 50 mole% of EPPD, △, 70 mole% of EPPD.

mixtures with 50 and 70 mole% of EPPD. In the mixture with 20 mole% of EPPD the order parameter in the nematic phase at any relative temperature is lower than that of pure 7CB. On the other hand addition of 50 mole% of EPPD gives rise to a large increase in its value. The order parameters of 7CB at specific relative temperatures as a function of the concentration of EPPD are shown in Figure 7. 7CB has a molecular length $l \simeq 19.2$ Å and EPPD has $l \simeq 28.2$ Å as measured using Dreiding models. 7CB is a highly polar compound and as we mentioned earlier its molecules can be expected to form antiparallel pairs.[22] These pairs are more symmetric than the individual molecules which are highly asymmetric because of the presence of the alkyl chain. From X-ray scattering studies it has been found[22] that ~150 molecules of 7CB form smectic-like cybotactic groups. As we have discussed for system I, the smectic-like short range order can enhance the orientational order parameter of 7CB in the nematic phase.

When about 20 mole% of EPPD is added to 7CB an induced smectic A phase with monolayer structure is obtained below 30°C. Even when $T_{NI} - T = 15°$ the temperature is considerably higher than T_{NA} (induced) so that the induced smectic A like short range order appears to be unimportant. The length of the 7CB molecule is significantly smaller than that of EPPD, and the S value reduces as expected from theoretical models.[4,20]

For the two other compositions, the induced A-like short range order has a clear influence on the S values in the nematic phase (Figures 6 and 7). The pronounced peak in S seen for the 50% mixture at $T_{NI} - T = 15°$ is a consequence of the proximity of the A-N transition point.
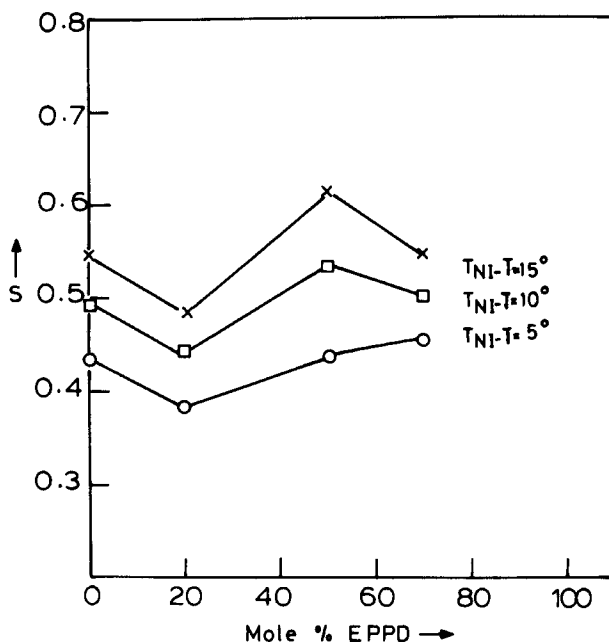

FIGURE 7   Variation of the order parameter S as a function of the concentration of EPPD at three relative temperatures.

Further, X-ray studies on a monolayer compound[26] and measurements on the ratio of the elastic constants k_{33}/k_{11} of a binary mixture exhibiting an induced smectic A phase[27] have shown that $\xi_{\parallel}/\xi_{\perp}$, the ratio of the smectic-like correlation length $\parallel$ and $\perp$ to the director decreases as the temperature is increased in the nematic phase. The smectic-like cybotactic groups can thus have lower shape anisotropy which allow them to have stronger orientational fluctuations at higher temperatures. This could of course reduce the measured value of the orientational order parameter. We can thus expect that both the decrease of smectic-like short range order and of $\xi_{\parallel}/\xi_{\perp}$ at higher temperatures can reduce the value of S considerably as the temperature is increased in the N phase. Indeed the S value of the 50% mixture shows the strongest temperature dependence (Figure 6), as in the case of 80CB in system I.

CONCLUSION

The order parameters of two cyanobiphenyls in several mixtures belonging to two binary systems were measured using the infrared dichroism method. The experimentally measured values of S of 80CB in the nematic range of pure 80CB which has an A phase at lower temperatures (system I) and the values of S of 7CB in the 50 mole% mixture (system II) which exhibits an induced A phase have an enhancement which is due to the smectic like short range order. The S value strongly decreases as the temperature is increased in the nematic phase. This can arise partly from a progressive decrease in the smectic like short range order and partly from a reduction of the value of the ratio $\xi_{\parallel}/\xi_{\perp}$, thus reducing the geometrical anisotropy of the cybotactic groups.

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