

## CHAPTER III

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### DETERMINATION OF THE ORIENTATIONAL ORDER PARAMETERS OF ONE OF THE COMPONENTS IN BINARY MIXTURES USING THE INFRARED DICHOISM METHOD

#### 3.1 INTRODUCTION

Uniaxial nematic liquid crystals are characterised by an orientational order parameter  $S = \frac{1}{2} \langle 3\cos^2 \theta - 1 \rangle$  when the molecules are considered to be cylindrically symmetric. As mentioned in Chapter I, the Maier-Saupe theory accounts for the nematic-isotropic transition and yields a universal value of  $S = 0.429$  at the N-I transition point. This theory has been extended to multicomponent systems containing axially symmetric molecules by Humphries et al. (1971, 1973) and the theory has been used to predict phase diagrams of binary mixtures of nematogens. Martire et al. (1976) have also proposed theories for binary systems based on a lattice model as well as the Maier-Saupe type of treatment for axially symmetric molecules and studied the nature of the phase diagrams. Palfy-Muhoray et al. (1984) have given a more rigorous extension of the Maier-Saupe theory by calculating the chemical potentials. The above theory, in addition to predicting a two phase region close to the N-I transition, leads to the result that the order parameters of the components in the mixture usually differ. These results will be discussed later.

All the above theoretical treatments are for cylindrically

symmetric molecules. But in reality most molecules do not possess this symmetry. Alben et al. (1972) have shown that two order parameters are then required to describe the uniaxial nematic phase.

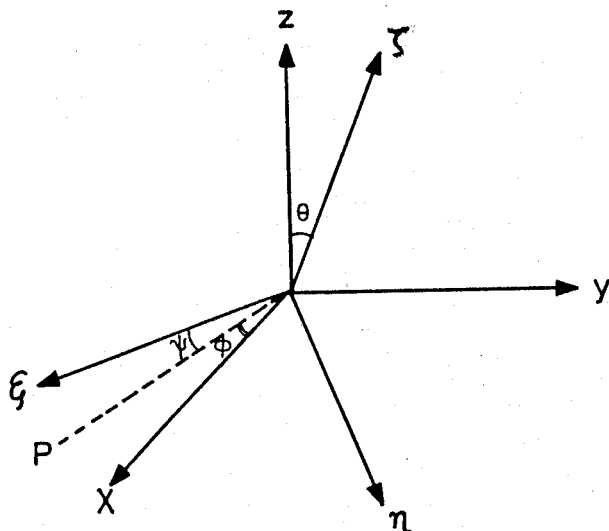
### 3.2 ORIENTATIONAL ORDER PARAMETERS OF A UNIAXIAL NEMATIC WITH BIAxIAL MOLECULES

In general for a molecule of arbitrary shape the nematic phase can be characterised by the tensor order parameter (Saupe 1964)

$$S_{ij}^{\alpha\beta} = \frac{1}{2} \langle 3i_{\alpha} j_{\beta} - \delta_{\alpha\beta} \delta_{ij} \rangle \quad (3.1)$$

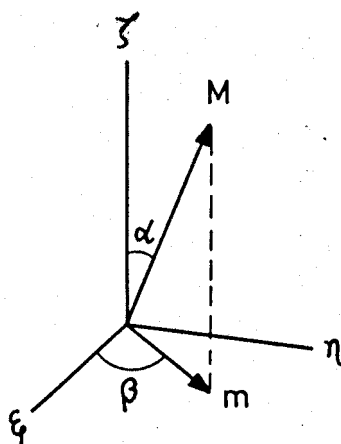
where  $\alpha, \beta = x, y, z$  refer to a laboratory fixed coordinate system and  $i, j = \xi, \eta, \zeta$  refer to the frame linked to the molecule.  $i_{\alpha}$ ,  $j_{\beta}$  denote the projection of the unit vectors  $i$  and  $j$  along  $\alpha$  and  $\beta$  respectively and  $\delta_{ij}$  and  $\delta_{\alpha\beta}$  are the Kronecker deltas. The orientational state of the molecules is completely determined by the three Euler angles  $\theta$ ,  $\psi$  and  $\phi$  (Fig. 3.1), where  $\theta$  is the angle between the  $z$ -axis and  $\zeta$ -axis,  $\psi$  is the angle between the  $\xi$ -axis and the normal to the  $z$ - $\zeta$  plane, describing a rotation of the molecule around its long axis.  $\phi$  is the angle between the  $x$ -axis and the normal to the  $z$ - $\zeta$  plane, describing a rotation of the whole molecule around the director. In the uniaxial phase  $\phi$  can take all values with equal probability,  $S_{ij}^{\alpha\beta}$  is a symmetric tensor in  $i, j$  and  $\alpha, \beta$  and has zero trace.

The director is assumed to be along the  $z$ -axis and the mole-



**Figure 3.1**

Illustration of the Eulerian angles  $\theta$ ,  $\psi$  and  $\phi$ .



**Figure 3.2**

Angles specifying the orientation of the transition moment  $M$  with respect to the molecular axes  $\xi$ ,  $\eta$  and  $\zeta$  ( $m$  is the projection of  $M$  on the  $\xi - \eta$  plane).

cular long axis is along the  $z$  axis.  $\xi$ ,  $\eta$  and  $\zeta$  are the principal axes of the rotational diffusion tensor of the molecule. To describe the average orientation of the molecule with respect to the director, we have to consider the components  $\zeta_z$ ,  $\eta_z$  and  $\xi_z$ . Now  $\zeta_z = \cos \theta$ ,  $\eta_z = \sin \theta \cos \psi$  and  $\xi_z = \sin \theta \sin \psi$ .

From eqn. (3.1)

$$S_{ij}^{zz} = \frac{1}{2} \langle 3i_z j_z - \delta_{ij} \rangle \quad (3.2)$$

Omitting the superscripts  $zz$  in subsequent expressions we have

$$\begin{aligned} S_{\xi\xi} &= \frac{1}{2} \langle 3\xi_z^2 - 1 \rangle \\ S_{\eta\eta} &= \frac{1}{2} \langle 3\eta_z^2 - 1 \rangle \\ S_{\zeta\zeta} &= \frac{1}{2} \langle 3\zeta_z^2 - 1 \rangle \end{aligned} \quad (3.3)$$

From which the two order parameters  $S$  and  $D$  for a uniaxial nematic medium made up of biaxial particles are obtained as

$$\begin{aligned} S &= S_{\zeta\zeta} = \frac{1}{2} \langle 3\zeta_z^2 - 1 \rangle = \frac{1}{2} \langle 3\cos^2 \theta - 1 \rangle \\ D &= S_{\eta\eta} - S_{\xi\xi} = \frac{1}{2} \langle 3(\eta_z^2 - \xi_z^2) \rangle \\ &= \frac{3}{2} \langle \sin^2 \theta \cos 2\psi \rangle \end{aligned} \quad (3.4)$$

A finite  $D$  indicates that there is a difference in tendency of the two transverse molecular axes to project on the  $z$ -axis.

A convenient method of measuring the orientational order

parameters experimentally is by Infrared dichroism measurements. Isolated and pronounced bands available in the Infrared spectra of the compounds can be used for this purpose, if the orientation of the related transition moment with respect to the molecular geometry is known.

Saupe and Maier (1961) assumed the molecules constituting the nematic phase to be cylindrically symmetric and derived the relation between the dichroic ratio and the order parameter  $S$ . Korte (1983) has later discussed the contribution of  $D$  to the dichroic ratio.

There are two geometries in which the order parameters can be measured by the Infrared technique. One method makes use of polarised radiation and a planar aligned sample (For e.g., Saupe and Maier 1961, Maier and Englert 1960). The order parameters are evaluated from the two integrated absorption coefficients  $A_{||}$  and  $A_{\perp}$  where the subscripts  $||$  and  $\perp$  indicate that the incident radiation is polarised parallel or perpendicular to the direction of alignment. However a simpler technique is to make use of a homeotropically aligned sample (Kelker et al. 1973, Fernandes and Venugopalan 1976). The use of polarised radiation can thus be avoided.

### 3.3 RELATION BETWEEN THE DICHROIC RATIO AND THE ORDER PARAMETERS .

Consider a sample aligned homeotropically along the  $z$  direction of a space fixed coordinate system  $(x,y,z)$ . Let  $\xi$ ,  $\eta$  and  $\zeta$

be the principal axes of the rotational diffusion tensor of the molecule (Saunders et al 1984, Keifer and Baur 1984). As mentioned before the long axis of the molecule is along the  $\zeta$  axis and the director is parallel to the  $z$  axis. The orientation of the molecular axes are described by the Euler angles  $\theta$ ,  $\psi$  and  $\phi$  as defined before.

The transition moment forms an angle ' $\alpha$ ' with the  $\zeta$  axis and its projection on the  $\xi\eta$  plane forms an angle  $\beta$  with the  $\xi$  axis of the molecule (Fig. 3.2). The components of the oscillator strength  $f$  which is proportional to the square of the transition moment are

$$\begin{aligned} f_{\xi} &= f \sin^2 \alpha \cos^2 \beta \\ f_{\eta} &= f \sin^2 \alpha \sin^2 \beta \\ f_{\zeta} &= f \cos^2 \alpha \end{aligned} \quad (3.5)$$

The components parallel to the  $x, y, z$  axes respectively can be obtained by using the Euler transformations (for e.g., Goldstein 1950). Thus we have

$$\begin{aligned} f_x &= f[(\cos \phi \cos \psi - \cos \theta \sin \phi \sin \psi)^2 \sin^2 \alpha \cos^2 \beta \\ &\quad + (\cos \phi \sin \psi + \cos \theta \sin \phi \cos \psi)^2 \sin^2 \alpha \sin^2 \beta \\ &\quad + \sin^2 \theta \sin^2 \phi \cos^2 \alpha] \\ f_y &= f[(\sin \phi \cos \psi + \cos \theta \cos \phi \sin \psi)^2 \sin^2 \alpha \cos^2 \beta \\ &\quad + (\sin \phi \sin \psi - \cos \theta \cos \phi \cos \psi)^2 \sin^2 \alpha \sin^2 \beta \\ &\quad + \sin^2 \theta \cos^2 \phi \cos^2 \alpha] \end{aligned}$$

$$f_z = f[\sin^2 \theta \sin^2 \psi \sin^2 a \cos^2 \beta + \sin^2 \theta \cos^2 D \sin^2 a \sin^2 \beta + \cos^2 \theta \cos^2 \alpha] \quad (3.6)$$

By introduction of ensemble averages

$$\begin{aligned} \langle f_x \rangle &= f\left[\frac{1}{2} \sin^2 \alpha + \frac{1}{2}\left(1 - \frac{3}{2} \sin^2 a\right)(\langle \sin^2 \theta \rangle - \langle t \rangle) + \frac{1}{4} \sin^2 a \cos 2\beta (\langle \sin^2 \theta \cos 2\psi \rangle + \langle V \rangle)\right] \\ \langle f_y \rangle &= f\left[\frac{1}{2} \sin^2 \alpha + \frac{1}{2}\left(1 - \frac{3}{2} \sin^2 \alpha\right)(\langle \sin^2 \theta \rangle + \langle t \rangle) + \frac{1}{4} \sin^2 a \cos 2\beta (\langle \sin^2 \theta \cos 2\psi \rangle - \langle V \rangle)\right] \\ \langle f_z \rangle &= f\left[1 - \sin^2 a - \left(1 - \frac{3}{2} \sin^2 \alpha\right)\langle \sin^2 \theta \rangle - \frac{1}{2} \langle \sin^2 \theta \cos 2\psi \rangle \sin^2 a \cos 2\beta\right] \end{aligned} \quad (3.7)$$

where  $t = \sin^2 \theta \cos 2\phi$  and

$$V = (1 + \cos^2 \theta) \cos 2\phi \cos 2\psi - 2 \cos \theta \sin 2\phi \sin 2\psi$$

For a uniaxial phase,  $\langle f_x \rangle$  and  $\langle f_y \rangle$  have to be equal, i.e., terms involving  $t$  and  $V$  in (3.7) vanish.  $D = \frac{3}{2} \langle \sin^2 \theta \cos 2\psi \rangle$  is the additional order parameter necessary for characterising the uniaxial nematic phase made of biaxial molecules. Substituting the order parameters  $S$  and  $D$  in eqn. (3.7)

$$\langle f_x \rangle = \langle f_y \rangle = \frac{1}{3} f \left[ 1 - S \left( 1 - \frac{3}{2} \sin^2 a \right) + \frac{1}{2} D \sin^2 \alpha \cos 2\beta \right]$$

and

$$\langle f_z \rangle = \frac{1}{3} f \left[ 1 + 2S \left( 1 - \frac{3}{2} \sin^2 \alpha \right) - D \sin^2 a \cos 2\beta \right] \quad (3.8)$$

For the homeotropically aligned sample, if the radiation is incident along the  $z$  direction (which is also the direction of alignment of the molecules) the absorption due to the molecule is given by

$$\begin{aligned} A &= f[\langle f_x \rangle + \langle f_y \rangle] \\ &= \frac{2}{3} f \left[ 1 - S \left( 1 - \frac{3}{2} \sin^2 a \right) + \frac{1}{2} D \sin^2 a \cos 2\beta \right] \\ &= A_{LC} \end{aligned} \quad (3.9)$$

i.e., the absorption in the liquid crystalline phase.

In the isotropic phase  $S$  and  $D$  are zero. Therefore

$$A_{iso} = \frac{2}{3} f \quad (3.10)$$

the dichroic ratio  $R = A_{LC}/A_{iso}$ . Substituting for  $A_{LC}$  and  $A_{iso}$  from eqns. (3.9) and (3.10)

$$R = \left[ 1 - S \left( 1 - \frac{3}{2} \sin^2 a \right) + \frac{1}{2} D \sin^2 a \cos 2\beta \right]$$

or

$$1 - R = S \left( 1 - \frac{3}{2} \sin^2 a \right) - \frac{1}{2} D \sin^2 a \cos 2\beta \quad (3.11)$$

The dichroic ratio involves the integrated absorption intensity and not just the peak absorption coefficients. Also the experimental absorption profile has to be corrected for the effects of finite spectral slit width (Ramsay 1952). Following Ramsay's procedure the true absorption profile can be represented by a Lorentzian function. The corrected integrated absorption strength is calculated using the experimentally observed values of the peak intensity,



the width of the absorption profile at half peak height  $\Delta\nu_{1/2}$  and the spectral slit width  $S$  of the instrument. If  $I_0$  is the intensity value corresponding to the base line and  $I$  is the intensity value corresponding to the absorption peak,  $\Delta\nu_{1/2}$  is the width corresponding to the intensity  $(II_0)^{1/2}$ . The integrated absorption of the band is equal to

$$K \ln(I_0/I) \Delta\nu_{1/2} \quad (3.12)$$

Ramsay (1952) has constructed a table to obtain the values of  $K$  for specific values of  $\ln(I_0/I)$  and  $S/\Delta\nu_{1/2}$ . We found that the values of  $\Delta\nu_{1/2}$  obtained for the C  $\equiv$  N bond in the isotropic and liquid crystalline phases are the same. The same slit width has been chosen when recording the spectra in the isotropic and liquid crystal phases. This leads to identical values for  $K$  in the isotropic and liquid crystalline phases. We have therefore neglected the terms  $K$  and  $\Delta\nu_{1/2}$  in eqn. (3.12) as these terms cancel out, when the ratio of the integrated absorption intensities in the isotropic and liquid crystalline phases are taken to obtain the dichroic ratio  $R$ . The experimental value of  $R$  would in general be different from the true value because the refractive indices of the mesophase are different from those of the isotropic liquid. Also the local field in the mesophase is anisotropic in nature. The error involved in these factors has been estimated to be  $-2\%$  (Fernandes and Venugopalan 1976) and has thus been neglected as this is less than the uncertainty involved in our experimental

measurements which is -5%.

If the transition moment chosen for the experiment is not along the long axis, i.e., if  $a \neq 0$  in eqn. (3.11) the measured intensity values have contributions from both S and D. In order to determine S and D separately it is essential to have two bonds in the same molecule whose transition moments active in the Infrared region make different angles with the long axis. The equations

$$1 - R_1 = S(1 - \frac{3}{2} \sin^2 \alpha_1) - \frac{1}{2} D(\sin^2 \alpha_1 \cos 2\beta_1) \quad (3.13)$$

$$1 - R_2 = S(1 - \frac{3}{2} \sin^2 \alpha_2) - \frac{1}{2} D(\sin^2 \alpha_2 \cos 2\beta_2) \quad (3.14)$$

can be solved to obtain both S and D.

Our main aim was to study the order parameters of the components in binary mixtures. This requires a total of four bonds, two from each of the components, without any overlap of the absorption bands due to the transition moments. It is difficult to obtain four such isolated bands. Even if it is possible to obtain four such bonds, as the  $\xi$  and  $\eta$  axes cannot be uniquely fixed the determination of the absolute values of D is difficult. However if a single bond from one of the components which has a transition moment along the long axis is chosen,  $a$  is equal to zero in Eqn. (3.11). Therefore there is no contribution from D and the order parameter S of that particular component can be uniquely determined.

As our experimental studies do not take into consideration

the contributions from D, we now present the results of Palffy-Muhoray et al. (1984) for order parameters of the components, pertaining to only cylindrically symmetric molecules.

### 3.4 COMPONENT ORDER PARAMETERS IN BINARY MIXTURES

As mentioned in Chapter II, the single particle pseudo potential generalised to a two component mixture consisting of  $N_1$  molecules of species 1 and  $N_2$  molecules of species 2 is given by

$$\begin{aligned} \epsilon(\hat{n}_1) = & -\frac{1}{2} \gamma_{11} \rho_1 - \frac{1}{2} \gamma_{12} \rho_2 - \left[ \frac{2}{3} u_{11} \rho_1 S_{\alpha\beta}^{(1)} \right. \\ & \left. + \frac{2}{3} u_{12} \rho_2 S_{\alpha\beta}^{(2)} \right] \times \left[ \sigma_{\alpha\beta}^{(1)} - \frac{1}{2} S_{\alpha\beta}^{(1)} \right] \end{aligned} \quad (3.15)$$

where  $\hat{n}_1$  is the unit vector with components  $n_\alpha^{(1)}$  specifying the orientation of a molecule of species 1,  $\rho_1$  and  $\rho_2$  are the number densities of the two species,  $\gamma_{ij}$  and  $u_{ij}$  are isotropic and anisotropic interaction strengths between molecules of species  $i$  and  $j$ ,  $\sigma_{\alpha\beta}^{(i)} = \frac{1}{2}(3n_\alpha^{(i)} n_\beta^{(i)} - \delta_{\alpha\beta})$ ,  $S_{\alpha\beta}^{(i)} = \langle \sigma_{\alpha\beta}^{(i)} \rangle$  and  $\langle \rangle$  denotes an ensemble average. The single particle pseudo potential for molecules of species 2 is obtained by interchanging the indices 1 and 2 in eqn. (3.15). The free energy density of the system is given by

$$\begin{aligned} F = & -kT \left[ \rho_1 \ln \left( \frac{1}{\rho_1} \int \exp(-\epsilon(\hat{n}_1)/kT) d\Omega \right) \right. \\ & \left. + \rho_2 \ln \left( \frac{1}{\rho_2} \int \exp(-\epsilon(\hat{n}_2)/kT) d\Omega \right) \right] \end{aligned} \quad (3.16)$$

where  $d\Omega$  is an element of solid angle. Minimisation of this free energy leads to the self consistent equation for the order parameter

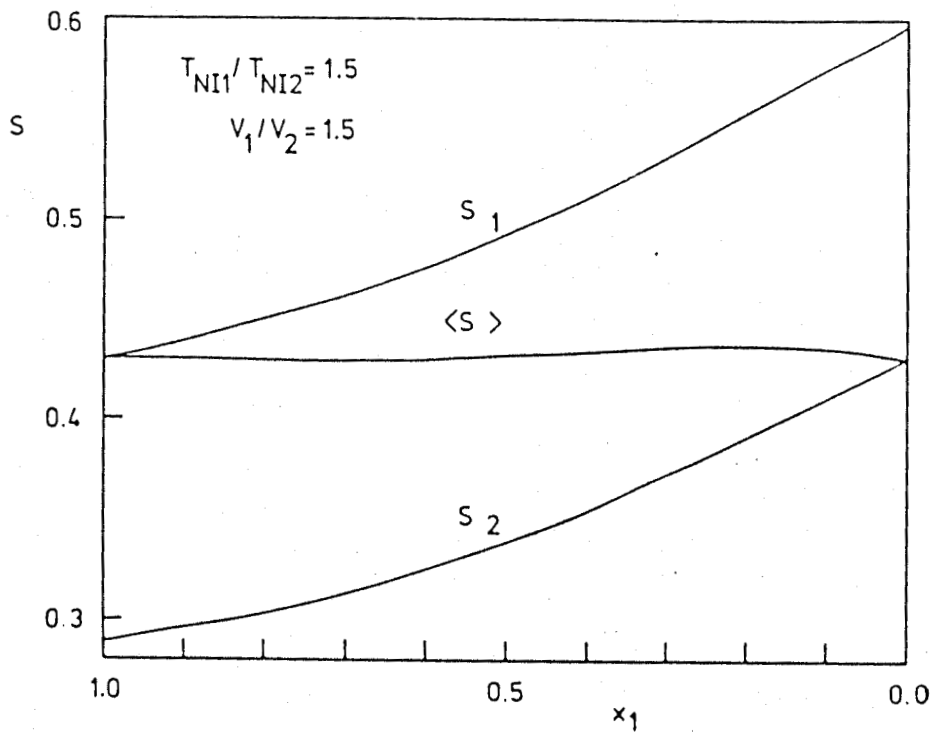
given by

$$S_{\alpha\beta}^{(i)} = \frac{\int \sigma_{\alpha\beta}^{(i)} \exp[-\epsilon(\hat{n}_i)/kT] d\Omega}{\int \exp[-\epsilon(\hat{n}_i)/kT] d\Omega} \quad (3.17)$$

where  $i = 1, 2$  refers to the two components or species.

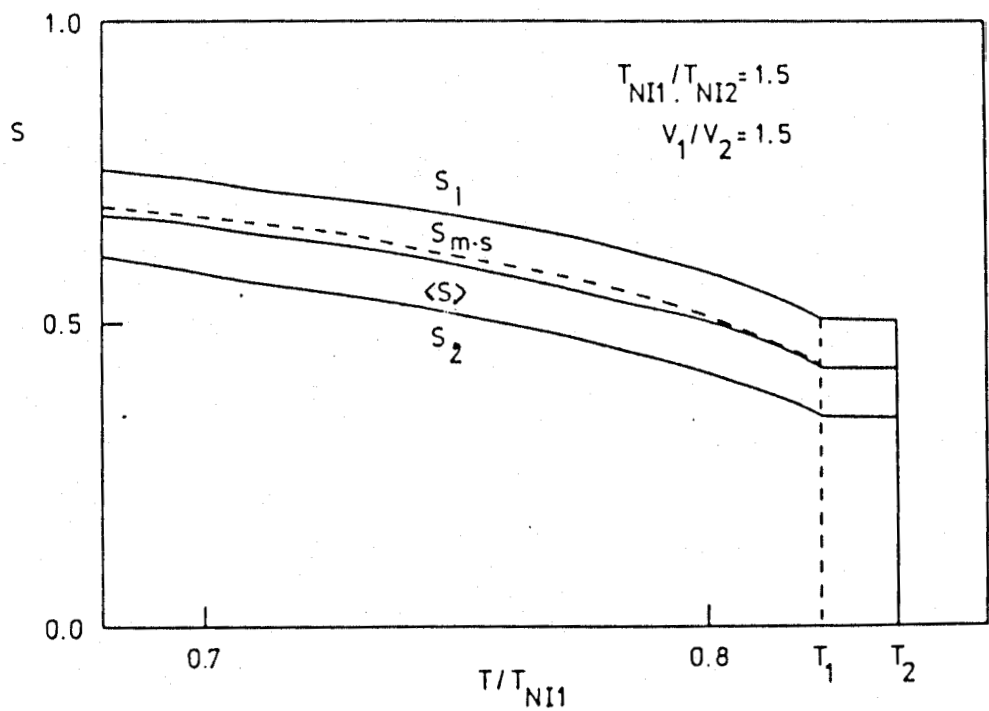
Palfy-Muhoray et al. have made calculations illustrating the typical behavior of the order parameters of the components in a binary mixture of two nematogens. The ratio of the nematic-isotropic transition temperatures of the two components 1 and 2, i.e.,  $T_{NI_1}/T_{NI_2}$  is assumed to be 1.5 and the ratio of the molar volumes  $V_1$  and  $V_2$  is also assumed to be equal to 1.5 for this case. The order parameters of the components  $S_1$ ,  $S_2$  and the volume averaged order parameter  $\langle S \rangle$  plotted against  $x_1$  evaluated along the N-I coexistence curve are shown in Fig. 3.3a. It is seen that the order parameters  $S_1$  and  $S_2$  in the mixtures are significantly different from the Maier-Saupe value of  $S_{m-s} = 0.429$ . The temperature behavior of the order parameters of the components ( $S_1$  and  $S_2$ ) and the volume averaged order parameter ( $\langle S \rangle$ ) are shown in Fig. 3.3b. The Maier-Saupe value ( $S_{m-s}$ ) has been indicated for comparison. The curve representing  $\langle S \rangle$  is seen to be close to the Maier-Saupe curve whereas the curves for  $S_1$  and  $S_2$  differ from the Maier-Saupe curve. In the two phase region  $T_2 < T < T_1$ , though the nematic composition changes, the order parameters remain nearly constant.

They have also made some experimental measurements of **refrac-**



**Figure 3.3a**

Volume averaged order parameter:  $\langle S \rangle$  and order parameters of the components:  $s_1$  and  $s_2$  evaluated along the N - I coexistence curve (From Palfy-Muhoray et al. 1984).



**Figure 3.3b**

Order parameters  $s_1$ ,  $s_2$  and  $\langle S \rangle$  as functions of reduced temperature (From Palfy-Muhoray et al. 1984).

tive indices of a couple of binary systems. Only the volume averaged order parameters of the mixture can be obtained from the birefringence measurements and hence a detailed comparison with theory is not possible.

In a system exhibiting the induced smectic phase, a significant increase in the order parameters in the nematic phase of the mixture relative to those of the pure component was found by the same authors.

In summary this theory yields the separate order parameters of the components in a mixture. The order parameter of one of the components is greater and that of the other less than the Maier-Saupe value for pure components. The volume averaged mixture order parameters is approximately equal to the Maier-Saupe value.

We have experimentally measured the temperature variation of the order parameter of one of the components for two binary systems. The two systems consist of mixtures of two non-cyano compounds with two cyano biphenyls. In both cases the  $C \equiv N$  stretching mode of the nitrile group situated at one end of the cyano biphenyl molecule has been studied. It gives rise to a strong vibrational band which is distinct and free from overlap of other bands. The transition moment of this band is parallel to the long axis of the molecule. This enables us to examine the behavior of the order parameter  $S$  of the cyanobiphenyl component in the binary mixtures. Since one of the systems studied by us exhibits an induced smectic

A phase, we now make a few remarks on the induced smectic A phase.

### 3.5 THE INDUCED SMECTIC A PHASE

The induced smectic A phase is usually exhibited by mixtures which consist of terminal polar and terminal non-polar compounds, both of which exhibit only a nematic phase in the pure state (Dave et al. 1966, Schroeder and Schroeder 1968, Bock et al. 1976, Heppke and Richter 1978) (see for e.g., Fig.1.7). Park et al. (1975) have suggested that the induced A phase is due to a charge transfer interaction between the components. A charge transfer complex formation takes place between the two kinds of molecules. The highly polar component acting as the acceptor and the other component as the donor. Evidence for the interaction has been detected by an additional absorption band with negative dichroism in the visible/UV spectrum of some mixtures exhibiting the induced smectic A phase (Sharma et al. 1980). The interaction gives rise to a strong lateral attraction between the two types of molecules resulting in a layered arrangement, which is characteristic of smectic phases. The induced smectic A phase is known to have a monolayer structure.

The smectic A phase exhibited by highly polar compounds is of a partial bilayer type, i.e., the layer spacing is considerably greater than the molecular length (Leadbetter 1979). This structure arises due to a strong antiparallel correlation between the neighbouring molecules of terminal polar compounds (Madhusudana and Chandrasekhar 1973). The strongest intermolecular attractions are



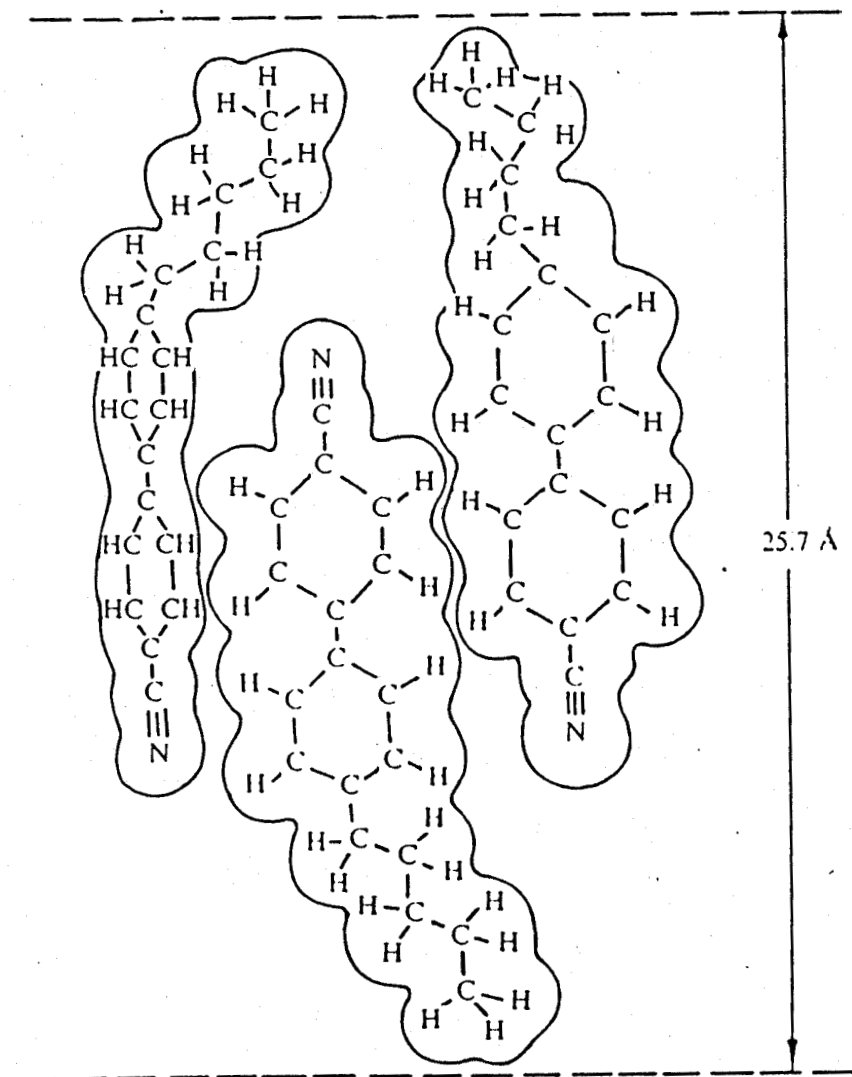
confined to the rigid molecular cores and the additional polar interactions favor an antiparallel orientation. Such a structure leads to the formation of antiparallel pairs. These pairs are more symmetric than the individual molecules which are highly asymmetric due to the presence of the alkyl chain at one end of the aromatic core. Many compounds with strong polar end groups exhibit the smectic A phase (de Jeu 1982). If the chain length is too short to form an A phase, a strong smectic like short range order can be found in the nematic phase. For e.g., Leadbetter et al. (1975) have made X-ray diffraction studies on the pentyl and heptyl cyanobiphenyls both of which exhibit only the nematic phase. These studies indicate that both these materials (particularly heptyl cyanobiphenyl) have a quasi smectic A ordering on a local scale. Fig. 3.4 shows the schematic diagram of antiparallel local structure in pentyl cyanobiphenyl (Leadbetter et al. 1975).

With this background we now discuss our experimental studies. We start with the description of the experimental technique used by us.

### **3.6 EXPERIMENTAL METHOD**

#### **Phase Diagrams**

Specific mixtures for studying the phase diagrams were prepared by the procedure described in Chapter II. The transition temperatures were noted under a Leitz polarising microscope (Model Ortholux II Pol BK) in conjunction with a Mettler hot stage (Model FP-52).



**Figure 3.4**

Schematic diagram of antiparallel local structure in pentyl cyano biphenyl (From Leadbetter et al. 1975).

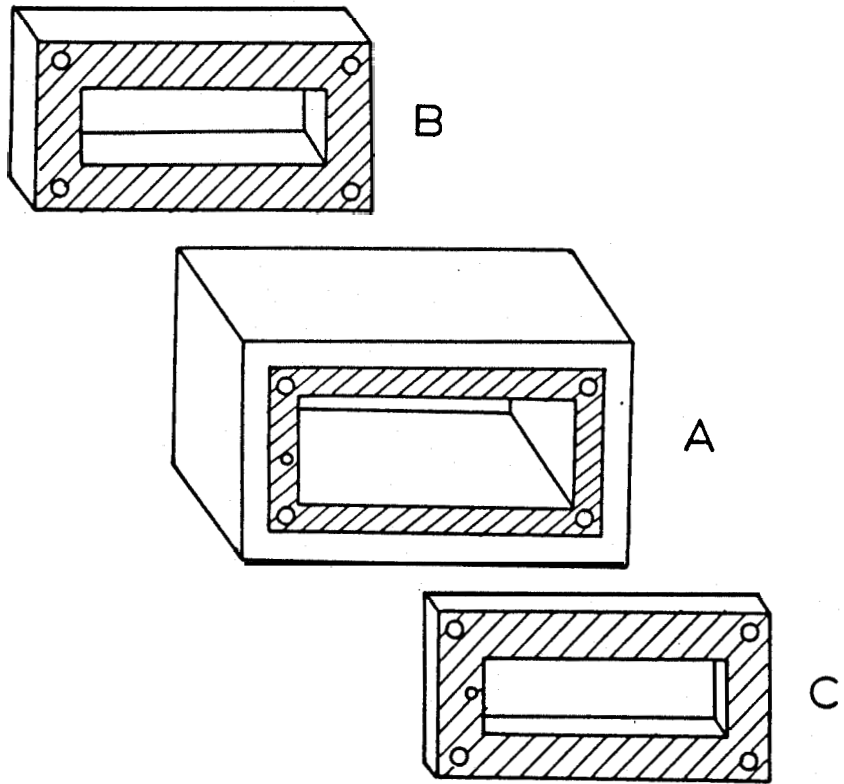
The complete phase diagram involving the determination of the eutectic point, etc., was not investigated as our main interest was in the liquid crystalline phases above the ambient temperature. The samples were not studied below room temperature as the heater used for the Infrared measurements could not be taken to subambient temperatures.

### **The Infrared Cell**

Our studies are concerned with the temperature variation of the order parameters. Hence it was essential to confine the liquid crystal samples in suitable cells whose temperature could be varied. NaCl plates were used as cell windows. These possess good transmission in the required frequency range. They also possess good mechanical and thermal ruggedness. Flat, scratch free windows were obtained by the following procedure. After initial grinding using a saturated solution of NaCl in distilled water, the windows were polished on chamois leather which was held tightly on a glass plate. Red rouge was used as a polishing agent and brine solution served as a lubricant. After the polishing, the surface smoothness was checked by observing the quality of the reflected image - a sharp image over the entire area of the window indicated a well polished surface.

### **Heating System**

The cells were mounted in a suitable heater. The heater consists of a rectangular copper frame A (Fig. 3.5) which is insulated



**Figure 3.5**

Schematic diagram of the heater used in the Infrared studies.

with mica on the sides. Nichrome wire is wound all around it. This is covered with layers of plaster of Paris over which asbestos sheets are placed, in order to reduce heat losses. Another smaller frame B is fixed on one side of the frame A. Frame C is identical to frame B and can be screwed on to frame A after mounting the cell. The widths of the frames B and C are smaller than that of A and the cell can be held firmly within the frame A.

The temperature of the heater can be changed by varying the voltage supplied to it. A regulated DC power supply(Digireg-233) was used for this purpose.

The temperature close to the sample was measured using a copper-constantan thermocouple in conjunction with a voltmeter (Keithley 181 Nanovoltmeter). The hot junction of the thermocouple was inserted through a groove cut in one of the sides in frame A, such that it was in contact with the cell. There was a variation of  $\pm 0.2^{\circ}\text{C}$  within the time required to record the spectrum.

#### **Alignment of the Sample**

Good homeotropic alignment could be obtained for most samples by rubbing the NaCl plates on chamois leather in a random manner. In cases where the rubbing did not give a good alignment a thin film of lecithin was coated on the plates.

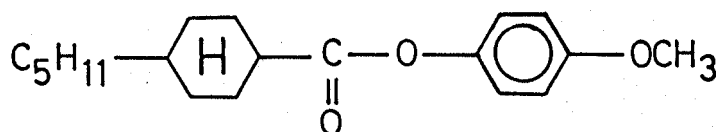
A 23  $\mu\text{m}$  thick mylar spacer was used in the cells. The temperature of the cell was maintained about  $15^{\circ}$  higher than the nematic-

isotropic temperature of the liquid crystal and the sample was allowed to flow into the cells in the isotropic phase. Before placing the heater with the cell in the beam of the spectrophotometer, the alignment in the nematic phase was checked under a polarising microscope.

The spectra were recorded in the isotropic phase (about  $15^\circ$  above  $T_{NI}$ ) and at various temperatures in the liquid crystalline phases using the Infrared spectrophotometer (Shimadzu IR-435). The slit width was chosen such that a good intensity of the band could be obtained. The order parameters of the different mixtures have been plotted as functions of the relative temperatures ( $T_{NI} - T$ ). As there is a small range of coexistence of the isotropic and nematic phases,  $T_{NI}$  in our studies is taken to be the temperature at which the nematic phase just begins as the temperature is lowered from the isotropic phase.

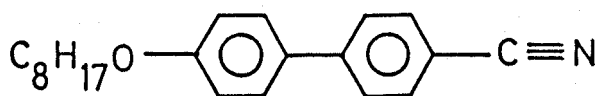
### 3.7 EXPERIMENTAL RESULTS

System I studied by us consists of mixtures of methoxyphenyl-trans-pentyl cyclohexyl carboxylate (MPPC) and 4'-n-octyloxy-4-cyanobiphenyl (8OCB). The structural formulae and transition temperatures of these compounds are shown in Fig. 3.6. As mentioned before the complete phase diagram has not been studied as only the thermal range of the nematic and smectic phases obtained on cooling the sample are of interest. Fig. 3.7 shows the phase diagram which gives the transition temperatures determined on cooling the sample.



Methoxy phenyl trans pentyl cyclohexyl carboxylate ( MPPC)

K 40°C N 71°C I



4'-n - Octyloxy - 4 - cyanobiphenyl ( 80 CB)

K 54.5°C S<sub>A</sub> 67°C N 80°C I

Figure 3.6

Structural formulae and transition temperatures of, the  
compounds MPPC and 80CB (System I).

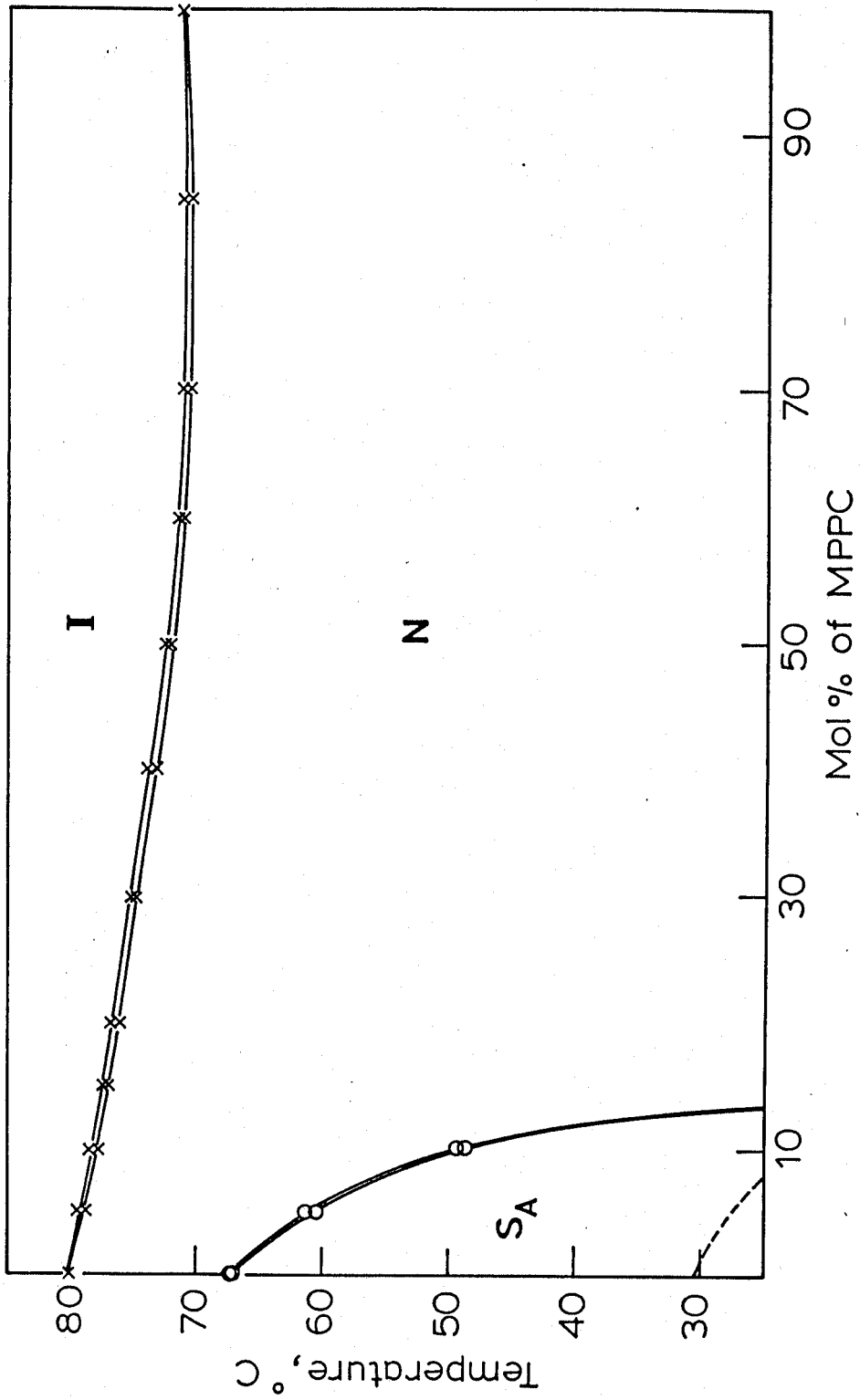


Figure 3.7. Phase diagram of mixtures of MPPC and 80CB (transition temperatures determined on cooling only).



There is a very narrow coexistence range of **I** and **N** phases of about  $0.5^\circ$ . The partial bilayer smectic A phase of the pure 80CB is seen to be suppressed beyond  $-13$  mol % of MPPC. The dotted line indicates the temperatures at which the smectic phase starts crystallising.

As we discussed earlier usually when terminal polar compounds are mixed with non-polar or weakly polar compounds an induced smectic A phase can be expected to occur. However in the temperature range in which we have studied the phase diagram such an induced phase is not found in the present system. The MPPC molecule consists of one cyclohexyl ring and only one phenyl ring. Compared to compounds with 2 phenyl rings there is a decrease in the dipole-induced dipole interactions and charge transfer complexing. Indeed in other binary systems, a reduction in the nematic-smectic A transition temperature is found when one of the benzene rings in the polar component is substituted by a cyclohexyl ring (Moodithaya 1981). Thus one cannot rule out the possibility that the System **I** studied by us also exhibits an induced A phase below room temperature.

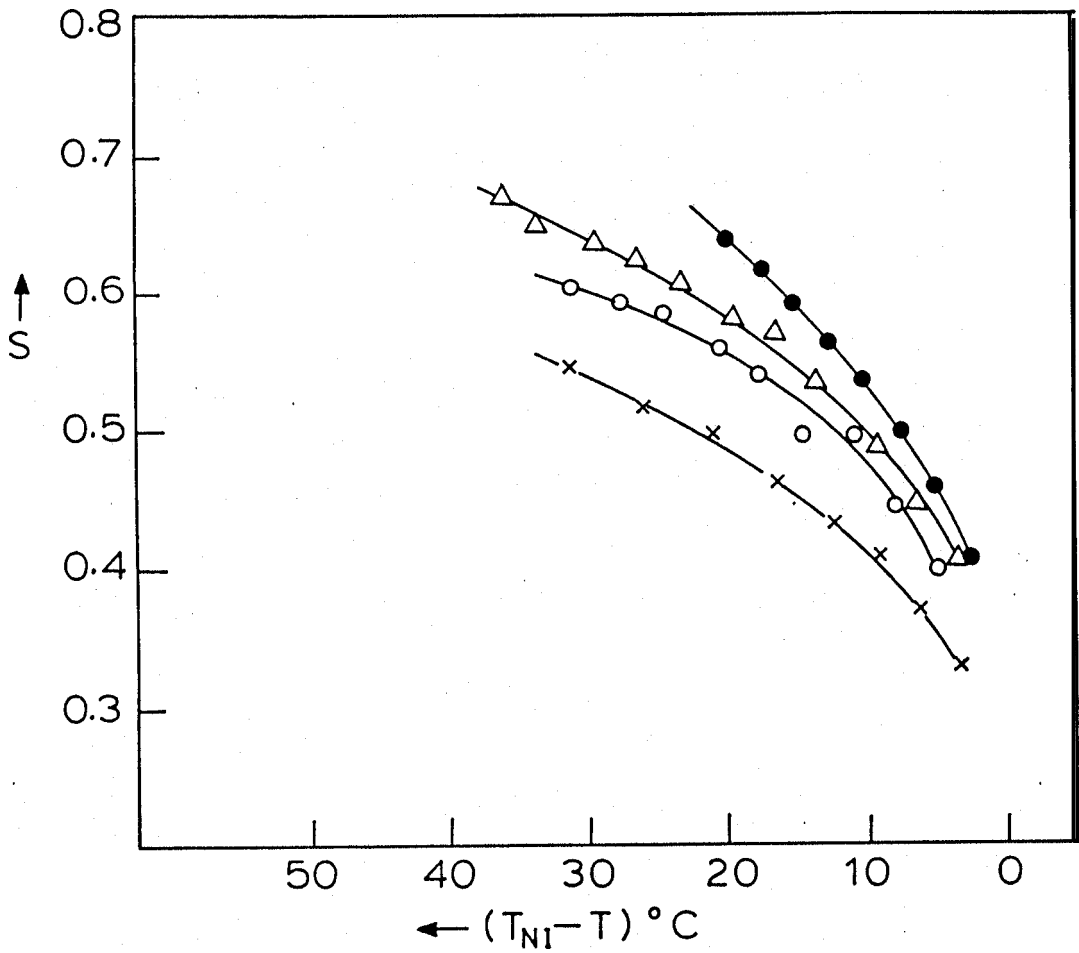
We have studied the Infrared dichroism of the mixtures with 20, 50 and 70 mol % of MPPC. These mixtures exhibit only the nematic phase down to room temperature.

There is a clear reduction in the intensity of the  $C \equiv N$  band from the isotropic to the nematic phase as the orientational ordering sets in. Typical Infrared spectra will be illustrated for the System **II**. In order to decrease errors in the measurement of the

intensities, the wave number corresponding to the peak and the width of the absorption profile at half peak height, the wave number scale was expanded. A slit width of 0.15 mm was found to give a good absorption peak for the  $C \equiv N$  stretching band and the peak was found to correspond to a value of  $2228 \text{ cm}^{-1}$ .

The order parameter  $S$  of 80CB as a function of temperature in the three mixtures and that of pure 80CB as measured by Prasad and Venugopalan (1981) by the same technique, have been shown in Fig. 3.8. Pure 80CB is seen to have the highest order parameters. An addition of 20 mol % of MPPC decreases the orientational order parameter considerably. Further addition of MPPC is found to again increase the value of  $S$ . In Fig. 3.9 we have plotted the variation of  $S$  with concentration of MPPC at three relative temperatures. The results can be interpreted as follows.

In the theory of Palffy-Muhoray et al. the order parameters of the components at any temperature in the nematic range of the mixture are found to be different as shown by the curves drawn for  $S_1$  and  $S_2$  in Fig. 3.3a. Indeed the component order parameter of the longer molecule can be expected to be higher than that of the shorter molecule purely for geometrical reasons. It is easier for the shorter molecules to have orientational fluctuations and hence a lower order parameter. This is known from experimental studies on the order parameters of anisotropic dye molecules dissolved in various nematic hosts (Saunders et al. 1984).



**Figure 3.8**

Variation of the order parameter  $S$  of 80CB as a function of the relative temperature.

- : pure 80CB
- x : Mixture with 20 mol % of MPPC
- : Mixture with 50 mol % of MPPC
- △ : Mixture with 70 mol % of MPPC.

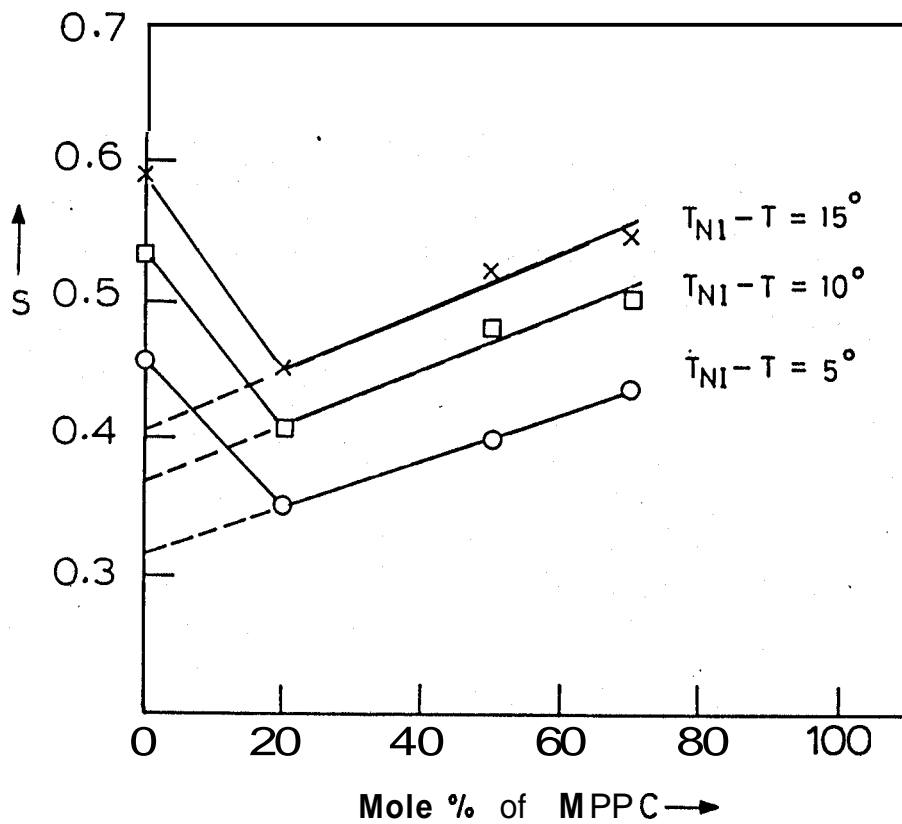


Figure 3.9

Variation of the order parameter  $s$  as a function of the concentration of MPPC, at three relative temperatures.

We have calculated the molecular lengths ' $l$ ' of 80CB and MPPC using the Dreiding models.  $l = 20.9 \text{ \AA}$  for 80CB and is equal to  $19.5 \text{ \AA}$  for MPPC. Therefore the component order parameter of 80CB can be expected to be somewhat higher than that of MPPC. Following the theoretical prediction (Fig. 3.3a) its value should increase as the concentration of 80CB in the mixture decreases. At any given relative temperature the part of the curve for a concentration  $>20 \text{ mol } \%$  of MPPC shows a variation almost similar to the theoretical result given by Palffy-Muhoray et al. (Fig. 3.3a) increasing practically linearly with the concentration of MPPC. However pure 80CB exhibits a relatively high value of  $S$  compared to the value linearly extrapolated from the order parameters of mixtures with  $>20 \text{ mol } \%$  of MPPC. The values of the order parameter in the mixtures correspond to the component order parameters of 80CB which occurs as individual molecules, or, if there is a weak charge transfer interaction with MPPC, has an essentially monolayer type of cybotactic structure. If these curves are extrapolated to  $0 \text{ mol } \%$  of MPPC (i.e., pure 80CB) as indicated by dashed lines the values obtained are much lower than that obtained by experiments. According to the Maier-Saupe theory which does not take into account the geometrical anisotropy of the molecule, the order parameters of the pure components have a universal value at  $T_{NI}$ . The theoretical curves (Fig. 3.3a) of the component order parameters have been derived by a generalisation of the Maier-Saupe theory.

Due to antiparallel correlations, 80CB 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 (Leadbetter 1975). Theories which take into account the geometrical anisotropy of molecules predict that the order parameter at  $T_{NI}$  increases weakly as the length to breadth ratio is increased (Savithramma and Madhusudana 1980). Even though the 80CB dimer has a length 1.4 times the molecular length, the average breadth of the dimer has also increased by a similar amount and the length to breadth ratio of a dimer is not very different from that of a monomer. Thus the origin of the increase in the order parameter of pure 80CB is not due to an increase in length due to the formation of dimers. We note that 80CB exhibits both nematic and smectic A phases. McMillan (1971) extended the Maier-Saupe theory of the nematic phase to smectic liquid crystals taking into consideration the translational order of the latter. Assuming that in the smectic phase the orientational and translational orders are coupled he showed that the orientational order parameter is enhanced in the smectic A phase compared to the Maier-Saupe value.

In the Landau type phenomenological theory later developed by de Gennes (1973) a similar assumption is made about the enhancement of  $S$  in the smectic A phase. If the orientational order in the nematic phase is given by  $S_o(T)$ , in the smectic phase there is a coupling between the strength of the smectic order denoted

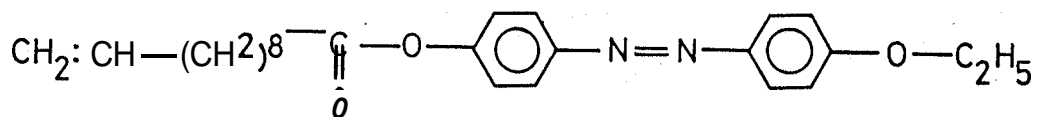
by  $\Psi$  and  $S$ . If the alignment measured by  $S$  increases, the average attractions between neighbouring molecules in a smectic layer also increases. This enhancement of  $S$  in the smectic phase has been confirmed experimentally (Doane et al. 1972 and Fernandes and Venugopalan 1979). But the above mean field theories do not predict any enhancement of the orientational order parameter in the nematic phase exhibited by the smectogenic compounds compared to the Maier-Saupe value. None of the mixtures of 80CB and MPFC studied by us exhibits a smectic A phase at least down to room temperature. Hence the value of  $S$  of pure 80CB extrapolated from those of the mixtures, as shown by the dashed line (Fig. 3.9) corresponds to the orientational order parameter of a hypothetical 80CB which exhibits only a nematic phase, but not a smectic A 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 Fig. 3.8 it is clearly seen that the order parameter curve in the nematic phase of pure 80CB, which exhibits a smectic A phase at a lower temperature rises more steeply with decrease in temperature than the curves for the three mixtures which do not have any smectic phase down to room temperature.

System 11 studied by us consists of mixtures of 4-(4'-ethoxy-

phenylazo)phenyl undecylenate (EPPD) and heptyl cyano biphenyl (7CB). Both the compounds exhibit only the nematic phase in the pure state. The structural formulae and transition temperatures of the compounds are given in Fig. 3.10. The binary system exhibits an induced smectic A phase. Fig.3.11 shows the phase diagram which gives the transition temperatures determined on cooling the sample. As in system I the complete phase diagram has not been studied and only the thermal range of nematic and smectic phases useful in the Infrared studies have been indicated. As the sample was cooled from the I phase a small coexistence of the I and N phases extending over 2-3° was observed before the entire sample was transformed to the nematic phase. A slight maximum is present in the I - N coexistence curve. 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 mol % of EPPD. The smectic phase obtained on further cooling starts crystallising at temperatures of 15 - 18° below that at which the whole sample goes over to the smectic A phase. The dotted lines in Fig. 3.11 indicate the temperatures at which the crystallisation begins. In particular we have made measurements of Infrared dichroism on mixtures with 20, 50 and 70 mol % of EPPD.

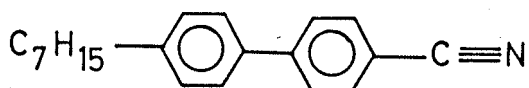
Typical spectra recorded in the isotropic, nematic and smectic phases for the mixture 7CB : EPPD (30 : 70 mol %) are shown in Fig.





p-p'-Ethoxyphenyl azo) phenyl undecylenate (EPPD)

K 65.3°C N 108.1°C I

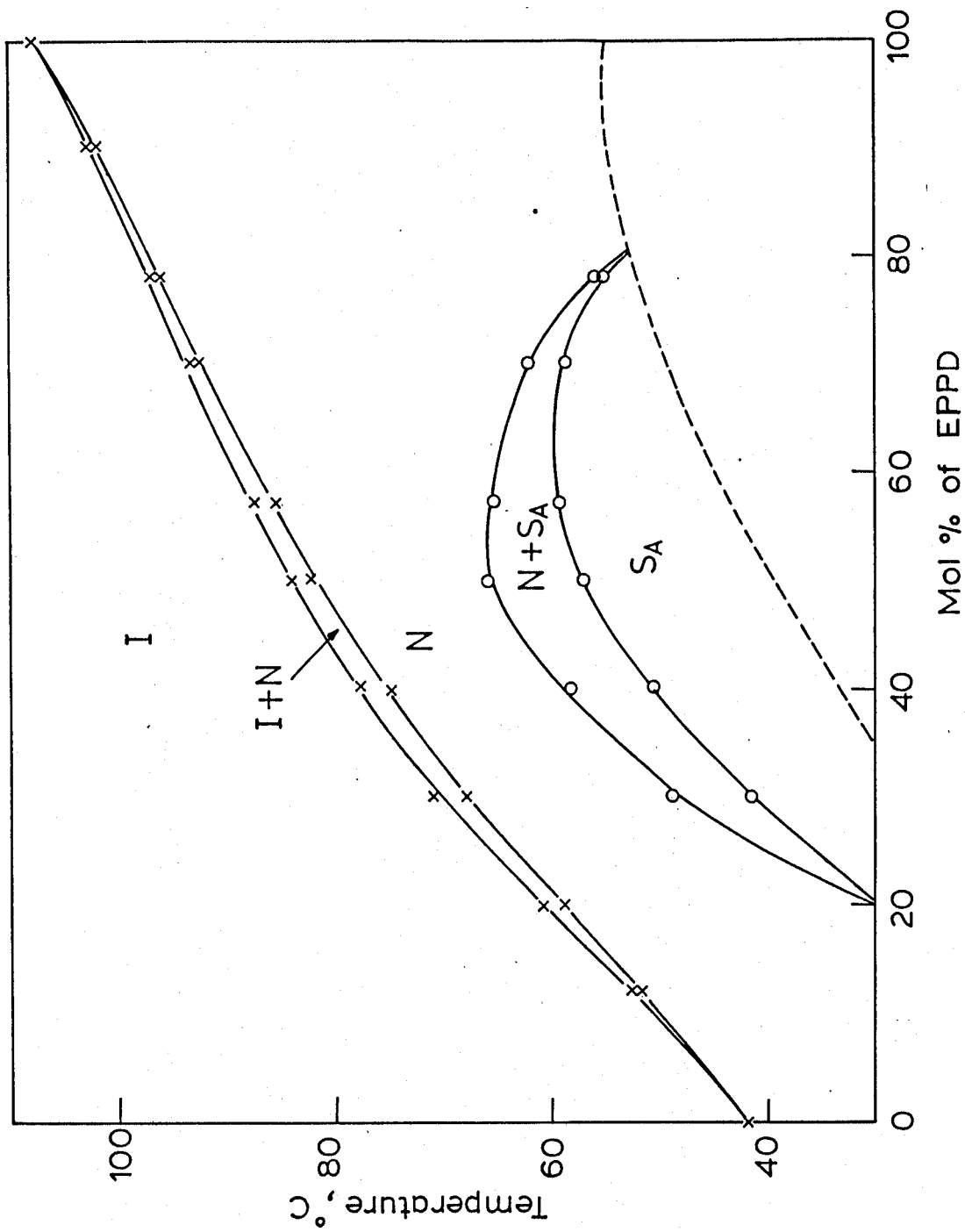


4'-n-heptyl-4-cyanobiphenyl (7CB)

K 28.5°C N 41.8°C I

Figure 3.10

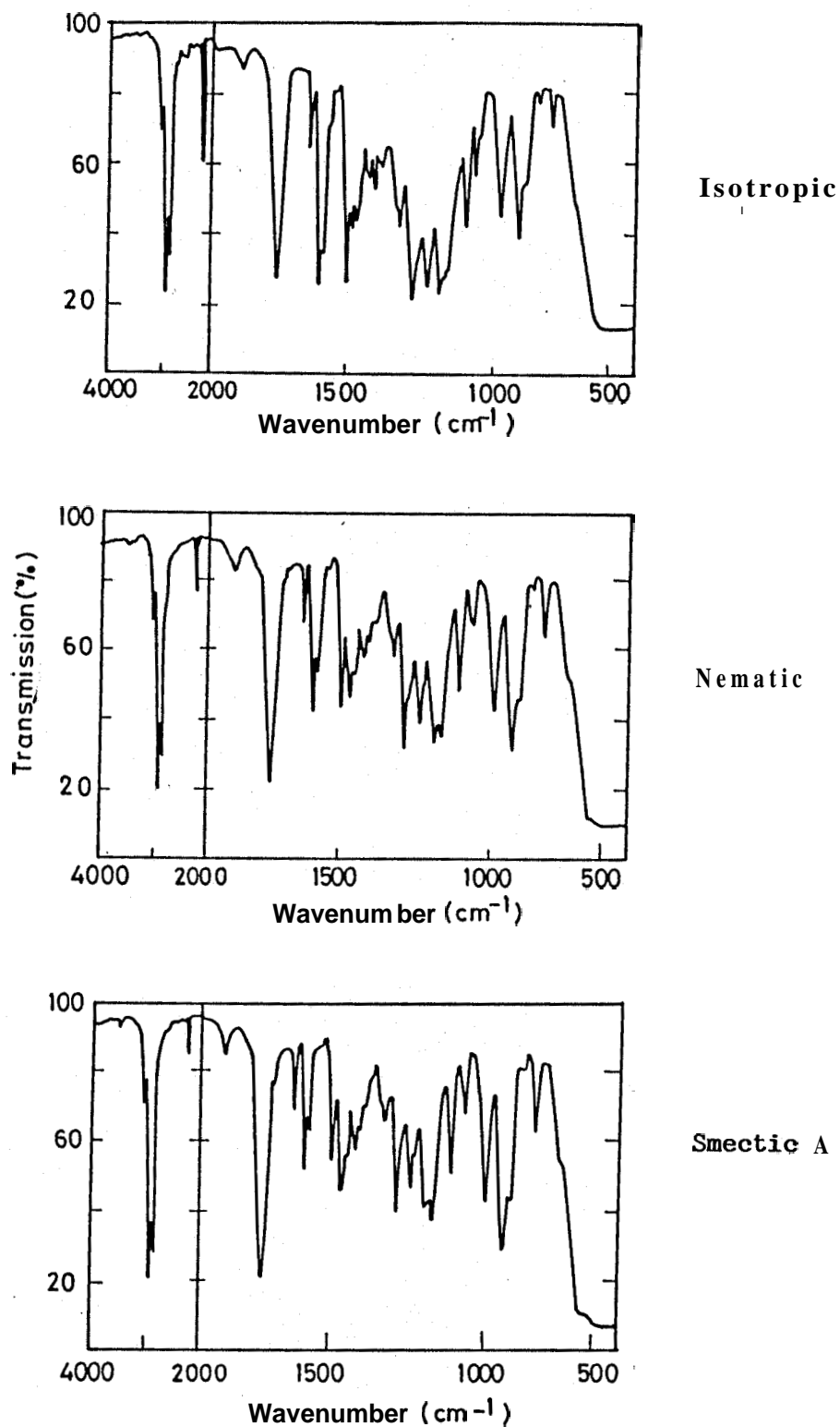
Structural formulae and transition temperatures of the compounds  
EPPD and 7CB (System II).



**Figure 3.11.** Phase diagram of mixtures of EPPD and 7CB. (Transition temperatures determined on cooling).

3.12. The variation of the intensity of the  $C\equiv N$  band in the three phases can be clearly seen. As mentioned before the wave number scale has been expanded for reducing the errors in measurement (Fig. 3.13). The variation with temperature of the order parameter  $S$  of 7CB in the three mixtures mentioned before, along with the values of  $S$  obtained by the same technique for pure 7CB by Prasad and Venugopalan (1981) have been shown in Fig. 3.14. A considerable increase in the values of  $S$  in the smectic A phase is observed for mixtures with 50 and 70 mol % of EPPD. When only 20 mol % of EPPD is added to 7CB the order parameter at any relative temperature is seen to drop to values lower than that of pure 7CB. On the other hand addition of 50 mol % of EPPD gives rise to a large increase in the value of the order parameter. Further addition of EPPD again lowers the values of  $S$ . The order parameters of 7CB, at specific relative temperatures as a function of the concentration of EPPD are shown in Fig. 3.15.

In order to interpret these results as in the previous case let us first compare the molecular lengths ' $l$ ' of the two types of molecules. 7CB has an  $l \approx 19.2 \text{ \AA}$  and EPPD  $\approx 28.2 \text{ \AA}$  as measured using Dreiding models. Therefore the order parameter of 7CB which is composed of shorter molecules can be expected to be lower than that of EPPD in the mixture. Indeed when a small amount of EPPD ( $\sim 20$  mol %) is added to the pure 7CB the value of  $S$  does decrease in agreement with the theoretical prediction (see Fig. 3.3a). The



**Figure 3.12**

Typical spectra. in the isotropic, nematic and smectic A phases for the mixture with 70 mol % of EPPD.

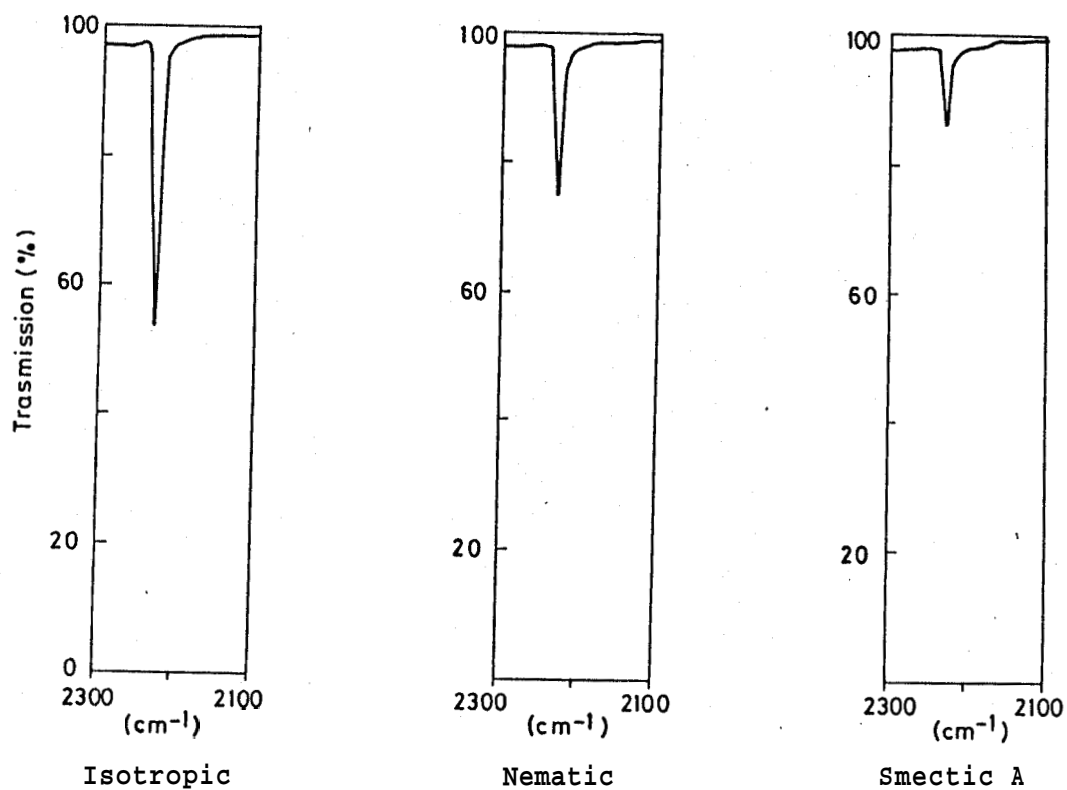


Figure 3.13

Spectra of the cyano band in the isotropic, nematic and smectic A phases. The wave number scale has been expanded (x4).

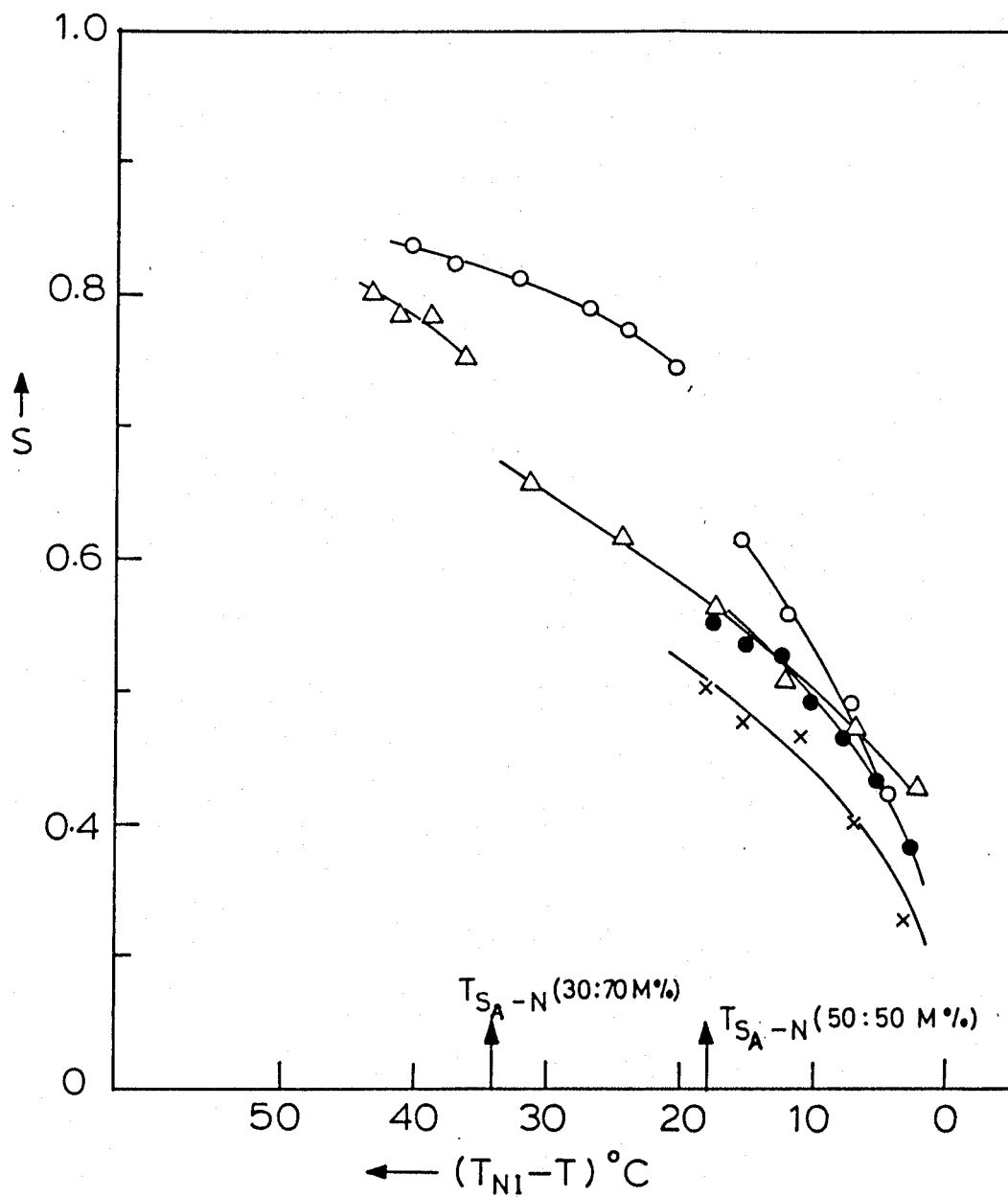
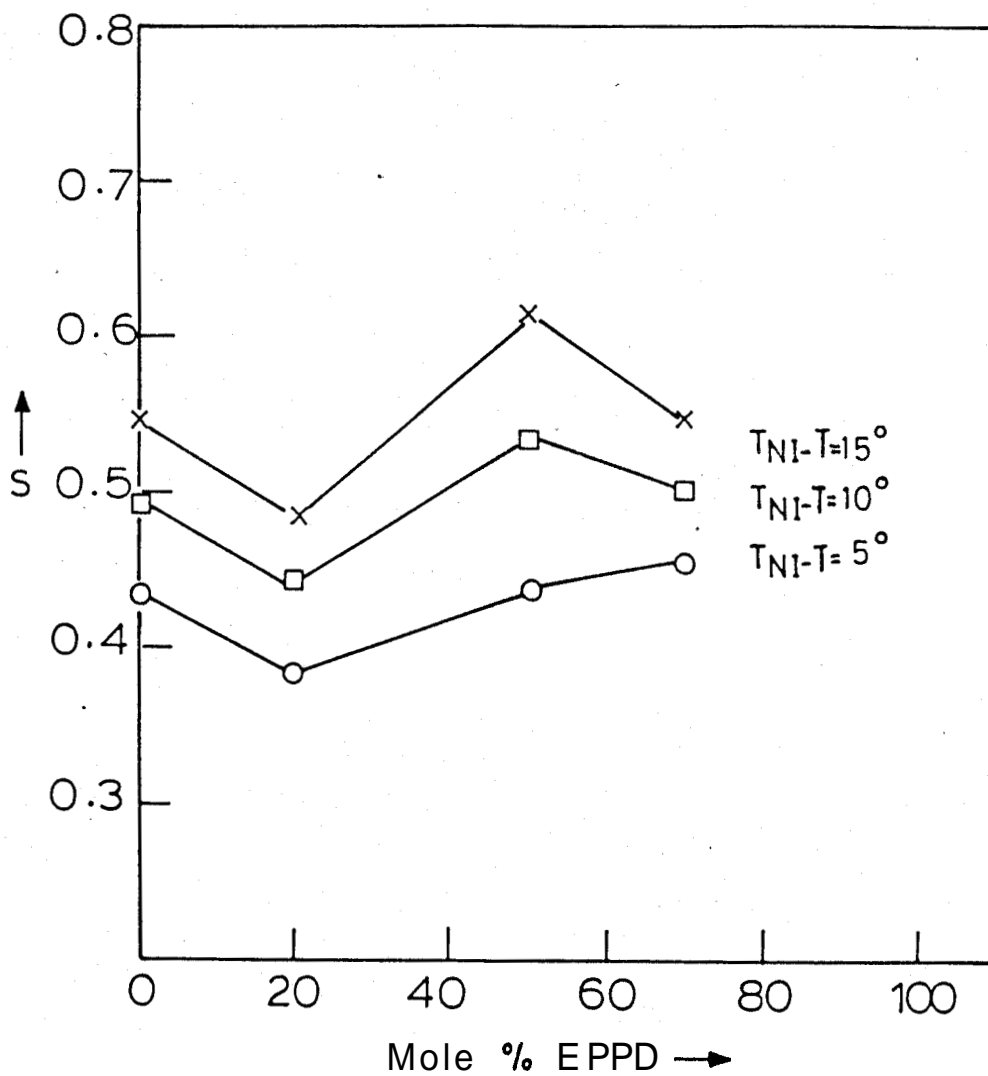


Figure 3.14

Variation of the order parameter  $S$  of 7CB as a function of the relative temperature.

- : pure 7CB
- x : Mixture with 20 mol % of EPPD
- : Mixture with 50 mol % of EPPD
- △ : Mixture with 70 mol % of EPPD.



**Figure 3.15**

Variation of the order parameter  $s$  as a function of the concentration of EPPD at three relative temperatures.

order parameter of pure 7CB can however be enhanced for yet another reason discussed below.

Like 8OCB, 7CB is a highly polar compound with a central aromatic core which is quite rigid. As mentioned earlier an antiparallel arrangement of molecules is favoured in this compound also, leading to the formation of antiparallel pairs. 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 Ceadbetter et al. (1975) found that  $\sim 150$  7CB molecules form smectic-like cybotactic groups. As we have discussed for System I, the smectic-like short range order can increase the orientational order parameter of 7CB in the nematic phase.

When about 20 mol% of EPPD is added to 7CB an induced smectic A phase with a monolayer structure is obtained below room temperature. This means that the partial bilayer smecticlike short range order of 7CB is completely lost in this mixture. The induced smectic-like short range order does not appear to be strong enough to enhance the S value of 7CB for this composition. As the concentration of EPPD is increased from 20 to 70 mol % there is an overall increase in the value of S (Fig. 3.14). From the phase diagram (Fig. 3.11) we see that  $T_{AN}^u$  (the upper temperature limit of the coexistence of the nematic and induced smectic phases) peaks around 50 mol % of EPPD and is equal to 65.5°C. Though  $T_{AN}^u$  (= 62.5°C) for the mixture with 70 mol % of EPPD is lower than that of the 50 mol % mixture, it is still higher than that of the 20 mol % mixture



(for which  $T_{AN}^u$  is below room temperature  $\approx 30^\circ\text{C}$ ). Indeed the  $S$  of 7CB for a relative temperature  $T_{NI} - T = 15^\circ$  shows an exactly similar trend (see Fig. 3.15), i.e.,  $S_{50} > S_{70} > S_{20}$ , where the subscript denotes the concentration of EPPD in the mixture.

As the temperature is increased the enhancement in the value of  $S$  for the mixture with 50 mol % of EPPD decreases. The dependence of  $S_{7CB}$  on composition is almost linear for a relative temperature of  $T_{NI} - T = 5^\circ$  (Fig. 3.15). In fact this can also be seen in System I (Fig. 3.8). 80CB which exhibits a smectic A phase has the strongest variation of the orientational order parameter in the nematic phase.

We could expect a rapid decrease in the smectic-like short range order above  $T_{AN}^u$  in the 50 % mixture (or  $T_{AN}$  in 80CB). The enhancement of the orientational order  $S$  due to the smectic-like short range order also would decrease rapidly with increase of temperature, as seen in the experiment. Indeed measurements of integrated intensities of diffuse X-ray scattering profiles above  $T_{AN}$  clearly demonstrates the decrease of the smectic-like short range order above  $T_{AN}$  (Chan et al. 1985). While this reduction of the short range order should make an important contribution to the rapid reduction of  $S_{50}$ , we feel that another possible contributory mechanism can also be noted. The elastic constant ratio  $K_{33}/K_{11}$  above  $T_{AN}^u$  of another binary mixture exhibiting the induced smectic A phase shows a very remarkable trend (Madhusudana and Moodithaya 1983). At temperatures just above  $T_{AN}^u$ ,  $K_{33}/K_{11}$  attains

large values as the bend elastic constant is enhanced due to smectic-like short range order. The ratio decreases with the strength of the short range order at higher temperatures and actually takes values  $< 1$  at higher temperatures. This has been attributed by the authors to a reduction of  $\xi_{||}/\xi_{\perp}$ , the ratio of the correlation lengths  $||$  and  $\perp$  to the director of regions with smecticlike short range order at higher temperatures. Again, X-ray studies on a monolayer compound, viz., N-[4-(n-butyloxy)benzylidene]-4'-(n-heptyl)aniline (Garland et al. 1983) have shown that  $\xi_{||}/\xi_{\perp}$  decreases from 22 to 11 in just  $3^{\circ}$  above  $T_{AN}$ , while the molecular length to breadth ratio  $\approx 7$ . The reduction of  $K_{33}/K_{11}$  to values  $< 1$  in the mixtures exhibiting induced smectic A phase shows that in these,  $\xi_{||}/\xi_{\perp}$  must be quite low. The smectic-like cybotactic groups can thus have lower shape anisotropy which allow them to have orientational fluctuations relatively easily. This could of course reduce the measured orientational order parameter. We can thus expect that both the decrease of smectic-like short range order and that of  $\xi_{||}/\xi_{\perp}$  at higher temperatures reduce the  $S_{50}$  considerably at higher temperatures and lead to the trends shown in Fig. 3.15.

### 3.8 CONCLUSION

The order parameters of two cyanobiphenyls in several mixtures belonging to two binary systems were measured using the Infrared dichroism method. In System I, all the mixtures for which the order parameters have been measured exhibit only the nematic phase down

to room temperature. The variation of the order parameter of 8OCB in the mixtures has a trend similar to the theoretical curves of Palffy-Muhoray et al. However, the experimentally measured values of  $S$  in the nematic range of pure 8OCB which exhibits a smectic A phase are much higher than that got by extrapolation of the values obtained in the mixtures. This enhancement in the orientational order parameter is due to the smectic-like short range order present in 8OCB which has a partial bilayer structure. Mixtures of the second system show an induced smectic A phase even though the pure components exhibit only the nematic phase. Because of the presence of the induced smectic A phase there is an increase in the smectic-like short range order at lower temperatures in the nematic range of such systems. This enhances the value of the orientational order parameter  $S$ . But at temperatures close to  $T_{NI}$ , the smectic-like short range order decreases as also evidenced by X-ray scattering measurements on other systems. This leads to a reduction in the enhancement of the value of  $S$  at higher temperatures. Another contributory factor for this reduction could be due to a decrease in the value of the ratio  $\xi_{||} / \xi_{\perp}$ , thus reducing the geometrical anisotropy of the cybotactic groups. We have quoted evidences of such a decrease by both X-ray studies on a monolayer compound exhibiting the smectic phase and also by a strong reduction in the ratio of  $K_{33}/K_{11}$  in another system exhibiting the induced smectic A phase.

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