

## CHAPTER III

## DISCUSSION

III.1 General Theoretical Considerations

A theory of the optical birefringence of nematic liquid crystals has been developed in terms of the intermolecular interactions. When there are more than one component in a system, however, the interactions between the various molecules can arise from so many different contributions. Clearly, the interactions between molecules of the same kind ~~must differ from~~ those between molecules of different kinds. Chandrasekhar et al.<sup>1</sup> have classified the intermolecular interactions as consisting of the dipole-dipole, anisotropic dispersion, induction, and repulsion interactions.

Chatelain and Pellet<sup>2,3</sup> have given a theoretical interpretation of the values of the ordinary and extraordinary refractive indices of a nematic liquid crystal involving the polarizability of molecules. Under the assumptions that there were spherical regions in the nematic melt, and the molecules on the surface of each sphere had a random orientation with respect to the molecule at the center of the sphere, they have shown that

$$\frac{n_e^2 - 1}{n_e^2 + 2} + 2 \frac{n_o^2 - 1}{n_o^2 + 2} = \frac{4\pi}{3} N (A + B + C) \dots\dots\dots (1)$$

<sup>1</sup> S. Chandrasekhar, D. Krishnamurti and N. V. Madhusudana, Mol. Cryst. Liquid Cryst., 8 (1969), 45

<sup>2</sup> P. Chatelain and O. Fellet, Bull. Soc. Franc. Minéral. Cryst., 73 (1950), 154

<sup>3</sup> P. Chatelain, Bull. Soc. Franc. Minéral. Cryst., 78 (1955), 262

where  $N$  is the number of molecules per unit volume, and  $A$ ,  $B$  and  $C$  are their principal polarizability components. This equation satisfies Born's relation;

$$\frac{1}{3\rho} \left[ \frac{n_e^2-1}{n_e^2+2} + 2 \frac{n_o^2-1}{n_o^2+2} \right] = \frac{1}{\rho_i} \frac{n_i^2-1}{n_i^2+2} \dots\dots\dots (2)$$

where  $\rho$  and  $\rho_i$  are respectively the densities of the liquid crystal and the isotropic liquid,  $n$  the refractive index, the suffixes  $e$ ,  $o$  and  $i$  denoting extraordinary, ordinary and isotropic.

In the case of a similar orientation of the molecules on the surface of the sphere with respect to the central molecule, Chatelain and Pellet<sup>4</sup> gave the relation between the effective polarizabilities  $A'$ ,  $B'$ ,  $C'$  and  $A$ ,  $B$ ,  $C$  as

$$n_e^2 - 1 = 4\pi N \left[ C' - \left( C' - \frac{A'+B'}{2} \right) I_3 \right] = 4\pi N \alpha'_z$$

$$n_o^2 - 1 = 4\pi N \left[ \frac{A'+B'}{2} + \frac{1}{2} \left( C' - \frac{A'+B'}{2} \right) I_3 \right] = 4\pi N \alpha'_x$$

where

$$A' = A \left( 1 - \frac{4\pi N A}{3} \right)^{-1}$$

$$B' = B \left( 1 - \frac{4\pi N B}{3} \right)^{-1}$$

$$C' = C \left( 1 - \frac{4\pi N C}{3} \right)^{-1}$$

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<sup>4</sup> P.Chatelain and O.Pellet, Bull.Soc.Franc.Minéral.Cryst., 73 (1950), 154

In general, the effective molecular polarizability in the direction parallel or perpendicular to the optic axis, viz.;  $\alpha'_{\parallel}$  or  $\alpha'_{\perp}$  may be taken to be of the form

$$\alpha'_{\parallel} = \alpha_{\parallel} (1 - P_1 N \alpha_{\parallel})^{-1} \quad \text{or} \quad \alpha'_{\perp} = \alpha_{\perp} (1 - P_2 N \alpha_{\perp})^{-1}, \quad \text{respectively,}$$

where  $P_1$  and  $P_2$  are not necessarily equal to  $4\pi/3$  as given in the Lorentz-Lorenz relation. Chandrasekhar et al<sup>5</sup> have shown that

$$n_e^2 - 1 = 4\pi N \left[ \alpha'_{\parallel} + \frac{(\alpha'_{\parallel} - \alpha'_{\perp})}{2} \left( \frac{2h_1^2}{45} + \frac{4h_2^2}{45} + \frac{8h_2^2}{945} + \frac{8h_4^2}{105} + \dots \right) \right] \dots \textcircled{3}$$

$$n_o^2 - 1 = 4\pi N \left[ \alpha'_{\perp} - \frac{(\alpha'_{\parallel} - \alpha'_{\perp})}{2} \left( \frac{2h_1^2}{45} + \frac{4h_2^2}{45} + \frac{8h_2^2}{945} + \frac{8h_4^2}{105} + \dots \right) \right] \dots \textcircled{4}$$

where  $\alpha_{\perp} = \frac{A+B}{2}$ ,  $\alpha_{\parallel} = C$ ,  $\alpha = (\alpha_{\parallel} + 2\alpha_{\perp})/3$ ,  $h_1 = u_1/kT$ ,

$h_2 = u_2/kT$ , etc., and  $u_1, u_2$  etc. are the contributions of dispersion effects of successively higher order to the molecular interactions. Therefore, equation (2) will be only approximately satisfied. It is seen that the extraordinary index consists of a sum of two terms both of which diminish with temperature. On the other hand the ordinary index consists of difference of two similar terms. They also observed the fact that  $dn_e/dT$  is large and negative and  $dn_o/dT$  comparatively small and positive. Equations (3) and (4) then lead to

$$n_e^2 - n_o^2 = 4\pi N (\alpha'_{\parallel} - \alpha'_{\perp}) \left( \frac{h_1^2}{15} + \frac{2h_2^2}{15} + \frac{4h_2^2}{315} + \frac{4h_4^2}{35} + \dots \right) \dots \textcircled{5}$$

<sup>5</sup> S.Chandrasekhar, D.Krishramurti and N.V.Madhusudana, Mol. Cryst. Liquid Cryst., 8 (1969), 45

Chandrasekhar et al<sup>6</sup> have drawn some important conclusions regarding the relative contributions of the different forces to the optical birefringence of nematic liquid crystals. In particular, they have found that the temperature variation of the birefringence is determined mainly by the repulsion and dispersion forces.

The temperature dependence of  $n_e$  and  $n_o$  and the different temperature coefficients of double refraction in the several liquid crystals can be explained in terms of their structures. According to the Lorentz-Lorenz formula,

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} \frac{\rho}{M} N\alpha$$

the refractive index is dependent on the density  $\rho$  and the polarizability  $\alpha$ . In a liquid crystal,  $n_e$  is determined by the mean value of the polarizability parallel to the optic axis ( $\bar{\alpha}_{\parallel}$ ) of a homogeneously oriented uniaxial sample,  $n_o$  is determined by the mean polarizability perpendicular to the optic axis ( $\bar{\alpha}_{\perp}$ ). The magnitude of double refraction is determined by the mean polarizability anisotropy ( $\bar{\alpha}_{\parallel} - \bar{\alpha}_{\perp}$ ).

When the temperature increases, the  $\alpha_{\parallel}$  decreases whereas the  $\alpha_{\perp}$  increases. Since the density also decreases with rising temperature, so  $n_e$  and the double refraction ( $n_e - n_o$ ) generally diminish with rising temperature. On the other hand  $n_o$  can either increase or decrease. It is clear that the temperature change of  $\bar{\alpha}_{\perp}$  is larger than that of the density. The temperature change of density largely determines the negative temperature coefficient of  $n_o$ .

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<sup>6</sup> S.Chandrasekhar, D.Krishnamurti and N.V.Madhusudana, Mol., Cryst. Liquid Cryst., 8 (1969), 45

Further theoretical investigations of the variation of the refractive indices and birefringence of nematic liquid crystals have been made by Chandrasekhar et al<sup>7</sup>. In particular, an explanation has been given for the rapid variation of  $n_e$  and relatively slow variation of  $n_o$  with changing temperature.

### III.2 Discussion of Experimental Results

From the experimental data, it is shown that the ordinary refractive indices are only slightly dependent on temperature. The temperature variation of the birefringence in this observation agrees well with that obtained in previous investigations, that is, the birefringence falls rapidly as the temperature increases. The isotropic transition temperatures of the nematic mixtures investigated are in the range between the nematic-isotropic transition temperatures of their pure components.

The relationships between the extraordinary index, the ordinary index and the relative temperature agree qualitatively with the previous conclusions from the experimental results of Brunet-Germain only in the cases of the binary mixtures of PAA and PHAB ; and PAA and BEPCPC. But in the cases of the binary mixtures of MBAPA and EPPU ; and the mixtures of BEPCPC and EPP-Hep , the relationships between the extraordinary index , the ordinary index and the relative temperature the situations are different. The curves of the extraordinary index and of the ordinary index of mixtures of various compositions of EPPU and MBAPA are between the curves of the indices of pure EPPU and MBAPA , but are not arranged in an orderly manner. In the mixtures of BEPCPC and EPP-Hep , the extraordinary refractive indices of the pure nematic liquid crystals at the same relative temperature are nearly identical ; so the relationship between the extraordinary index and the relative temperatures at various

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<sup>7</sup> S.Chandrasekhar, D.Krishnamurti and N.V.Madhusudana, Mol. Cryst. Liquid Cryst., 8 (1969), 45

compositions are not arranged between those of the pure substances.

The contours of the extraordinary refractive indices in the temperature-composition plane of the systems PAA:PHAB and PAA:BEPCPC are qualitatively similar to those reported by Leelaprute<sup>8</sup> for other binary systems. But those for the systems EPPU:MBAPA and BEPCPC:EPP-Hep are quite different. In the system EPPU:MBAPA, the contour lines drop at the composition of 0.45 mole fraction of EPPU and then rise up and each has a highest point at the composition of 0.75 mole fraction of EPPU. In the system BEPCPC:EPP-Hep, the values of the extraordinary refractive indices rise up at the composition of 0.10 mole fraction of BEPCPC and drop at the composition of 0.48 mole fraction of BEPCPC.

In the system PAA:PHAB, the structural formulae of the constituent compounds are very similar and differ only in the number of carbon atoms in their side chains. The refractive indices of their mixtures agree quite well with the relations expressed by Chatelain and Brunet-Germain.

In the system PAA:BEPCPC, the nematic range is very narrow when the amount of PAA increases, especially in the range 50-80 mole percent PAA. Furthermore, it was found that at the temperature near the nematic-isotropic transition temperature, the two spectral lines of ordinary and extraordinary rays gradually blurred and finally disappeared at a few degrees below the transition temperature. When the temperature was raised further the isotropic spectrum slowly appeared. This effect is presumably due to the strong scattering of light by the irregular alignment of molecules near the transition temperature. From Table 3, it can be seen that

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<sup>8</sup> S. Leelaprute, Refractivity of Nematic Liquid Crystals., M.Sc. Thesis, Department of Chemistry, Mahidol University, Bangkok, Thailand, 1972.

the refractive indices of BEPCFC are lower than those of PAA at the same relative temperatures. This can be explained by the fact that the net dipole moment of the PAA molecule is larger than that of the BEPCFC molecule, so that the polarizability in the direction parallel to the long axis is also larger whereas the polarizability in the direction perpendicular to the long axis is less than that of BEPCFC. This implies that the refractive indices of PAA are higher than those of BEPCFC.

In the system EPP-Hep:BEPCFC, the refractive indices of EPP-Hep are higher than those of BEPCFC. From Fig.17, giving the contours of the extraordinary refractive indices, we see that the contour lines drop at the composition 0.48 mole fraction of BEPCFC, and from the Fig.21, showing the perspective plots of the refractive indices  $n_e$ ,  $n_o$  and  $n_i$  at different compositions and temperatures, the graphs have minima at the composition of 0.48 mole fraction of BEPCFC. This can be explained as follows. The existence of this point may be due to the correlation of the average intermolecular interaction, and the cis-trans isomerization of EPP-Hep and BEPCFC. It is well known that many of the trans-isomers could easily change into the corresponding cis-isomers, which would cause a decrease in the polarizability<sup>9</sup>. In each molecule, the dipole moment consists of two main components. In the cis-isomers they make an angle to each other, whereas in the trans-isomers they are oriented nearly parallel. Thus the dipole moment of the trans-isomers should be larger than that of the cis-isomers, which would lead to a lower polarizability of the cis-form. Therefore, the polarizability at this composition should be lower than that of its neighbouring one, and hence the contours of

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<sup>9</sup> L.Pdungsap, Phase Equilibria of Mixed Liquid Crystals, M.Sc. Thesis, Department of Chemistry, Mahidol University, Bangkok, Thailand, 1972.

the extraordinary refractive indices in the temperature-composition plane would drop at this composition.

In the last system EPPU:MBAPA, the refractive indices of EPPU at various temperatures are lower than those of MBAPA, and this can be explained in the following way. Since the  $\pi$ -electrons of the benzene rings can be easily dislocated or polarized, the refractive indices should depend on the number of benzene rings per unit volume. Each molecule contains two benzene rings, but EPPU has a longer chain-length than MBAPA. (see Table 1); hence, the number of benzene rings per unit volume of EPPU is less than that of MBAPA, and therefore the refractive index of EPPU is lower than that of MBAPA. Furthermore, from Fig.18 illustrating the contours of the extraordinary refractive indices in the temperature-composition plane, the contour lines drop at the composition of 0.45 and rise up at the composition of 0.75 mole fraction of EPPU. This is presumably due to the cis-trans isomerization of EPPU and MBAPA that can be explained in the same way as for the system of EPP-Hep and BEPCPC.

From Figs.23, 24, 25, 26, 27, 28 and 29, showing the temperature dependence of the refractive indices of six nematic liquid crystals and their mixtures, it can be seen that the average index and the isotropic liquid index are not joined smoothly in a straight line as previously concluded by Dolphin et al<sup>10</sup>. This observed feature may correspond to the discontinuities of the specific volume and other physical properties associated with the nematic-isotropic transition.

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<sup>10</sup> D.Dolphin, Z.Muljiani, J.Cheng and R.B.Meyer, J.Chem.Phys., 58 (1973), 2



We see from Figs. 30, 31, 32, and 33 that the double refraction ( $n_e - n_o$ ) of the four binary systems of six nematic liquid crystals decreases rapidly with rising temperature and drop down to zero discontinuously at the nematic-isotropic transition. The decrease is mainly due to the decrease of  $\alpha_{//}$  and the increase of  $\alpha_{\perp}$  as the temperature increases, which causes the extraordinary refractive index to decrease and the ordinary index to increase.

From the slopes of the graphs in Figs. 34, 35, 36 and 37, the coefficient of volume expansion ( $\beta$ ) of pure six nematic liquid crystals can be calculated by using the relations:

$$\beta = \frac{1}{V} \frac{dV}{dT} = -(d/dT) \ln \left[ \frac{(\bar{n}^2 - 1)}{(\bar{n}^2 + 2)} \right]$$

The results are given in Tables 6, 7, 8 and 9.

Table 6. The coefficients of volume expansion for the mixtures of PAA and PHAB

| Mole fraction of PAA<br>$\tau$ | Coefficient of volume expansion<br>$\beta$ ( $^{\circ}\text{C}$ ) |
|--------------------------------|---|
| Pure PAA                       | $(1.85 \pm 0.15) \times 10^{-3}$                                  |
| $\tau = 0.9$                   | $(1.90 \pm 0.03) \times 10^{-3}$                                  |
| $\tau = 0.8$                   | $(1.52 \pm 0.08) \times 10^{-3}$                                  |
| $\tau = 0.7$                   | $(0.91 \pm 0.08) \times 10^{-3}$                                  |
| $\tau = 0.6$                   | $(1.17 \pm 0.10) \times 10^{-3}$                                  |
| $\tau = 0.5$                   | $(0.99 \pm 0.12) \times 10^{-3}$                                  |
| $\tau = 0.4$                   | $(0.65 \pm 0.07) \times 10^{-3}$                                  |
| $\tau = 0.3$                   | $(0.59 \pm 0.09) \times 10^{-3}$                                  |
| $\tau = 0.2$                   | $(0.81 \pm 0.10) \times 10^{-3}$                                  |
| $\tau = 0.1$                   | $(0.93 \pm 0.07) \times 10^{-3}$                                  |
| Pure PHAB                      | $(1.00 \pm 0.15) \times 10^{-3}$                                  |

Table 7. The coefficients of volume expansion of the mixtures of PAA and BEPCPC

| Mole fraction of PAA<br>$\tau$ | Coefficient of volume expansion<br>$\beta$ ( $^{\circ}\text{C}$ ) |
|--------------------------------|---|
| Pure PAA                       | $(1.95 \pm 0.05) \times 10^{-3}$                                  |
| $\tau = 0.9$                   | $(2.20 \pm 0.20) \times 10^{-3}$                                  |
| $\tau = 0.8$                   | $(2.30 \pm 0.10) \times 10^{-3}$                                  |
| $\tau = 0.7$                   | $(1.00 \pm 0.02) \times 10^{-3}$                                  |
| $\tau = 0.6$                   | $(0.00 \pm 0.02) \times 10^{-3}$                                  |
| $\tau = 0.5$                   | $(2.65 \pm 0.05) \times 10^{-3}$                                  |
| $\tau = 0.4$                   | $(1.56 \pm 0.42) \times 10^{-3}$                                  |
| $\tau = 0.3$                   | $(2.60 \pm 0.20) \times 10^{-3}$                                  |
| $\tau = 0.2$                   | $(1.53 \pm 0.12) \times 10^{-3}$                                  |
| $\tau = 0.1$                   | $(1.25 \pm 0.14) \times 10^{-3}$                                  |
| Pure BEPCPC                    | $(1.44 \pm 0.21) \times 10^{-3}$                                  |

Table 8. The coefficients of volume expansion of the mixtures of EPP-Hep and BEPCPC

| Mole fraction of BEPCPC<br>$\tau$ | Coefficient of volume expansion<br>$\beta$ ( $^{\circ}\text{C}$ ) |
|-----------------------------------|---|
| Pure BEPCPC                       | $(1.28 \pm 0.04) \times 10^{-3}$                                  |
| $\tau = 0.9$                      | $(1.45 \pm 0.22) \times 10^{-3}$                                  |
| $\tau = 0.8$                      | $(2.00 \pm 0.02) \times 10^{-3}$                                  |
| $\tau = 0.7$                      | $(1.33 \pm 0.09) \times 10^{-3}$                                  |
| $\tau = 0.6$                      | $(1.46 \pm 0.04) \times 10^{-3}$                                  |
| $\tau = 0.5$                      | $(1.23 \pm 0.12) \times 10^{-3}$                                  |
| $\tau = 0.4$                      | $(1.17 \pm 0.03) \times 10^{-3}$                                  |
| $\tau = 0.3$                      | $(1.52 \pm 0.03) \times 10^{-3}$                                  |
| $\tau = 0.2$                      | $(1.37 \pm 0.16) \times 10^{-3}$                                  |
| $\tau = 0.1$                      | $(1.04 \pm 0.04) \times 10^{-3}$                                  |
| Pure EPP-Hep                      | $(0.99 \pm 0.14) \times 10^{-3}$                                  |

Table 9. The coefficients of volume expansion of the mixtures of EPPU and MBAPA

| Mole fraction of EPPU<br>$\tau$ | Coefficient of volume expansion<br>$\beta$ ( $^{\circ}\text{C}$ ) |
|---------------------------------|---|
| Pure EPPU                       | $(1.68 \pm 0.08) \times 10^{-3}$                                  |
| $\tau = 0.9$                    | $(1.40 \pm 0.20) \times 10^{-3}$                                  |
| $\tau = 0.8$                    | $(1.69 \pm 0.02) \times 10^{-3}$                                  |
| $\tau = 0.7$                    | $(2.00 \pm 0.02) \times 10^{-3}$                                  |
| $\tau = 0.6$                    | $(1.20 \pm 0.02) \times 10^{-3}$                                  |
| $\tau = 0.5$                    | $(2.00 \pm 0.02) \times 10^{-3}$                                  |
| $\tau = 0.4$                    | $(1.08 \pm 0.02) \times 10^{-3}$                                  |
| $\tau = 0.3$                    | $(2.00 \pm 0.02) \times 10^{-3}$                                  |
| $\tau = 0.2$                    | $(1.96 \pm 0.04) \times 10^{-3}$                                  |
| $\tau = 0.1$                    | $(1.98 \pm 0.02) \times 10^{-3}$                                  |
| Pure MBAPA                      | $(2.04 \pm 0.04) \times 10^{-3}$                                  |

### III.3 Concluding Remarks

From the present detailed study of birefringence of mixed nematic liquid crystals, it has been found that the mixtures generally exhibit strong birefringence in the whole nematic region of the temperature-composition plane with the refractive index of the extraordinary ray higher than that of the ordinary ray. On increasing the temperature, the ordinary refractive index will increase whereas the extraordinary refractive index will decrease. The main reason for this is that the increase of the ordinary refractive index according to the mean polarizability perpendicular to the optic axis ( $\bar{\alpha}_{\perp}$ ) is greater than that according to the polarizability parallel to the optic axis ( $\bar{\alpha}_{\parallel}$ ). Also the density is decreased when the temperature is increased. As the refractive

indices of liquid crystals depend on the density, dilatometric studies of the mixtures should be made in the future. Only then will the relationships among the refractive indices, the density, the temperature and the composition of liquid crystal mixtures be better understood.

An interesting result from the present experiments is that the refractive indices generally give minima in the eutectic region of the temperature-composition plane. This effect is presumably due to the specific arrangement of the molecules, the superstructures, the molecular association and clustering, and the special modes of packing of these molecular clusters. Certainly this problem needs further investigations.