

CHAPTER V

STUDIES ON SOME MIXTURES EXHIBITING INDUCED SMECTIC MESOMORPHISM

5.1 Introduction

Phase diagrams of binary mixtures of nematogenic compounds have been extensively studied. Commonly, when two compounds both of which exhibit only the nematic mesophase are mixed together, the mixtures exhibit only the nematic mesophase. The nematic-isotropic transition temperature T_{NI} of such mixtures usually lie between those of the pure components. When T_{NI} of the mixtures is plotted against composition a smooth curve is obtained. In fact, T_{NI} varies with composition almost linearly and only small deviations from linearity are observed (see, for example, Dave and Dewar 1954, 1955, Park et al 1975).

The Schroeder-van Laar equation (see, for example Gray et al 1973) is applicable to the melting transition of such mixtures as the components are miscible in the nematic phase and are not miscible in the solid phase. The van Laar equation is

$$\ln p_A = -\frac{\Delta H_A}{R} \left(\frac{1}{T_A} - \frac{1}{T} \right) \quad (5.1)$$

where p_A is the mole fraction of component A for which the heat of melting transition is ΔH_A . T_A is the melting point of the stable crystal form of component A and T is the melting point

of the mixture. For an n component mixture, n such equations exist. These can be solved simultaneously to give p_A and T for the eutectic mixture. In binary mixtures two such equations exist and obviously $p_A + p_B = 1$ where B stands for the second component of the mixture.

In the past few years, binary mixtures of nematogenic compounds showing a different type of phase diagram have been studied (Park et al 1975, Oh 1977, Engelen et al 1978, Bock et al 1978). One of the components of such mixtures consists of molecules having the strongly polar cyano end-group whereas the other consists of molecules which do not have the cyano end-group. Such mixtures exhibit a smectic A phase in some range of compositions even when each component by itself shows only the nematic mesophase. These smectic A phases are referred to as 'induced smectic A*' (denoted by the symbol A_I hereafter) phases (Engelen et al 1978).

We have studied the phase diagrams of a few binary mixtures exhibiting induced smectic A mesomorphism. We have also measured the orientational order parameter and elastic constants of some of these mixtures in the nematic phase with a view to study the correlations between these properties and the occurrence of induced smectic A phase.

5.2 Experimental

a) Study of binary mixtures. The two components of the

mixture were weighed into a glass cup provided with a ground glass stopper. The mixture was heated to the isotropic phase and mixed thoroughly by mechanical stirring. Then it was maintained in the isotropic phase for a few hours.

A slide was prepared by transferring the sample in the isotropic phase on to the slide. The transition temperatures were determined by examining the slide through a polarising microscope provided with a hot stage. Some of the transitions were found to occur over relatively wide ranges of temperature.

b) Determination of refractive indices. We have determined the ordinary and extraordinary refractive indices (n_o and n_e) of nematic liquid crystals by the prism method (Pellet and Chatelain 1950, Madhusudana et al 1971).

Construction of the prism. A small angled (angle $\sim 6^\circ$) hollow glass prism was constructed using two rectangular glass plates (11 mm x 7 mm) having perfectly parallel and flat surfaces. A goniometer spectrometer (Praxisionsmechanik Model SGo 1.1) provided with a gaussian eye-piece was used in making a proper selection of glass plates. The eye-piece is provided with a source of light. A beam of light from this source moves along the axis of the telescope and is reflected from the glass plate held in front of the telescope objective. The reflected light forms an image of an illuminated cross in the field of view of the telescope. When the surfaces of the glass plates are not

parallel to each other one could see two crosses produced by reflections at the two surfaces. If the surfaces are not flat, the images would be blurred. Only those glass plates which give a single, clear image of the cross when held in front of the telescope were selected.

The selected glass plates were cleaned thoroughly and dried. Then they were coated with SiO₂ at an oblique angle of $\sim 60^\circ$ with respect to the normal by the vapour deposition technique. This is done to facilitate homogeneous alignment of the liquid crystal. The coating was done such that the molecules align with their long axes parallel to the shorter edges of the glass plates.

The prism was constructed by placing the glass plates one on top of the other (such that the SiO₂ coated surfaces face each other) with a thin strip of glass of uniform thickness placed in between them at one end. The strip of glass was placed parallel to the width of the glass plates (figure 5.1) and is cemented to the two plates using araldite.

Oven and sample holder. The prism was kept with its edge vertical inside a small rectangular copper enclosure (Figure 5.2a). In order to see that there is no contamination of the sample by copper, thin sheets of teflon were placed around the prism (except at the refracting faces) so that the sample does not come in direct contact with copper. The copper enclosure was placed inside a massive copper chamber of rectangular cross-section

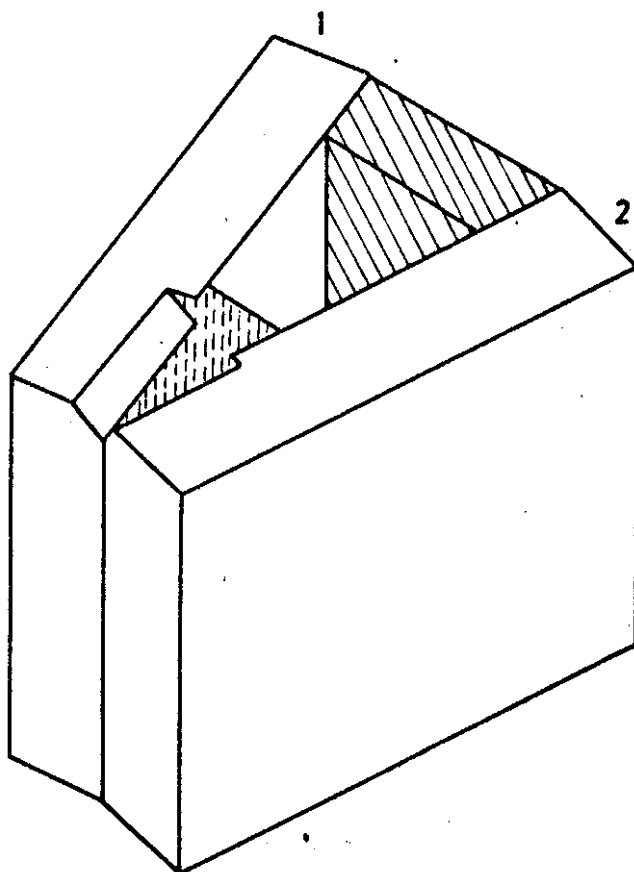
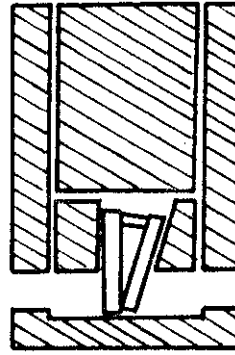
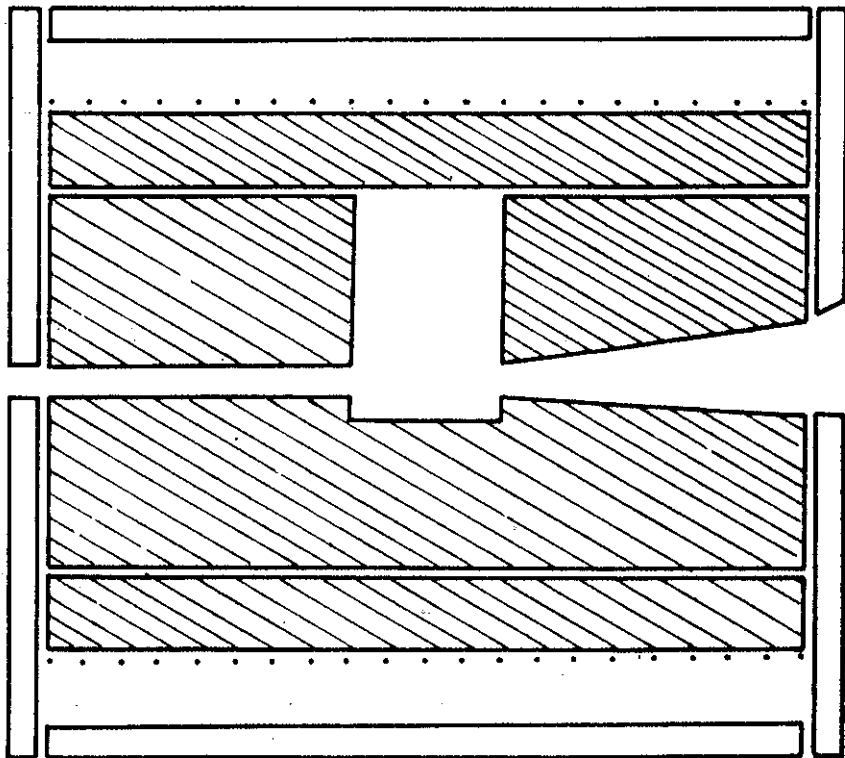


FIGURE 5.1

Small angled prism made of two optically flat glass plates 1 and 2 cemented together with a strip of glass (shown by the striped region) at one end. The glass plates are bevelled near the refracting edge of the prism to facilitate the filling of the sample.



(a)



(b)

**FIGURE 5.2: (a) Copper holder for the prism
(b) Cross-sectional view of the sample holder used in the measurement of refractive indices.**

(figure 5.2b). A narrow hole (~ 3 mm in diameter) present on one side of the chamber allows light to be incident on the prism and a suitable aperture present on the other side allows the passage of the refracted light beams. The copper chamber was placed inside an oven having 1 cm thick copper plates as the inner walls. The oven was heated by passing a direct current through the heating coil of the oven. On the two ends of the heater the copper blocks were covered by sheets of bakelite to avoid heat losses and to minimise temperature gradients.

The temperature of the sample was measured using a calibrated chromel-alumel thermocouple and a nanovoltmeter as described in chapter IV. The temperature could be maintained and measured to an accuracy of ± 0.025 °C.

The sample was introduced into the prism in the nematic phase by means of a capillary tube*. The sample got aligned homogeneously parallel to the edge of the prism and typically, it occupied a width of ~ 2 mm from the refracting edge.

The refractive indices were determined using a goniometer spectrometer which can measure angles to an accuracy of 2. Before taking any measurement the position of the prism was adjusted so that the refracting edge of the prism is perfectly vertical. This adjustment was done with the help of the gaussian eye-piece and the levelling screws of the prism table. The

light reflected from the plates 1 and 2 of the prism (figure 5.3) form two images of the illuminated cross. The levelling screws were adjusted to get the two images *in* a horizontal plane. Then the two plates of the prism would be vertical. The angle between the two reflected beams gives the angle θ of the prism.

A suitably attenuated laser beam ($\lambda = 6328 \text{ \AA}$) was incident normally on one face of the prism and the angles of deviation (D) were measured for the ordinary and extraordinary beams (figure 5.4). The refractive indices were calculated using the formula .

$$n = \frac{\sin(\theta + D)}{\sin \theta} \quad (5.2)$$

While taking each set of readings it was ascertained that the incident beam was exactly normal to the front face of the prism. The readings were taken at various steady temperatures in the nematic phase of the sample.

Measurement of elastic constants. The splay and bend elastic constants were determined by the Fredericksz transition technique (Chapter IV).

5.3 Results and discussion

a. Phase diagrams of binary mixtures. We have studied the , phase diagrams of the following mixtures.

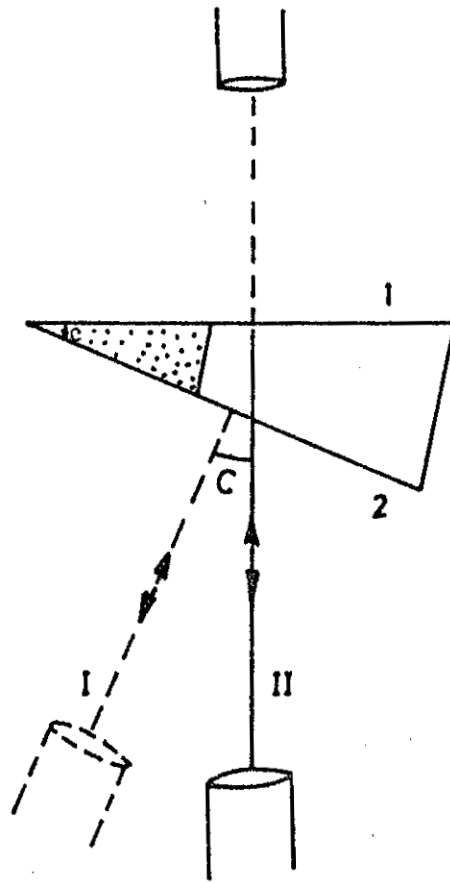


FIGURE 5.3

Schematic diagram of the setting of the prism for measuring the angle C of the prism.

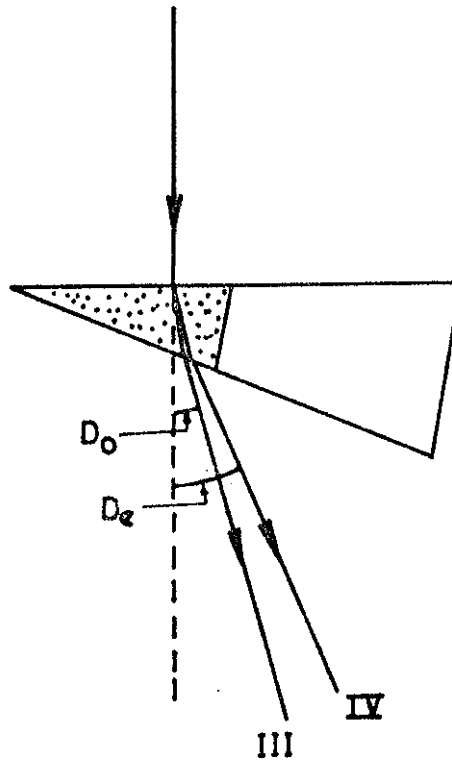


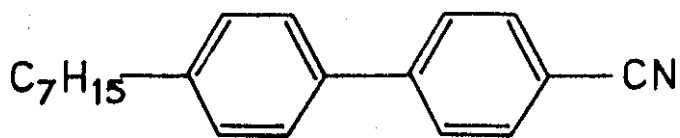
FIGURE 5.4

Refraction of light through the prism.
 D_o and D_e are the angles of deviation for
the ordinary and extraordinary rays.

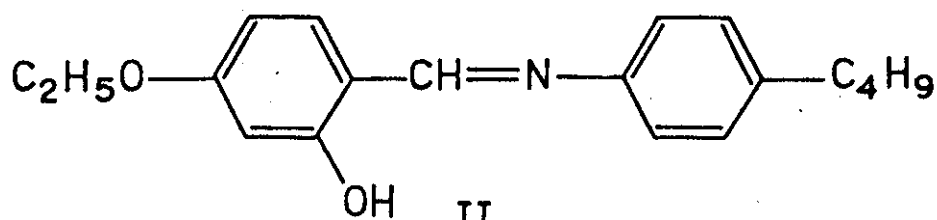
- i) 7CB (4'-n-heptyl-4-cyanobiphenyl) and OH-EBBA [(2-hydroxy)-p-ethoxybenzylidene-p'-butylaniline]
- ii) PCH-7 (4-cyanophenyl-trans-4'-n-heptylcyclohexane) and OH-EBBA, and
- iii) 7CB and HOAB (4,4'-diheptyloxyazobenzene).

The molecular structures of 7CB, OH-EBBA and HOAB are shown in figure 5.5.

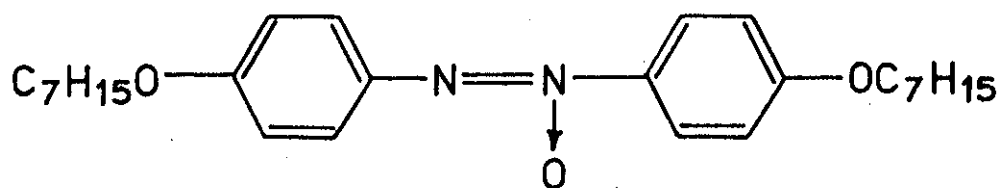
1) Mixtures of 7CB and OH-EBBA: The phase diagram for these mixtures is shown in figure 5.6. The two pure compounds show only the nematic (hereafter denoted by N) mesophase. But the mixtures having ~ 15-65% of 7CB exhibit A_I phase in addition to the N phase.  is typical of such mixtures, of A_I -N transition temperature curve peaks around some composition which in this case is ~ 35% of 7CB. The HI transition is also influenced by this as can be seen from the diagram. The NI transition curve has got a hump in it for almost the same composition as that corresponding to the peak in the A_I -N transition curve. For higher percentages of 7CB, the A_I -N transition takes place over fairly wide ranges of temperature. For these compositions, when the mixture is cooled down from the N phase, batonnets begin to appear in the field of view of the microscope at a certain temperature indicating that the NA_I transition has just started. The transition will be complete only after cooling the sample by a few degrees when the batonnets cover the entire area giving rise to a focal conic texture. For percentages of 7CB less than



I



II



III

FIGURE 5.5

Structural formulae of (I) 7CB, (II) OH-EBBA, and
(III) HOAB

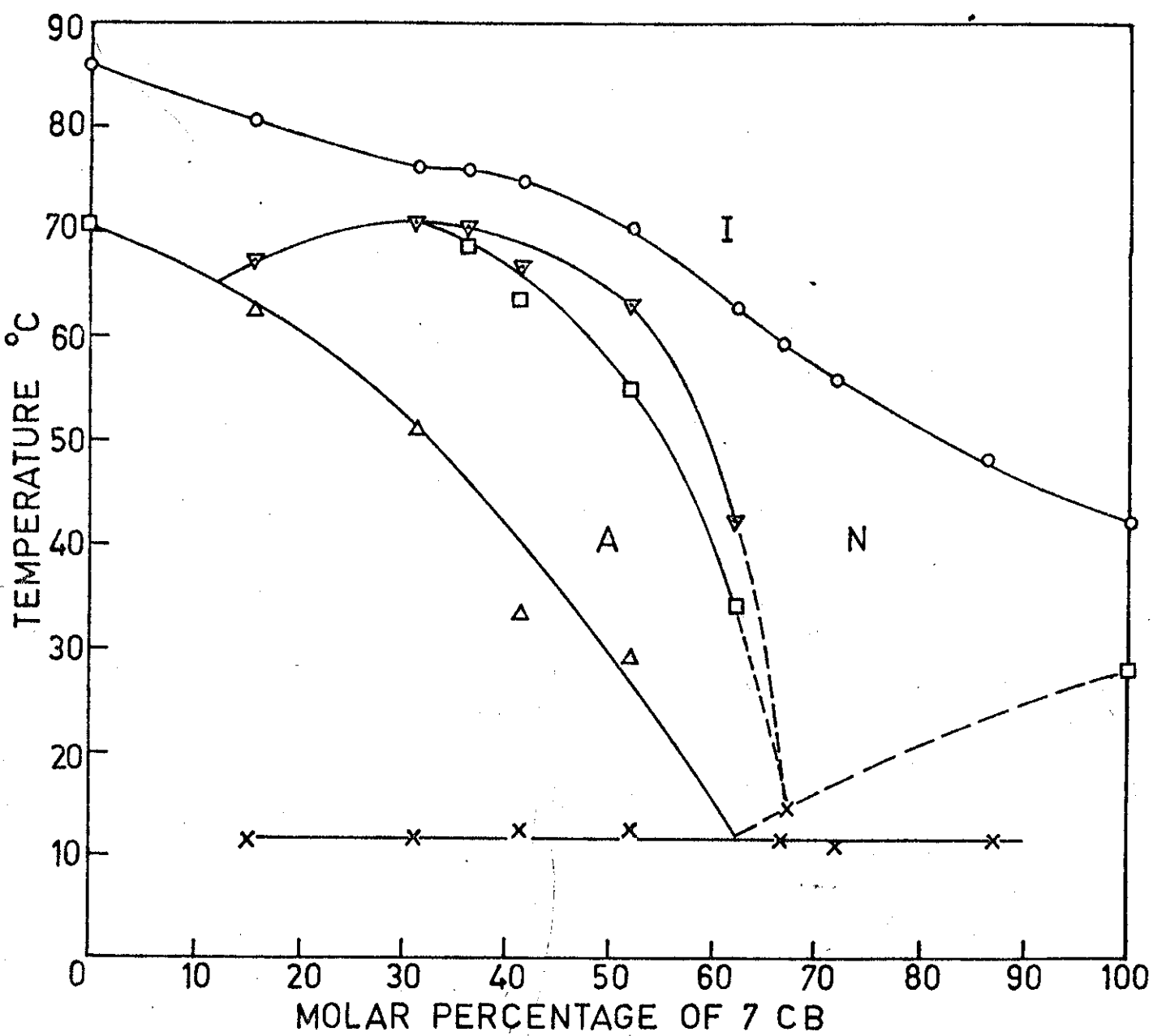


FIGURE 5.6

Phase diagram for the mixtures of 7CB and OH-EBBA

that corresponding to the peak in the ΔT_N transition curve, the ΔT_N transition takes place over a fairly short temperature range ($\sim 0.5 - 1^\circ\text{C}$) and this has not been explicitly shown in the diagram. For low concentrations of either of the α -nents ($< 10\%$ and $> 65\%$ of 7CB), the mixtures show only the N phase. For some 7CB-rich compositions, the ΔT_N and solid-smectic transition temperatures could not be determined accurately. These have been represented by dashed lines in the diagram.

ii) Mixtures of PCH-7 and OH-EBBA. In order to study the influence of the strongly polar component of the mixture on the formation of A_I phase, we have investigated the phase diagram of mixtures of PCH-7 and OH-EBBA. A PCH-7 molecule ($\text{C}_{15}\text{H}_{31}-\text{C}_6\text{H}_4-\text{CN}$) differs from a 7CB molecule in that the phenyl ring attached to the alkyl chain in the latter is replaced by a cyclohexane ring in the former. Consequently the polarisability of a PCH-7 molecule would be considerably less than that of a 7CB molecule. In the PCH-7/OH-EBBA system mixtures having a composition of $\sim 10-50\%$ of PCH-7 exhibit the A_I phase (figure 5.7). The NA_I transition curve is below the liquidus curve for all compositions. Hence we could measure NA_I transition temperatures only while cooling the sample. The NA_I transition point has a peak value ($\sim 60^\circ\text{C}$) for a composition of $\sim 25\%$ PCH-7. Both these values are less than the corresponding values ($\sim 70^\circ\text{C}$ and $\sim 35\%$ 7CB) for 7CB/OH-EBBA mixtures. Thus the effect of reducing the polarisability of the strongly polar

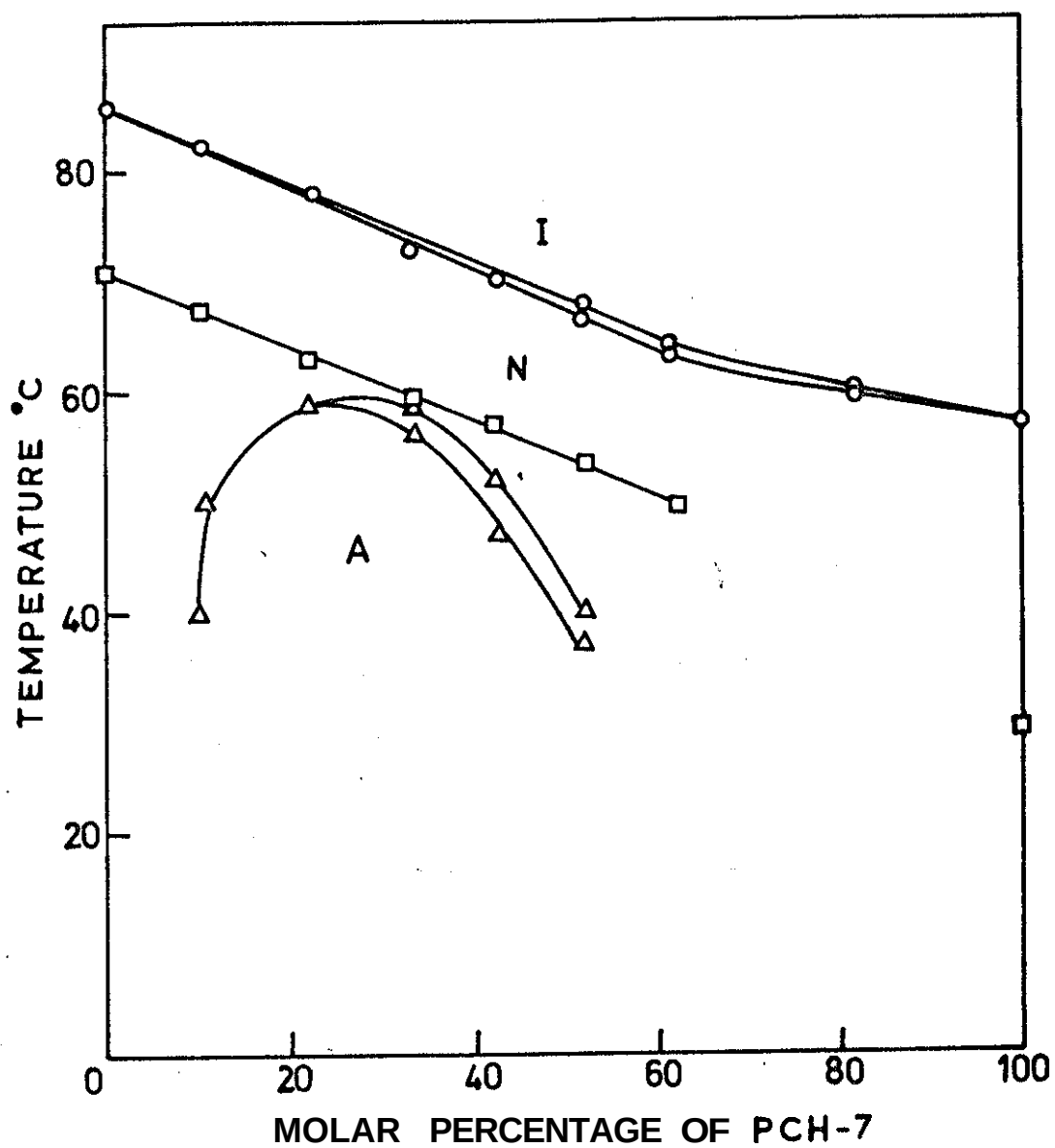


FIGURE 5.7

Phase diagram for the mixtures of PCH-7 and OH-EBBA

molecule is to lower the peak value of A_I -N transition curve and to reduce its concentration corresponding to the peak value. (Since we had a limited quantity of PQH-7 and our interest was only in the A_I phase we have not completed other parts of the phase diagram).

iii) Mixtures of 7CB and HOAB. The phase diagram of mixtures of 7aB and HOAB is shown in figure 5.8. Pure HOAB shows smectic C and nematic mesophases. Mixtures Rating less than $\sim 15\%$ of 7CB show nematic and smectic C phases. When the percentage of 7CB is more than 15, the mixtures exhibit A_I phase. There is a small composition range in which the mixtures exhibit smectic C, smectic A_I as well as N phases. At high percentages of 7CB (>90), the mixtures show only the N phase. For percentages of 7CB in the range 20-85, the A_I phase goes over directly to the isotropic phase. The smectic-isotropic transition curve peaks for a composition of $\sim 30\%$ of 7CB. For higher concentrations of 7CB, the A_I and isotropic phases coexist over fairly wide ranges of temperature. For lower concentrations, this temperature range is comparatively small. The solid- A_I transition temperatures could not be determined accurately in some mixtures. These have been represented by dashed lines in the diagram.

We have also found that some other mixtures like HOAB and 2 OMOPC (trans-p-n-ethyloxy- α -methylecyanophenyl cinnamate) and HOAB and 10 OMOPC (trans-p-n-decyloxy- α -methyl cyanophenyl cinnamate) exhibit induced smectic phases. We will have occasion

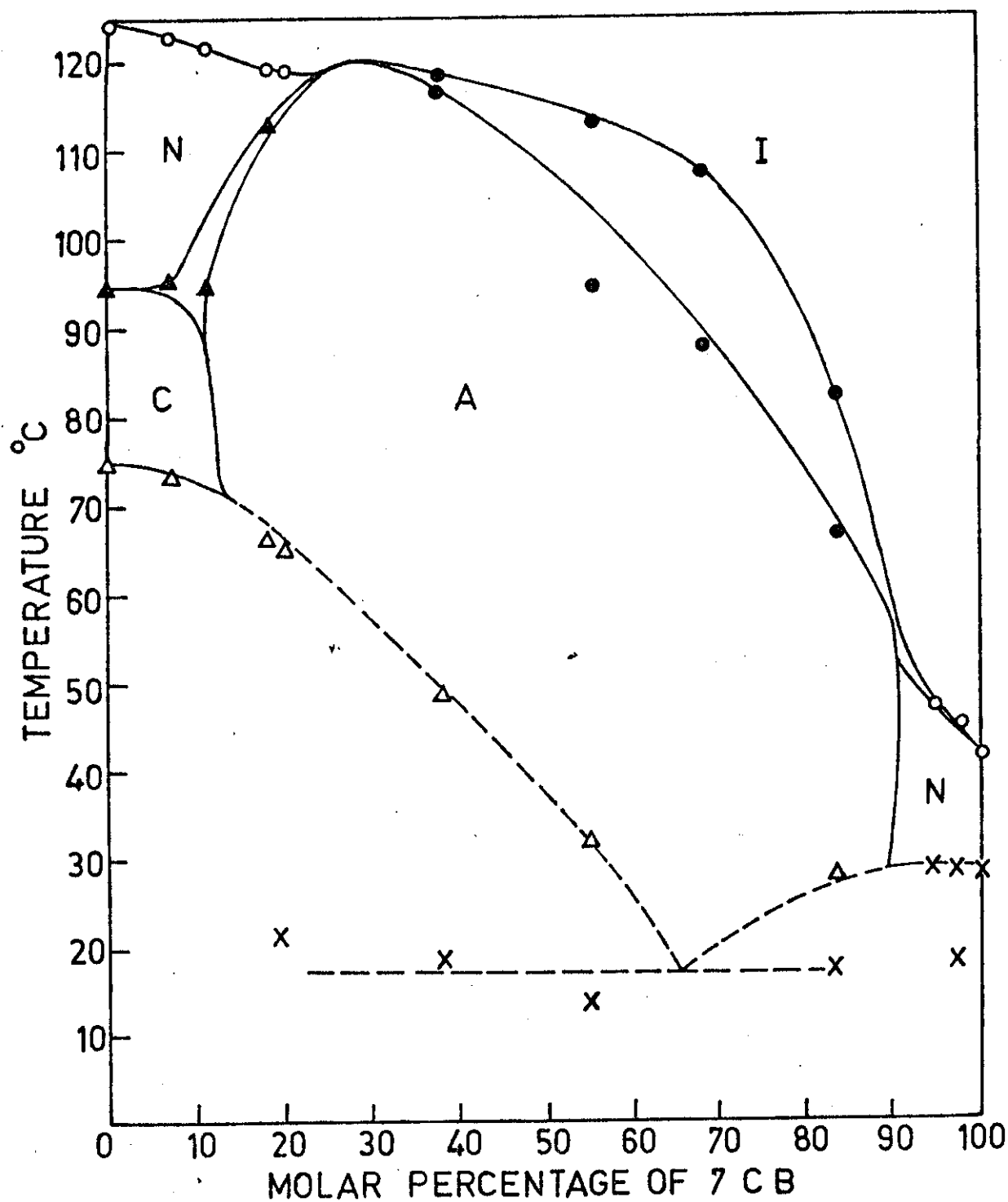


FIGURE 5.8

Phase diagram for the mixtures of 7CB and HOAB

to refer to these mixtures in a subsequent chapter (chapter VII).

As pointed out earlier, the phenomenon of induced smectic A mesomorphism is associated with the presence of the cyano $\text{C}\equiv\text{N}$ group in molecules of one of the components of the mixture. To elucidate this point further, we refer to the studies made by Engelen et al (1979) on binary mixtures of 4-n-pentylphenyl-4'-n-octyloxybenzoate (E.O.5) and N-p-cyanobenzylidene-p'-n-octyloxyaniline (CBOOA), the latter consisting of molecules with cyano end groups. The phase diagram for these mixtures is shown in figure 5.9a. One of the components, viz., CBOOA has got a smectic A phase in addition to the nematic phase. In the phase diagram, the smectic A phase of CBOOA is separated from the induced smectic A phase by a nematic phase. In some composition ranges, these mixtures also exhibit the re-entrant nematic phase which again is linked with the presence of molecules having cyano end-groups (see chapter II).

Engelen et al (1979) have also measured the layer spacing as a function of composition at temperatures represented by the dashed line in figure 5.9a. The layer spacing plotted against composition is shown in figure 5.9b. As the percentage of CBOOA in the mixture increases from zero, the spacing decreases almost linearly up to about 50% composition of CBOOA. If this line is extrapolated to pure CBOOA, a layer spacing comparable to the molecular length of CBOOA is obtained. Actually, however, beyond 50% composition of CBOOA the spacing increases quite

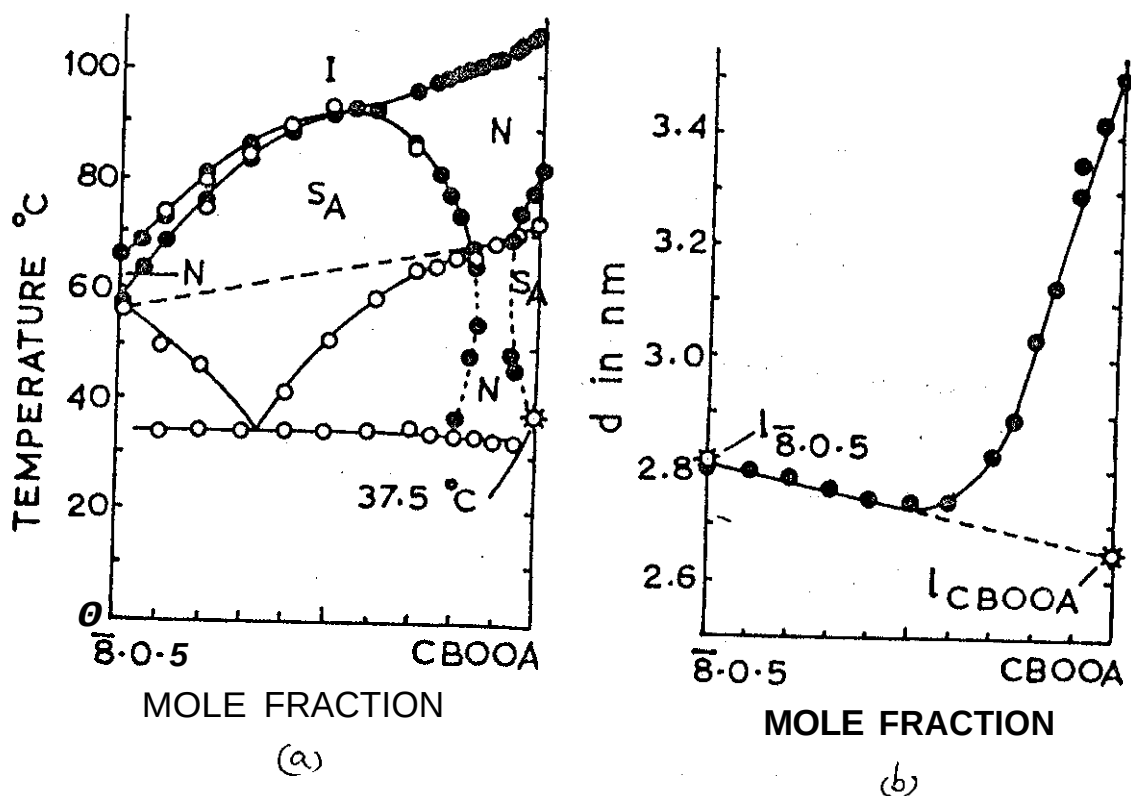


FIGURE 5.9

- (a) Phase diagram for the mixtures of 8.0.5 and CBOOA.
- (b) X-ray spacing plotted against composition for mixtures of 8.0.5 and CBOOA. The spacings correspond to the temperatures represented by a dashed line in fig. 5.9a. (Reproduced from Engelen et al 1979).

sharply approaching the bilayer spacing of pure CBOOA. It is interesting to note that the A_I -N transition curve peaks for about 50 per cent composition of CBOOA.

A similar trend in the variation of layer spacing can be expected to occur in the systems studied by us. Indeed, preliminary x-ray studies conducted in our laboratory have confirmed this trend in ^{the} 7CB-OH EBBA system. We can now try to understand the physical mechanism of the formation of the A_I phase. At low concentrations of 7CB, individual molecules of 7CB may be expected to be surrounded by OH-EBBA molecules. The strongly polar 7CB molecules polarise the neighbouring OH-EBBA molecules and this interaction should favour a collection of OH-EBBA molecules around a 7CB molecule thus favouring the formation of a layered arrangement. Beyond a certain concentration of 7CB, the layered arrangement takes on long-range characteristics giving rise to the A_I phase. As the concentration of 7CB is increased, some of the neighbours of a given 7CB molecule will be 7CB molecules themselves and beyond ~35% concentration (which corresponds to the peak in the A_I -N transition curve), a part of 7CB will retain the bilayer structure. As a consequence the average layer spacing starts to increase. Further, since pure 7CB shows only the nematic phase, the build up of the bilayer structure at the cost of the monolayer structure reduces the A_I -N transition point. Thus the medium containing more than 35% of 7CB consists

of a mixture of bilayer and monolayer species. The presence of both these species also explains the relatively wide ranges of coexistence of the A_I and N phases in the phase transition region.

We have calculated the eutectic temperature and eutectic composition of the mixtures using the van Laar equation. The calculated and observed values are given in table 5.1. It can be seen that the observed values of eutectic temperatures are lower (by $\sim 6-8^\circ$) than the calculated values. Also, the eutectic concentration of 7OB is considerably less (by $\sim 15-30\%$) than the calculated values. This is probably associated with the formation of induced smectic A phases in these mixtures.

b. Order parameters. The order parameters of the following systems have been measured in the nematic phase as functions of temperature.

- 1) OH-EBBA
- ii) Mixture I of 7OB and OH-EBBA (molar ratio 16:84)
- iii) Mixture II of 7OB and OH-EBBA (molar ratio 62:38)
- iv) 7OB.

Both the mixtures exhibit the A_I phase in addition to the N phase. The transition temperatures of the systems studied are given in table 5.2.

1) Refractive indices. The ordinary and extraordinary refractive indices of the systems plotted against temperature

are shown in figures 5.10, 5.11, 5.12 and 5.13. The values have been listed in tables 5.3, 5.4, 5.5 and 5.6.

ii) Densities. The densities of 7CB and OH-EBA were measured by the capillary tube method at some known temperature — (1.023 gm/cc for 7CB at 25°C and 1.07 gm/cc for OH-EBA at 90°C). Using this data the values of $\bar{\alpha}$ were calculated from equation 1.9. The values of $\bar{\alpha}$ for the mixtures were calculated using an additivity law (see equation 3.11). These data are given in table 5.7. Then using the value of $\bar{\alpha}$ the values of density at different temperatures were calculated using equation 1.9. These values are plotted in figure 5-14 and are given in tables 5.3, 5.4, 5.5 and 5.6. Further, knowing the densities of the pure compounds the values for the mixtures can also be calculated using an additive law for molar volumes. These values are found to agree quite well with the data obtained directly from optical measurements.

iii) Order parameters. The order parameters were calculated using equation 1.8, viz.,

$$S = \frac{\bar{\alpha}}{\Delta\alpha} \frac{n_e^2 - n_o^2}{n^2 - 1} \quad (5.3)$$

For 7CB, the value of $\bar{\alpha}/\Delta\alpha$ was obtained by normalising our results with the order parameter (0.524 at 26°C) obtained by Raman scattering studies (Prasad and Venugopalan 1980a).

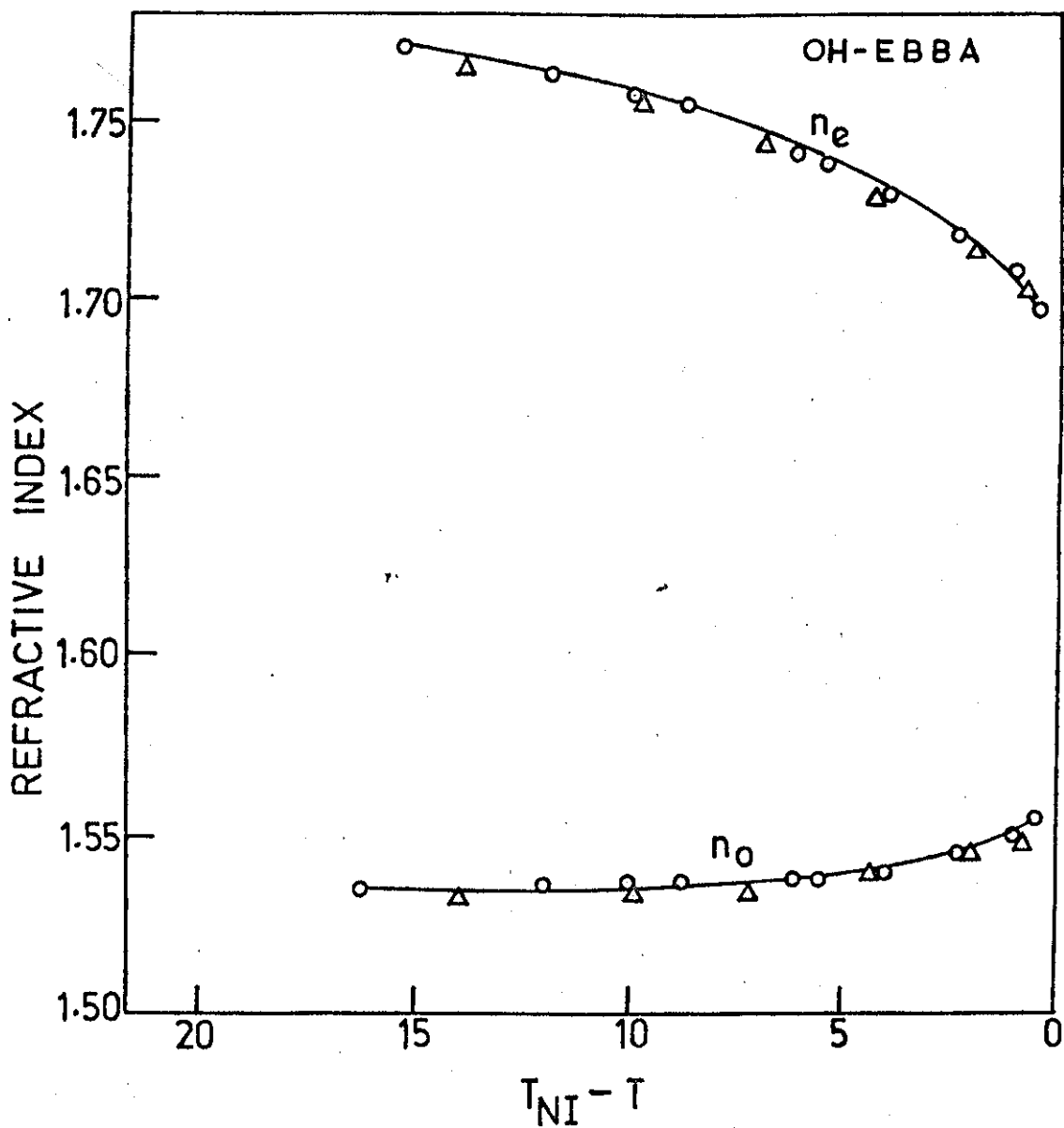


FIGURE 5.10

Ordinary and extraordinary refractive indices of OH-EBBA plotted against relative temperature (for $\lambda = 6328 \text{ \AA}$).

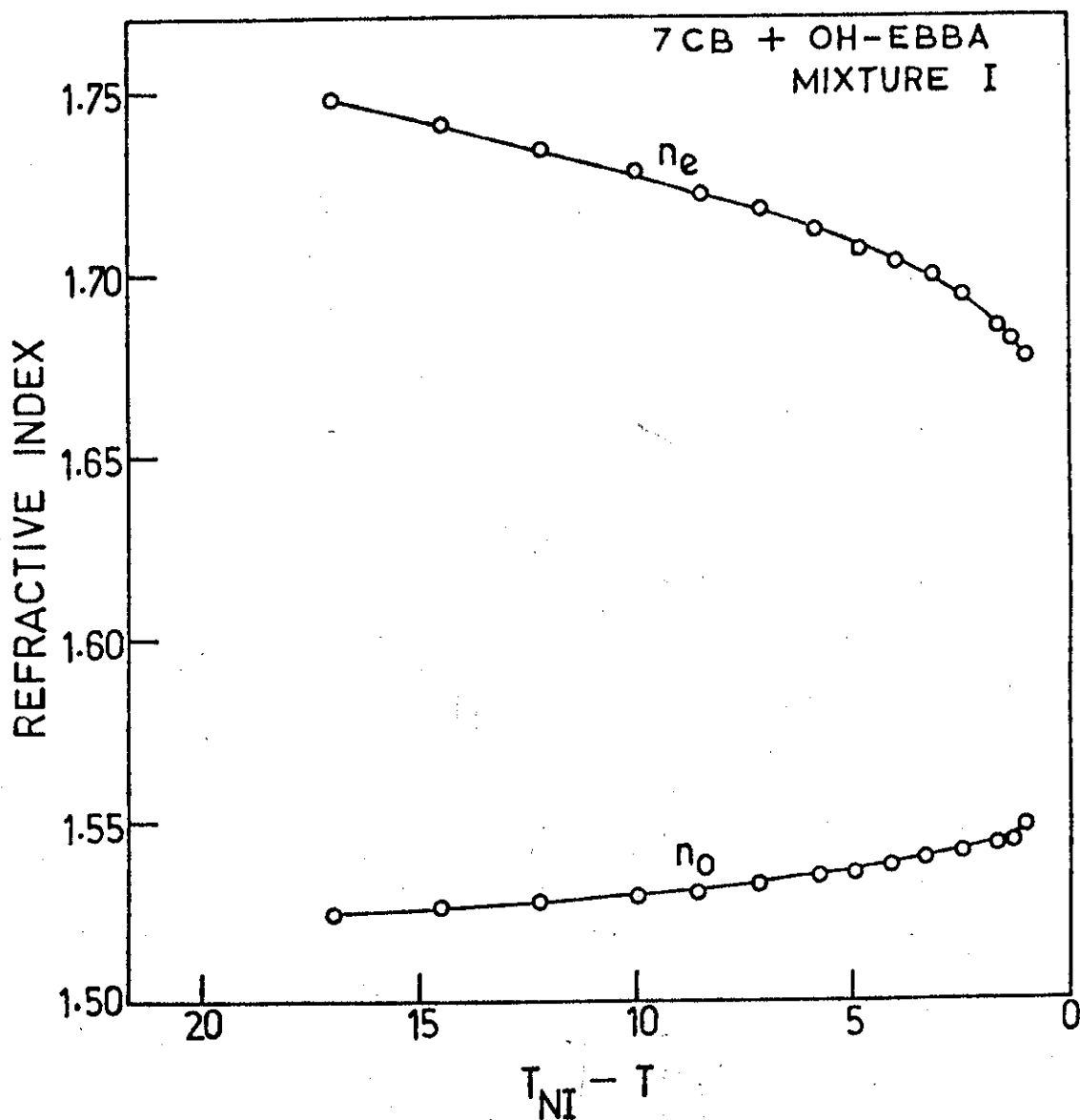


FIGURE 5.11

Ordinary and extraordinary refractive indices of mixture I plotted against relative temperature (for $\lambda = 6328 \text{ \AA}$)

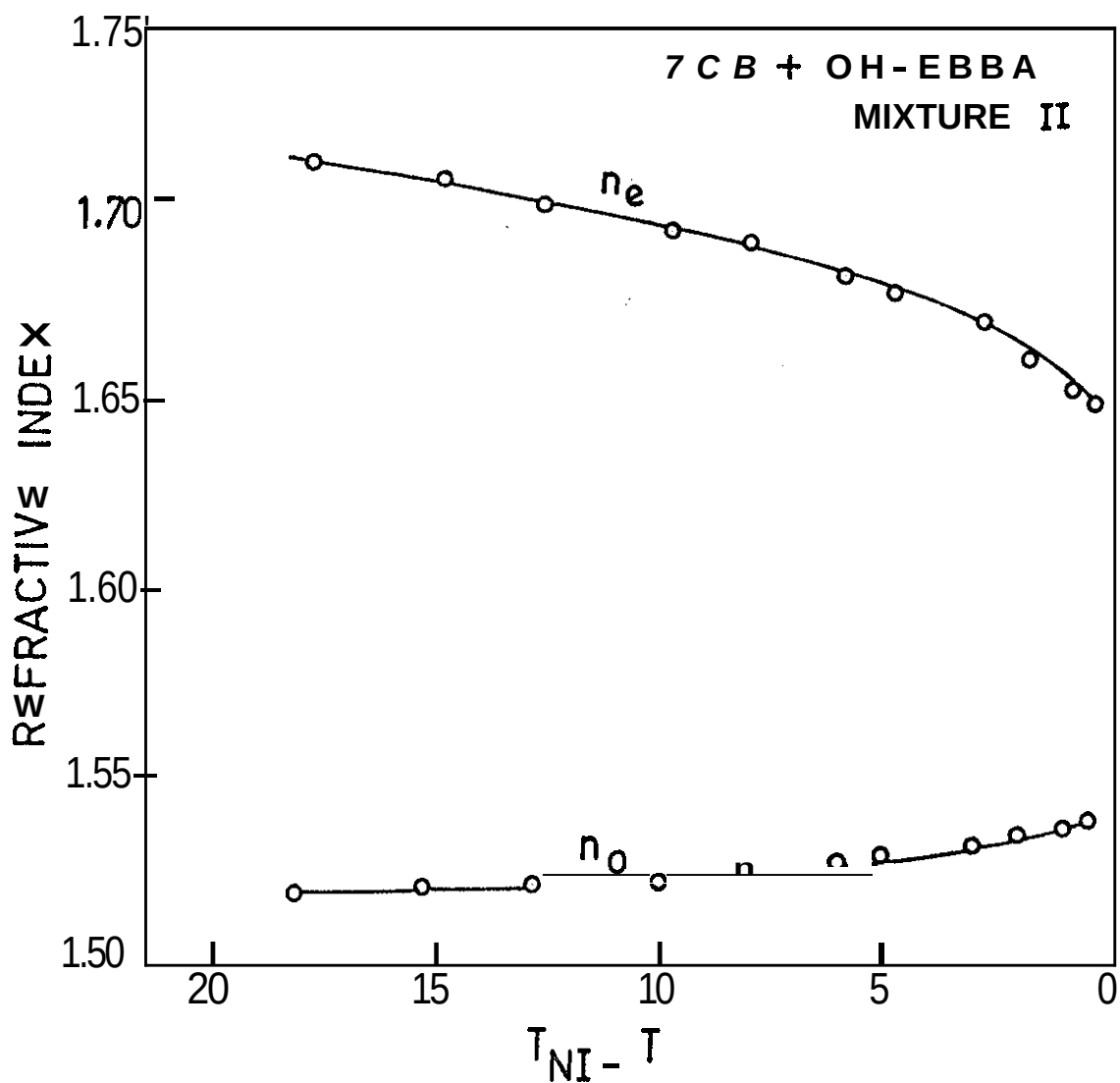


FIGURE 5.12

Ordinary and extraordinary refractive indices of *mixture II* plotted against relative temperature (for $\lambda = 6328 \text{ \AA}$)

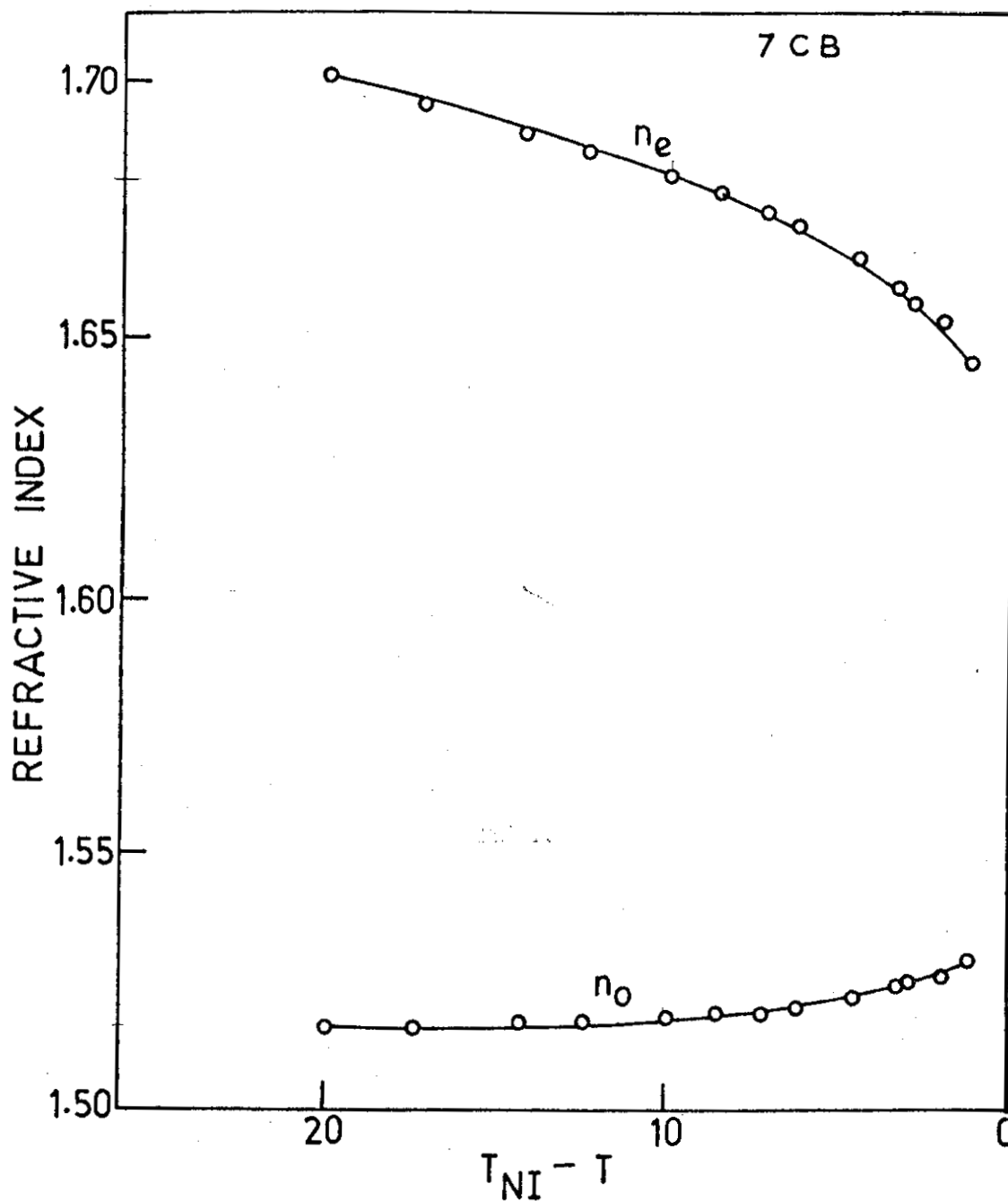


FIGURE 5.13

Ordinary and extraordinary refractive indices of 7CB plotted against relative temperature (for $\lambda = 6328 \text{ \AA}$), (Data taken from Karat and Madhusudana 1976)

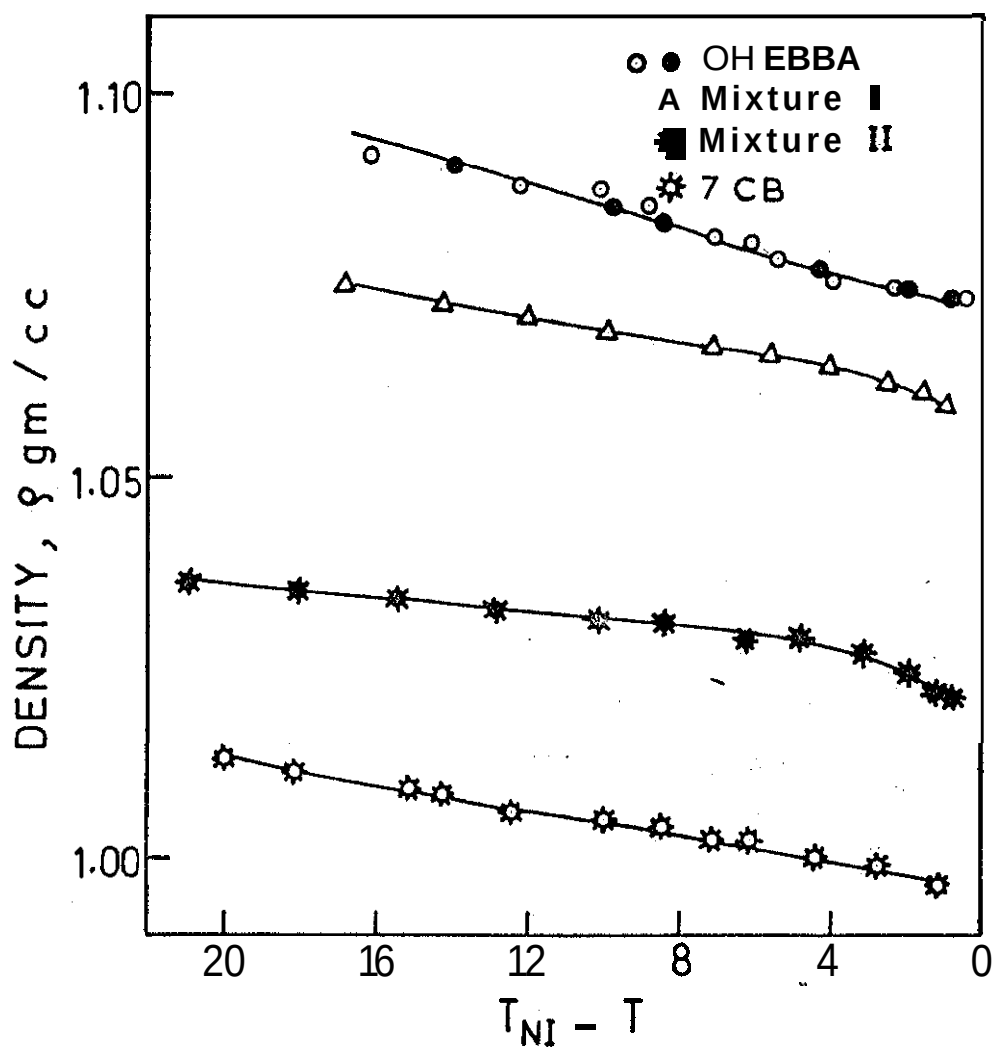


FIGURE 5.14

FIG.

Densities of OH-EBBA, mixture I, mixture II and 7CB plotted against relative temperatures.

A new extrapolation procedure. We have used a new extrapolation procedure to evaluate $\bar{\alpha}/\Delta\alpha$ from the temperature variation of relative order parameter of OH-EBBA. Haller et al (1973) found that when $\log(\alpha_e - \alpha_0)$ is plotted against $\log(T_{NI} - T)$, a straight line is obtained at the lower temperatures of the nematic phase. They extrapolated the straight line to the point corresponding to $T = 0$, to get the limiting value of $(\alpha_e - \alpha_0)$ which is assumed to be equal to $\Delta\alpha$. Subrahmanyam et al (1974) plot $\log \frac{\alpha_e}{\alpha_0}$ against $\log \frac{T_{NI}}{T}$ to get a straight line again at lower temperatures in the nematic phase. Extrapolating the straight line to $T = 0$ $\alpha_{||}/\alpha_{\perp}$ can be obtained. Knowing the value of $\bar{\alpha}$, α_e , and α_0 can be calculated. In both of these methods data in only a relatively small temperature range (i.e., at the lower temperatures sufficiently removed from T_{NI}) is useful for extrapolation and consequently the uncertainty in the estimated value of $\Delta\alpha$ tends to be somewhat large.

If the NI transition was of second order, the order parameter would have become zero at a temperature T_{NI}^* , say. Since the NI transition is actually a first order transition, the order parameter drops from a finite value to zero at a temperature T_{NI} which is somewhat lower than T_{NI}^* . To a reasonable approximation, the relation between α and $[(T_{NI}^* - T)/T_{NI}^*]$ can be expected to be of the form

$$\alpha = \left[\frac{(T_{NI}^* - T)}{T_{NI}^*} \right]^x \quad (5.4)$$

where x is a positive index. Equation (5.4) has been written so as to give the proper limiting values, viz., $s = 0$ at T_{NI}^* and 1 at 0°K .

Then, from equations (5.3) and (5.4), we get,

$$\log\left(\frac{n_e^2 - n_o^2}{n^2 - 1}\right) + \log \frac{\bar{\alpha}}{\Delta\alpha} = x \log \frac{T_{NI}^* - T}{T_{NI}^*}$$

By assuming different values of T_{NI}^* ($> T_{NI}$), we have plotted $\log[(T_{NI}^* - T)/T_{NI}^*]$ against $\log[(n_e^2 - n_o^2)/(n^2 - 1)]$ (figure 5.15). We find that the best straight line which passes through most of the points in the entire range of the nematic phase is obtained for $T_{NI}^* - T_{NI} = 0.2$ for OH-EBBA. By extrapolating the straight line to $T = 0$, we find that $\Delta\alpha = 29.1 \times 10^{-24} \text{ cc}$.

The values of $A\alpha$ for the mixtures are obtained by using an additive law. These values are given in table 5.7.

The values of s obtained for the different systems under study are given in tables 5.3, 5.4, 5.5, and 5.6. These values are plotted against relative temperature in figure 5.16. At any relative temperature, OH-EBBA has got a higher order parameter (by ~ 0.03) than that of 7CB. The s values of mixtures lie between those of the pure components. However, these values do not strictly follow a molar additivity law; the observed values are smaller (by ~ 0.03) than the

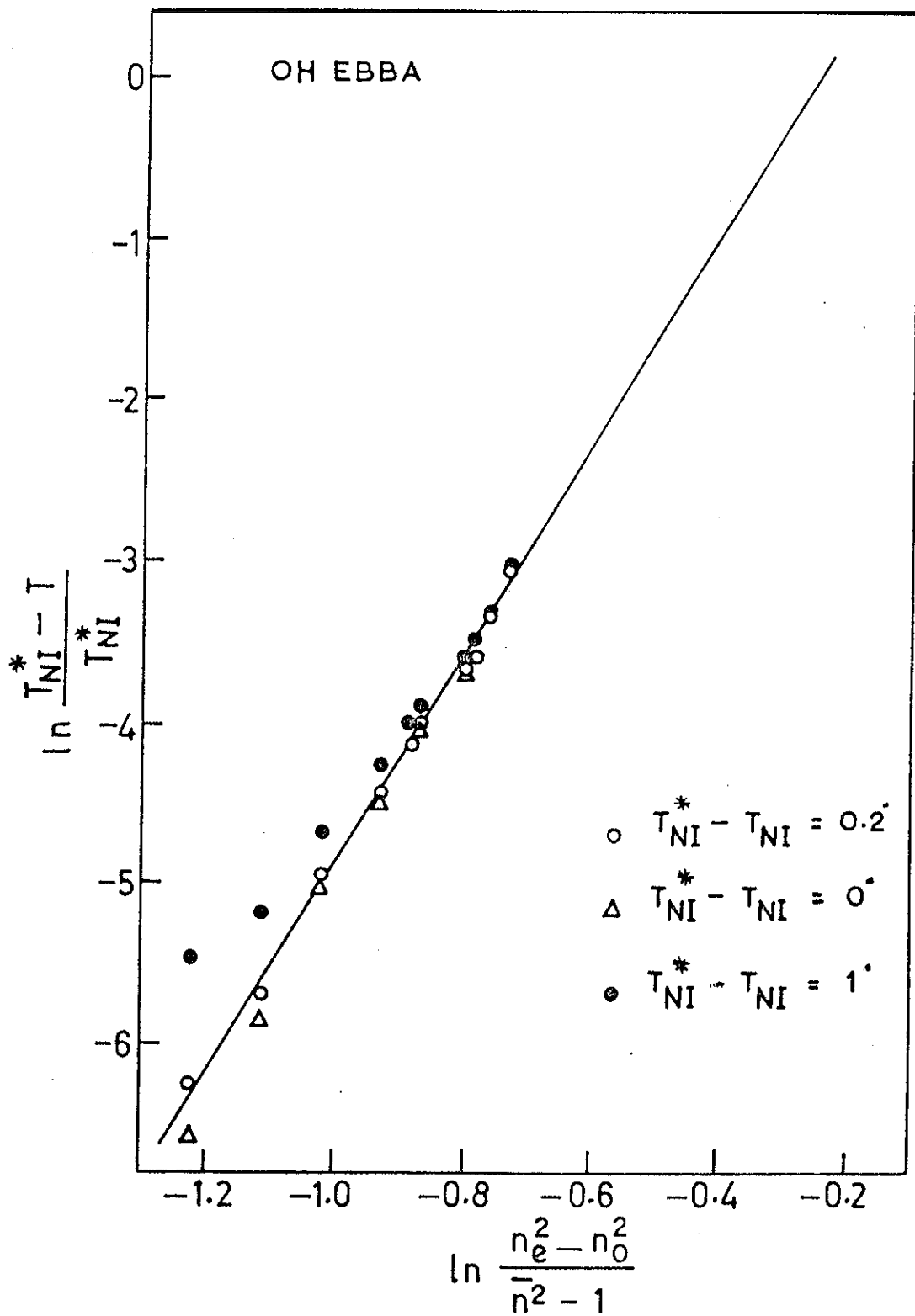


FIGURE 5.15

$\ln[(T_{NI}^* - T)/T_{NI}^*]$ plotted against $\ln[(n_e^2 - n_o^2)/(n^2 - 1)]$
for OH-EBBA

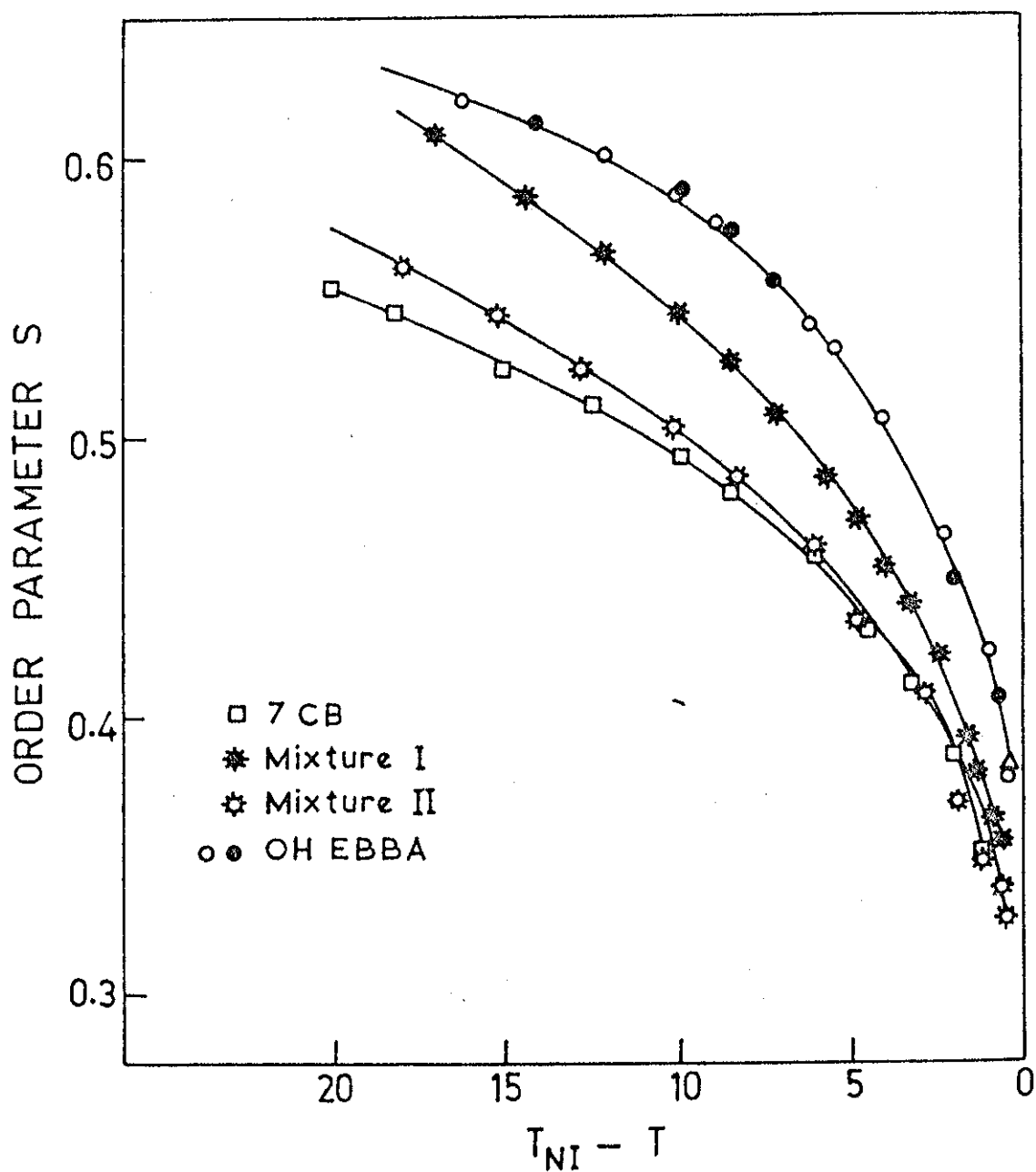


FIGURE 5.16

Order parameters of OH-EBBA, mixture I, mixture XI and 7CB plotted against relative temperature.

calculated values.

a, Elastic constants. The splay and bend elastic constants of the systems mentioned above were determined using the formula (see equations 4.6, 4.7 and 4.8)

$$k_{11} = \frac{x_0^2 H_0^2}{\pi^2} \frac{\Delta K}{H} \rho \quad (5.5)$$

The value of ΔK for 7CB was calculated by the method described in chapter IV. For OH-EBBA, this calculation was not possible as the principal susceptibilities of the C = N band are not known. Leenhouts (1979) has given a value of $54 \times 10^{-6} \text{ cm}^3/\text{mole}$ for ΔK of OH-MBBA, which is the lower homologue of OH-EBBA. We have made a reasonable assumption (Karat and Madhusudana 1979) that ΔK has the same value for both OH-EBBA and OH-MBBA. The values of ΔK for the mixtures were calculated using an additive law. These values are given in table 5.8.

The values of k_{11} for 7CB, OH-EBBA and the two mixtures are given in tables 5.9, 5.10, 5.11 and 5.12 and these are plotted against relative temperature in figure 5.17. At a given relative temperature the values of k_{11} for OH-EBBA is higher (~ 1.6 times) than those of 7CB. Mixture I which has got 16% 7CB has values of k_{11} which are higher (~ 1.2 times) than even those of pure OH-EBBA. The values of k_{11} for mixture II which has got 62% 7CB are intermediate.

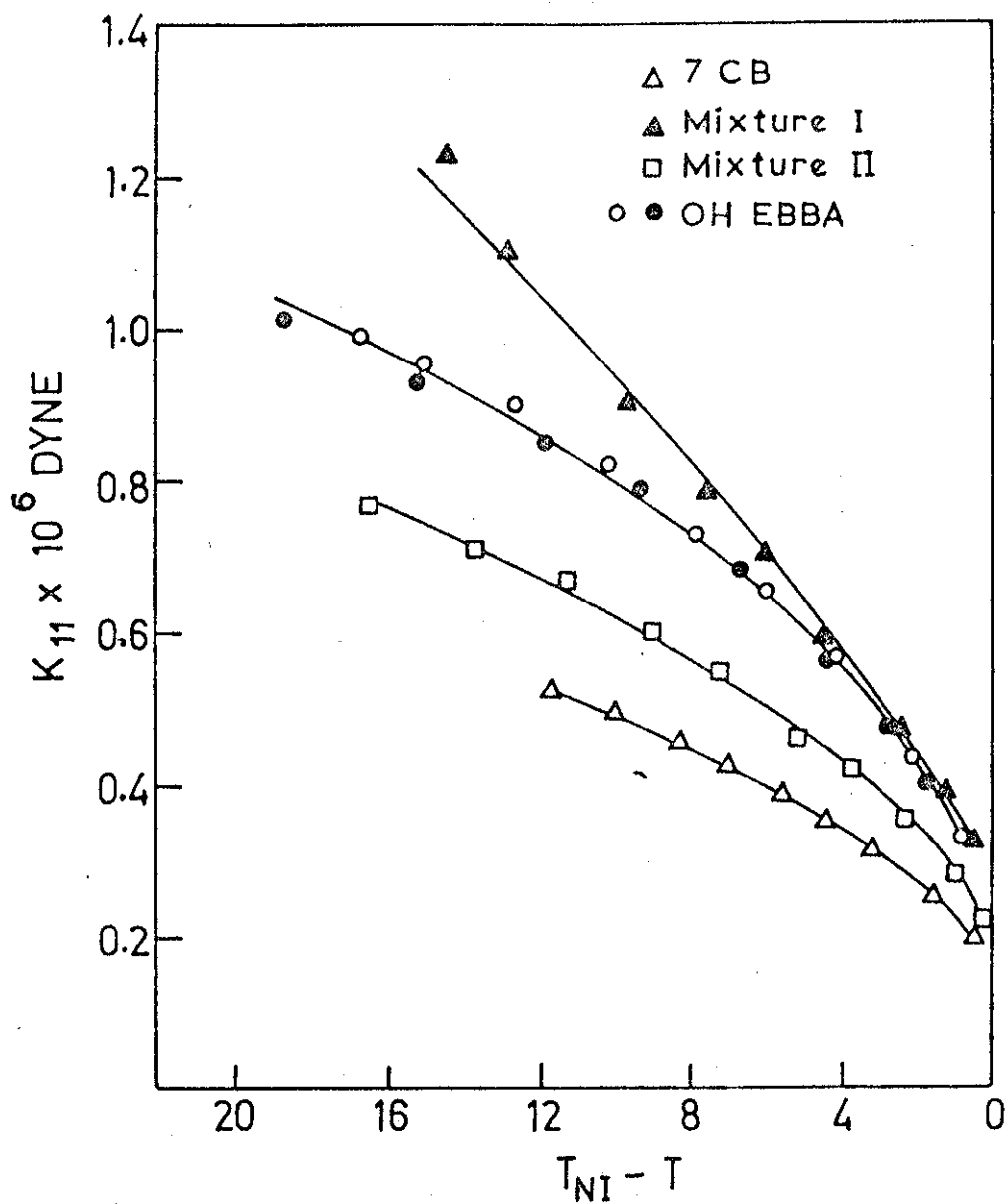


FIGURE 5.17

Splay elastic constants (k_{11}) of OH-EBBA, mixture I, mixture II and 7CB plotted against relative temperature.

between those of 7OB and OH-EBBA. An almost similar trend in the variation of k_{11} has been reported by Park and Labes (1977) who have measured the values of k_{11} in mixtures of MEBA and 8OB which show induced smectic mesomorphism. They have found that at the same relative temperature, as the concentration of 8OB increases in the mixture, k_{11} increases up to a certain concentration and thereafter remains almost constant.

In simple nematics, the elastic constants are expected to follow the predictions of the mean field theory, $k_{11} \propto s^2$ i.e., (Saupe 1960). However, in many cases, experimental results (see, for example, Karat and Madhusudana 1979) show considerable deviations from this relation. Hence we have tried to fit the results to a formula of the type $k_{11} = C a^x$ where x and C are constants. This was done by plotting $\log k_{11}$ against $\log a$. From the slope and intercept of the best straight line that could be drawn through the points, the values of x and C were obtained. The values so obtained are given in table 5.13. OH-EBBA and mixture I have got higher values (~ 2.5) of x compared to those of mixture II and 7OB (~ 2.2).

Tables 5.14, 5.15, 5.16 and 5.17 give the values of k_{33} for the systems under study. These values are plotted against relative temperatures in figure 5.18. As in the case of k_{11} at a given relative temperature OH-EBBA has got a higher

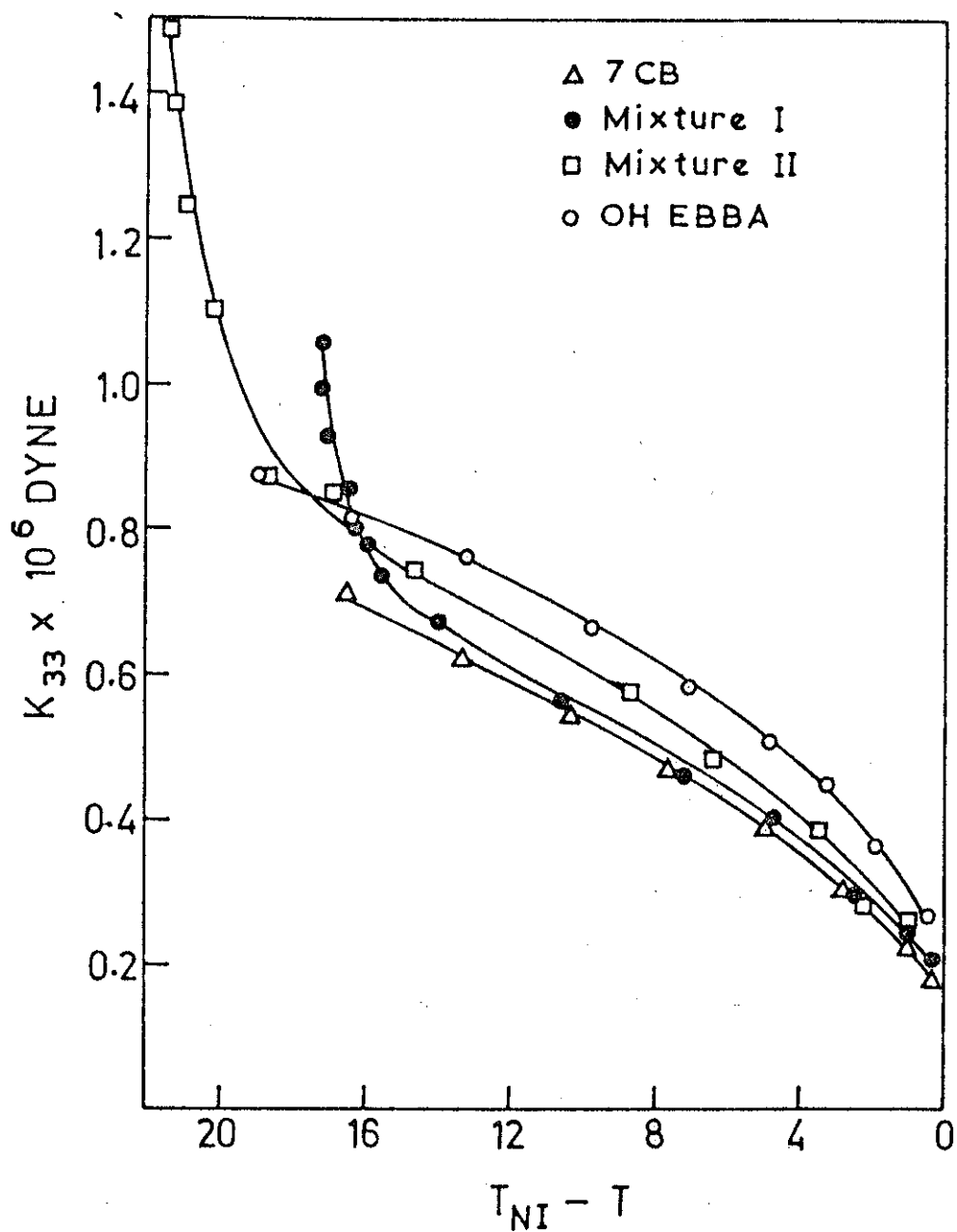


FIGURE 5.18

Bend elastic constants (k_{33}) of OH-EBBA, mixture I, mixture 11 and 7CB plotted against relative temperature.

(by ~ 1.25 times) value for k_{33} than for 7OB. The k_{33} values of the two mixtures are intermediate between those of 7OB and OH-EBBA at all relative temperatures except those which are close to the A_N transition point. Even though mixture XI has a higher percentage of 7OB, its k_{33} values are higher than those of mixture I. As pointed out earlier both the mixtures exhibit the A_I phase. As the A_I transition point is approached both of them show pretransitional increases in k_{33} .

In figures 5.19 and 5.20 we have plotted k_{11} , k_{33} and s against composition of the mixtures at two relative temperatures. The order parameter decreases steadily with increase in the concentration of 7OB. The figures bring out the notably high value of k_{11} and low value of k_{33} for mixture I (which has $\sim 16\%$ 7OB).

In figure 5.21, we have plotted k_{33}/k_{11} against relative temperature. $(k_{33}/k_{11}) < 1$ for OH-EBBA and it remains more or less independent of temperature. This result can be compared with the k_{33}/k_{11} ratio of OH-MBBA (Leenhouts et al 1979) which is slightly greater than 1 at lower temperatures and becomes less than 1 as the temperature approaches T_{NI} . Mixtures I and II also have $(k_{33}/k_{11}) < 1$ at temperature close to T_{NI} , the value being the lowest for mixture I. As the temperature is decreased, k_{33}/k_{11} decreases in mixture I attaining a value < 0.6 before it sharply increases as the

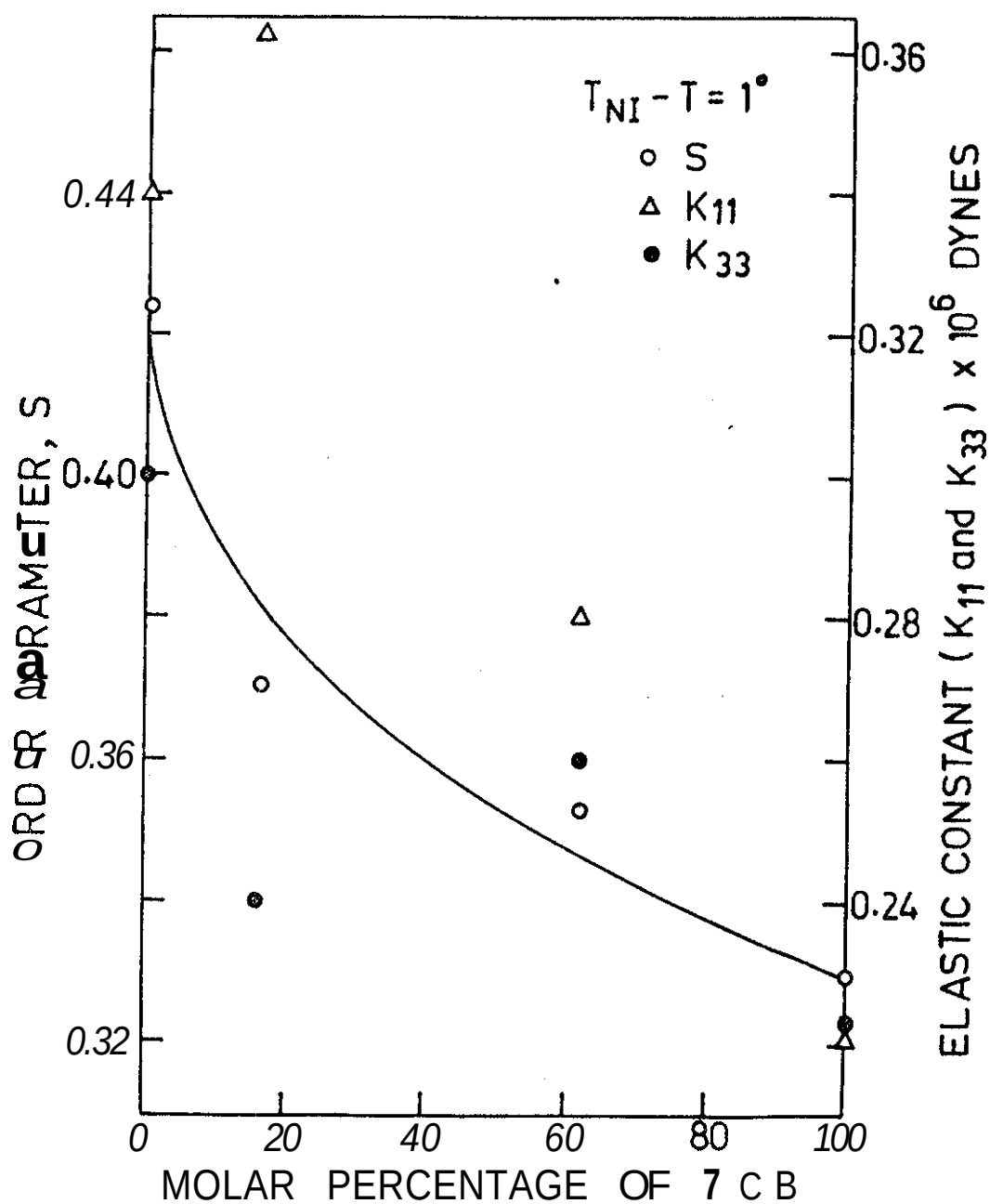


FIGURE 5.19

k_{11} , k_{33} and s plotted against concentration of 7CB in mixtures of 7CB and OH-EBBA for $T_{NI} - T = 1^\circ$.

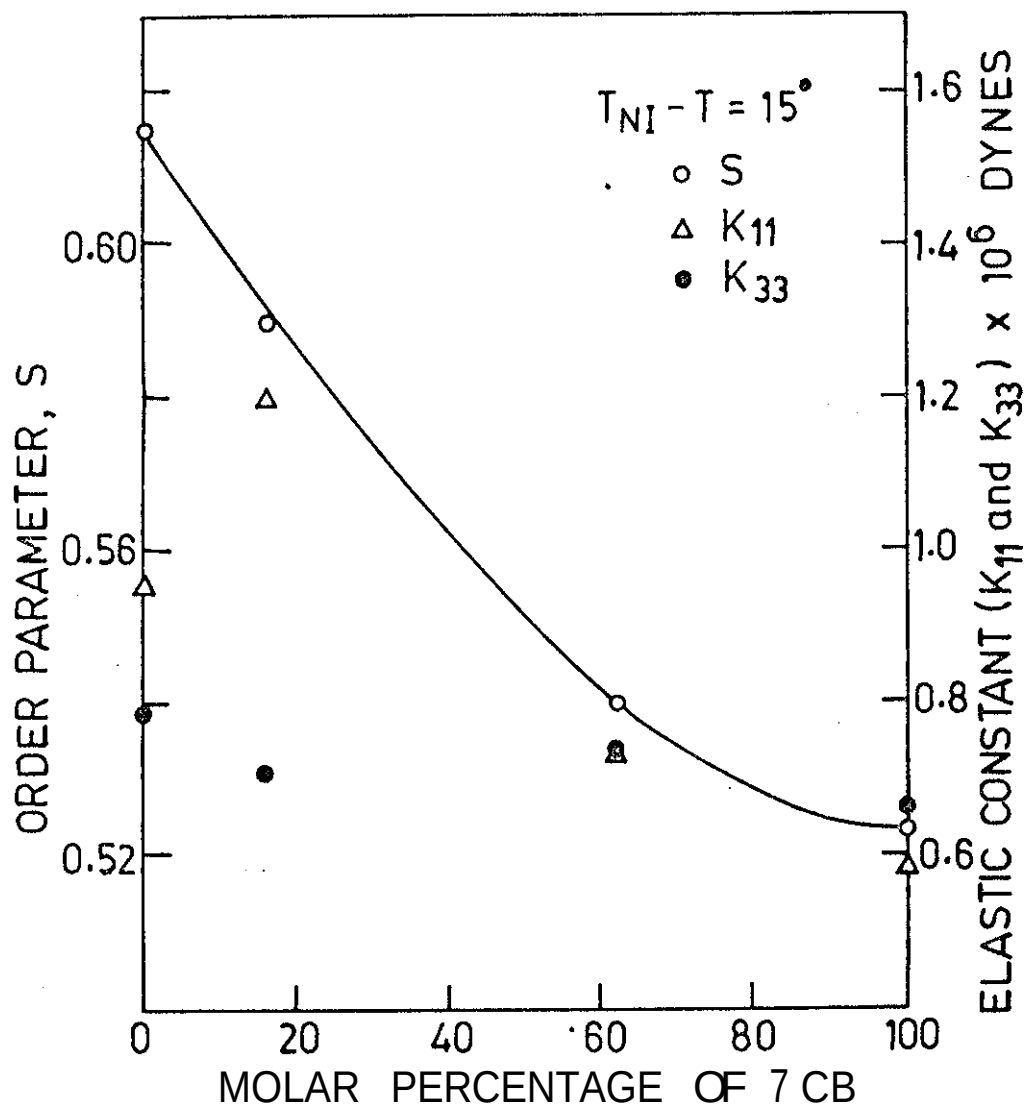


FIGURE 5.20

k_{11} , k_{33} and a plotted against concentration of 7CB in mixtures of 7CB and OH-EBBA for $T_{NI} - T = 15^\circ$.

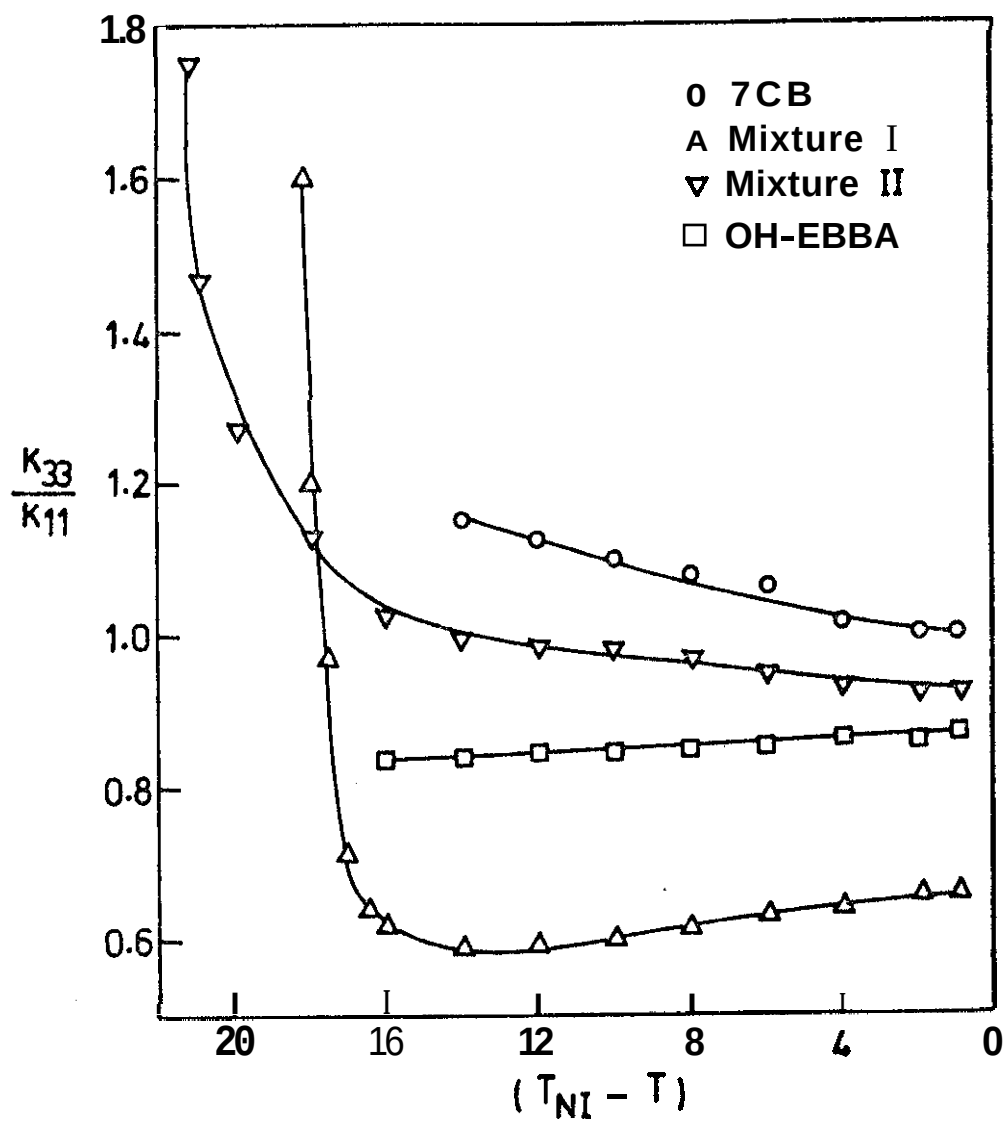


FIGURE 5.21

k_{33}/k_{11} of OH-EBBA, mixture I, mixture II and 7CB plotted against relative temperatures.

A_I^N point is approached. In mixture II, k_{33}/k_{11} slowly increases as the temperature is lowered from T_{NI} and shows the usual pretransitional increase close to the A_I^N transition temperature. In 7OB, $(k_{33}/k_{11}) \approx 1$ at temperatures close to T_{NI} and increases gradually as the temperature is decreased.

We can qualitatively understand some of these results in terms of Priest's (1973) theory of elasticity of nematic liquid crystals which is a detailed analysis based on the mean field theory (Saupe 1960). The specific results of the theory which can be compared with experimental data are the following.

$$\left. \begin{aligned} \frac{k_{11}}{\bar{k}} &= 1 + \Delta - 3\Delta' \frac{\bar{p}_4}{\bar{p}_2} + \dots \\ \frac{k_{22}}{\bar{k}} &= 1 - 2\Delta - \Delta' \frac{\bar{p}_4}{\bar{p}_2} + \dots \\ \frac{k_{33}}{\bar{k}} &= 1 + \Delta + 4\Delta' \frac{\bar{p}_4}{\bar{p}_2} + \dots \end{aligned} \right\} \quad (5.6)$$

where $\bar{k} = \frac{k_{11} + k_{22} + k_{33}}{3}$ and Δ and Δ' are molecular parameters depending on the nature of the compound and $\bar{p}_2 = a$ is the average second order Legendre polynomial and $\bar{p}_4$ is the average fourth order Legendre polynomial. Higher order terms ($\bar{p}_6$ etc.) should be included in principle, but, their contributions become progressively smaller.

If Δ and Δ' are positive, equations (3.6) lead to the result that when $(k_{33}/k_{11}) < 1$, $\bar{p}_4/\bar{p}_2$ is negative. This means that $\bar{p}_4$ is negative, since $\bar{p}_2$ is always positive. Such negative $\bar{p}_4$ values have been observed experimentally in Raman scattering studies (Miyano 1977, Prasad and Venugopalan 1980b) of some other compounds. However, no such data is available for the systems we have studied and hence no direct comparison could be made with Priest's theory. But we may point out that the negative values of $\bar{p}_4$ are compatible with the observed s values of the systems. The s values of mixtures calculated using the molar additive law come out to be more (by $\sim 8\%$) than the observed values. This implies that the peak of the actual distribution function of the molecule at $\theta = 0^\circ$ is not as sharp as the molar additivity law would suggest. Such a distribution could give rise to negative $\bar{p}_4$ values.

Further, Δ and Δ' are related to the length to breadth ratio (R) of the molecules. The higher the value of R the larger will be the value of k_{33}/k_{11} . Indeed, in a pure hard rod model (Priest 1973), A and A' are only functions of R and it turns out that as R goes below ~ 1.5 , k_{33}/k_{11} will be less than 1 even when $\bar{p}_4$ is positive. This has been experimentally confirmed (see for example, Leenhouts et al 1979, Karat and Madhusudana 1979). In figure 5.6, the composition of mixture I (16% 7CB) lies on the left side of the peak in the A_{TN} transition curve and hence the layer spacing corresponds

to an appropriate average length of single molecules, as we argued earlier. On the other hand, the composition of mixture 11 (62% 7OB) lies on the right side of the peak where the sample is supposed to be a mixture of monomolecular and bimolecular species. At any given relative temperature, the value of k_{33}/k_{11} for mixture I is lower than that of mixture II. This could either mean that $\bar{p}_4/\bar{p}_2$ is more negative in mixture I than in mixture II or, if it has comparable values in the two cases, the value of R is lower in mixture I than in mixture II. The latter explanation is to be preferred in view of x-ray results. Moreover, in these cases where short range order effects are strong, R has to be interpreted as equal to $\xi_{||}/\xi_{\perp}$ (Karat and Madhusudana, 1976; Gruler 1975) where $\xi_{||}$ and $\xi_{\perp}$ are the correlation lengths of the cybotactic groups along and perpendicular to the director respectively, rather than as Me length to breadth ratios of individual molecules (de Jeu et al 1975, Karat and Madhusudana 1979). The values of k_{33}/k_{11} for mixture II lie in between those of mixture I and 7OB. This is again a consequence of the fact that mixture 11 is indeed a mixture of monomolecular and bimolecular species.

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TABLE 5.1

Calculated and observed eutectic temperatures
for the mixtures under study

Mixture	Melting points °K	Heats of melting transition KJ/mole	Eutectic temperature		Eutectic composition (molar fraction)	
			Observed °K	Calculated °K	Observed	Calculated
7CB	301.5	19.0	286.0	291.5	0.63	0.77
OH-EBBA	344.8	23.16			0.37	0.23
PCH-7	303.0	6.4	-	294.8	-	0.74
OH-EBBA	344.5	23.16				0.24
7CB	301.5	19.0	290.5	297.6	0.65	0.91
HOAB	348.0	40.14			0.35	0.09

TABLE 5.2

Transition temperatures (in °C) of OH-EBBA, 7CB and some
mixtures

	<u>Smetic- nematic</u>	<u>Nematic- isotropic</u>
OH-EBBA	70.8	85.8
Mixture I (7CB : OH-EBBA = 16 : 84)	65 [*]	80.5
Mixture II (7CB : OH-EBBA = 62 : 38)	42 [*]	62.5
7CB	28.1	42.2

^{*} corresponds to the highest temperature at which A₁ phase
appears on cooling.

TABLE 5.3

Refractive indices, densities and order parameters
of OH-KBBA

$T_{NI} - T$	n_e	n_o	ρ gm/cc	s
<u>Trial No.1</u>				
0.5	1.697	1.555	1.072	0.377
1.0	1.708	1.549	1.072	0.423
2.3	1.719	1.545	1.074	0.463
4.0	1.730	1.540	1.075	0.505
5.5	1.738	1.538	1.077	0.531
6.2	1.742	1.538	1.080	0.539
8.8	1.755	1.537	1.085	0.575
10.0	1.759	1.537	1.087	0.585
12.1	1.763	1.536	1.088	0.598
16.3	1.771	1.535	1.092	0.620
<u>Trial No.2</u>				
0.45	1.695	1.552	1.073	0.381
0.85	1.701	1.549	1.073	0.405
2.00	1.712	1.545	1.075	0.445
4.35	1.724	1.540	1.077	0.491
6.15	1.730	1.537	1.080	0.530
7.20	1.743	1.534	1.081	0.556
8.40	1.749	1.533	1.083	0.574
9.80	1.755	1.532	1.085	0.591
14.00	1.764	1.532	1.090	0.613

[values of n_e and n_o correspond to $\lambda = 6328 \text{ \AA}$]

TABLE 5.4

Refractive indices, densities and order parameters of
 Mixture I
 (Values of n_e and n_o correspond to $\lambda = 6328 \text{ \AA}$)

$T_{NI} -$	n_e	n_o	$\rho \text{ gm/cc}$	a
0.7	1.676	1.547	1.059	0.355
1.0	1.678	1.546	1.059	0.363
1.4	1.681	1.544	1.059	0.377
1.6	1.685	1.543	1.060	0.390
2.5	1.694	1.541	1.062	0.420
3.4	1.699	1.539	1.064	0.439
4.0	1.703	1.538	1.065	0.453
4.9	1.706	1.535	1.064	0.470
5.8	1.711	1.534	1.066	0.486
7.2	1.717	1.532	1.067	0.507
8.5	1.721	1.529	1.066	0.527
10.1	1.728	1.529	1.069	0.545
12.2	1.734	1.527	1.011	0.566
14.5	1.741	1.526	1.073	0.587
17.0	1.748	1.524	1.075	0.611

TABLE 5.5

Refractive indices, densities and order parameters of
 Mixture II

$T_{NI} - T$	n_e	n_o	$\rho \text{ gm/cc}$	a
0.50	1.650	1.538	1.021	0.325
0.95	1.652	1.537	1.021	0.333
1.20	1.656	1.536	1.022	0.348
1.90	1.662	1.535	1.024	0.367
3.10	1.672	1.533	1.027	0.401
4.90	1.680	1.530	1.029	0.433
6.20	1.684	1.527	1.028	0.453
8.40	1.693	1.525	1.031	0.484
10.10	1.696	1.522	1.034	0.503
12.80	1.703	1.521	1.032	0.524
15.30	1.709	1.520	1.034	0.544
18.10	1.713	1.518	1.035	0.561
20.80	1.716	1.518	1.036	0.569

(values of n_e and n_o correspond to $\lambda = 6328 \text{ \AA}$)

TABLE 5.6

Refractive indices, densities and order parameters of 7OB

$T_{NI} - T$	n_e	n_o	ρ gm/cc	s
1.2	1.645	1.529	0.996	0.350
2.0	1.653	1.526	0.997	0.384
2.9	1.657	1.525	0.999	0.398
3.3	1.660	1.524	0.999	0.410
4.5	1.665	1.522	1.000	0.431
4.9	1.668	1.521	1.000	0.443
6.2	1.672	1.520	1.002	0.458
7.2	1.675	1.519	1.002	0.470
8.5	1.679	1.519	1.004	0.481
10.0	1.682	1.518	1.005	0.493
11.3	1.685	1.518	1.006	0.502
12.4	1.687	1.517	1.006	0.511
14.3	1.690	1.517	1.008	0.519
15.1	1.692	1.517	1.009	0.524
17.4	1.696	1.516	1.010	0.539
18.2	1.697	1.516	1.011	0.542
19.4	1.699	1.516	1.012	0.547
20.0	1.701	1.516	1.013	0.553

[values of n_e and n_o correspond to $\lambda = 6328 \text{ \AA}$]**TABLE 5.7** $\bar{\alpha}$ and $\bar{\alpha}/\Delta\alpha$ for the systems studied

Sample	$\bar{\alpha} \times 10^{24} \text{ cm}^3$	$\bar{\alpha}/\Delta\alpha$
OH-EBBA	37.59	1.284
Mixture I	37.36	1.306
Mixture II	36.69	1.349
7OB	36.13	1.390

TABLE 5.8

Anisotropy of molar diamagnetic susceptibilities

Sample	$\Delta K \times 10^6 \text{ cm}^3/\text{mole}$
OH-EBBA	54.0
Mixture I	51.6
Mixture II	44.7
7OB	39.0

TABLE 5.9

Spray elastic constants of OH-EBBA

$x_o = 23.5 \mu$

$T_{NI}-T$	H_o gauss	$k_{11} \times 10^6$ dynes
0.85	2725	0.320
1.90	2900	0.398
2.90	3025	0.475
4.50	3200	0.556
6.70	3400	0.683
9.60	3525	0.778
11.80	3625	0.852
15.30	3750	0.928
18.60	3838	1.009

$x_o = 23.6 \mu$

$T_{NI}-T$	H_o gauss	$k_{11} \times 10^6$ dynes
0.8	2750	0.326
1.9	3000	0.429
4.2	3200	0.566
6.0	3350	0.651
7.9	3450	0.732
10.2	3600	0.822
12.6	3675	0.902
15.0	3750	0.953
16.7	3800	0.985

TABLE 5.10Spray elastic constants of
Mixture I

$x_o = 28.1 \mu$

$T_{NI}-T$	H_o gauss	$k_{11} \times 10^6$ dynes
0.50	2500	0.319
1.25	2612	0.393
2.53	2750	0.471
4.50	2925	0.588
6.05	3100	0.699
7.60	3188	0.780
9.70	3350	0.902
12.75	3600	1.110
14.40	3750	1.233

TABLE 5.11Spray elastic constants of
Mixture II

$x_o = 27.0 \mu$

$T_{NI}-T$	H_o gauss	$k_{11} \times 10^6$ dynes
0.2	2450	0.217
1.0	2600	0.280
2.4	2775	0.352
3.75	2900	0.417
5.10	2988	0.462
7.30	3125	0.546
8.98	3200	0.600
11.30	3300	0.667
13.65	3350	0.712
16.45	3425	0.770

TABLE 5.12Spray elastic constants of 7CB
 $x_o = 31.5 \mu$

$T_{NI}-T$	H_o gauss	$k_{11} \times 10^6$ dynes
0.50	2075	0.196
1.50	2188	0.247
3.20	2338	0.314
4.40	2412	0.352
5.60	2475	0.386
6.95	2525	0.420
8.30	2575	0.449
10.10	2650	0.492
11.70	2688	0.521

TABLE 5.13The experimental values fitted to
the equation $k_{11} = CS^x$

Sample	x	a
OH-EBBA	2.50	3.29
Mixture I	2.54	3.27
Mixture II	2.12	2.72
7CB	2.20	2.75

TABLE 5.14

Bend elastic constants of
OH-EBBA $x_0 = 32.9\mu$

$T_{NI} - T$	H_0 gauss	$k_{33} \times 10^6$ dynes
0.43	1825	0.264
3.25	2075	0.363
4.88	2162	0.508
7.08	2225	0.579
9.80	2300	0.658
13.20	2425	0.762
16.43	2462	0.805
19.00	2550	0.874

TABLE 5.15

Bend elastic constants of
Mixture I $x_0 = 23.4 \mu$

$T_{NI} - T$	H_0 gauss	$k_{33} \times 10^6$ dynes
0.40	1675	0.204
1.00	1762	0.243
2.50	1888	0.289
4.80	2025	0.401
7.65	2100	0.463
10.60	2238	0.562
14.00	2400	0.672
15.70	2462	0.729
16.00	2525	0.771
16.35	2550	0.791
16.67	2650	0.858
16.95	2750	0.930
17.15	2925	1.057

TABLE 5.16

Bend elastic constants of
Mixture II $x_0 = 50 \mu$

$T_{NI} - T$	H_0 gauss	$k_{33} \times 10^6$ dynes
1.03	1325	0.246
2.23	1375	0.286
3.45	1500	0.376
6.37	1600	0.476
8.65	1700	0.570
13.45	1775	0.677
14.72	1838	0.739
16.78	1950	0.853
18.75	2050	0.969
20.25	2175	1.102
21.07	2300	1.237
21.33	2425	1.377
21.52	2500	1.467
21.60	25.75	1.560

TABLE 5.17

Bend elastic constants of 748

 $x_0 = 34.2 \mu$

$T_{NI} - T$	H_0 gauss	$k_{33} \times 10^6$ dynes
0.33	1825	0.175
0.94	1950	0.217
2.77	2125	0.299
5.00	2300	0.388
7.70	2425	0.464
10.33	2550	0.540
13.30	2675	0.619
16.50	2810	0.706