

# Chapter **4**

**Phase Diagram, Density and Optical Studies  
on Binary Mixture of a Cyanobiphenyl  
(11OCB) and a Benzoate Ester (ME6.O5)  
Showing Enhanced Smectic Phase**

## **4.1 Introduction:**

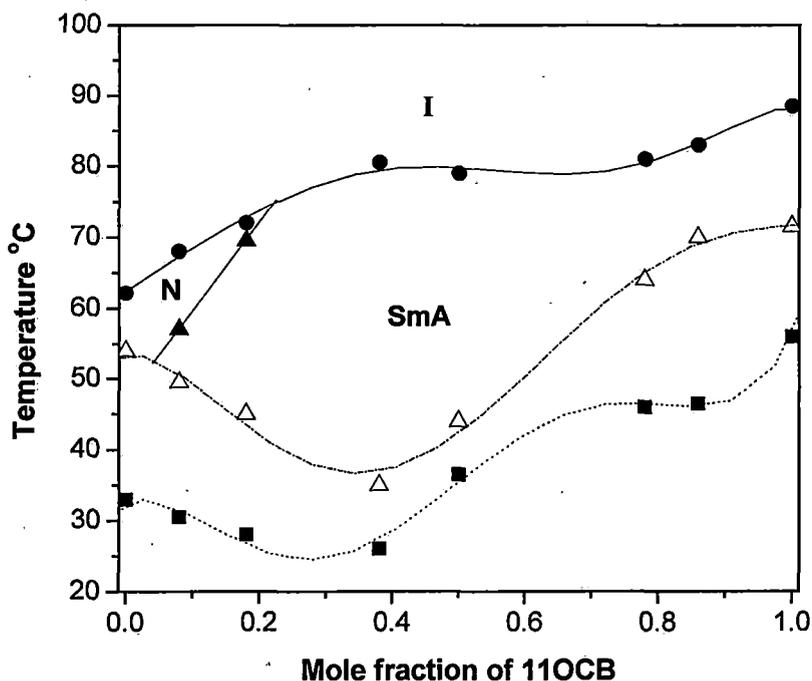
From the study of phase diagram in bicomponent and multicomponent systems, it has been found that smectic A phase can be strongly stabilized in mixtures [1,2]. The clearing temperature is increased compared to the corresponding temperature in the pure state, hence enhancing the respective phases. Some times, it has been observed that although none of the pure compounds is smectic, yet the mixtures of these compounds often show so-called induced smectic phase [3-5]. In many cases smectic phases existing in pure compounds of binary mixtures decrease their smectic stability and new phases of lower order are created. These phases are called 'phase created by depressing smectic stability' [6].

I have observed an enhanced smectic phase from the bicomponent mixtures of undecyloxy cyanobiphenyl (11OCB) and 4-n-hexyl phenyl-4-n'-pentyloxy benzoate (ME6.O5), where 11OCB and ME6.O5 show smectic A and nematic phases respectively. In this chapter, I have reported the phase diagram, density and refractive indices of the binary mixtures of 11OCB and ME6.O5 throughout the entire composition range. For better understanding of this phase, I have also calculated the variation of different physical parameters with molar concentration.

## **4.2 Phase diagram:**

The pure samples 11OCB and ME6.O5 were donated by E. Merck, U.K. and were used without further purification. The phase diagram of this system is obtained by studying the transition temperatures and textures of different

mixtures under crossed polariser with a polarizing microscope equipped with a hot stage (Mettler FP 80/82). The phase diagram of the binary system 11OCB + ME6.O5 are presented in figure 4.1.



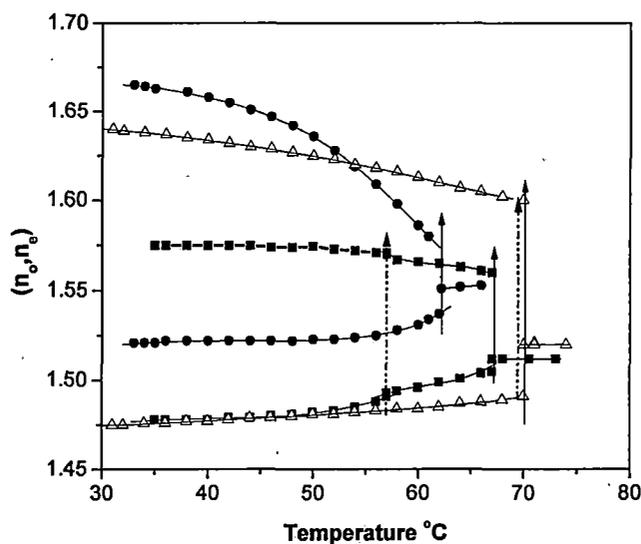
**FIGURE 4.1:** Phase diagram of the binary mixture of undecyloxy cyanobiphenyl (11OCB) and 4-n-hexyl phenyl-4-n'-pentyloxy benzoate (ME6.O5).  $x$  is the mole fraction of 11OCB. ● smectic or nematic to isotropic transition temperature; ▲ smectic to nematic transition temperature; △ melting temperature; ■ super cooled liquid crystal to solid transition.

The pure compounds 11OCB and ME6.O5 show only smectic and nematic phases respectively. From the phase diagram, it has been found that the smectic phase of 11OCB strongly influences the phase behaviour of the system. For mixtures having  $x > 0.15$  ( $x$  = mole fraction of 11OCB) the nematic phase is completely suppressed. For mixtures with  $0.03 < x < 0.15$  both smectic A and nematic phases are found to be present. Only nematic phase is found for  $x < 0.03$ . A strong positive and a negative deviation from

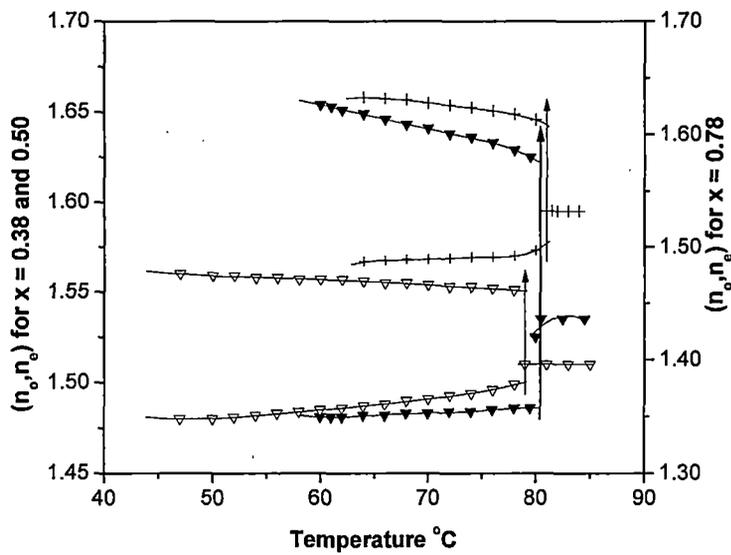
the linearity in the isotropic transition temperatures are obtained for mixtures with  $x \approx 0.4$  and  $0.8$  respectively. Positive deviation from the linearity has also been observed by Das et al [2]. Melting temperature shows a minimum around  $x \approx 0.4$ , where the thermal stability of the smectic A phase is maximum. The mixtures can be super-cooled by about  $20^\circ\text{C}$  in the mesomorphic phase before solidification and the solidification curve approximately follows trend of the melting curve.

### 4.3 Refractive index and density measurements:

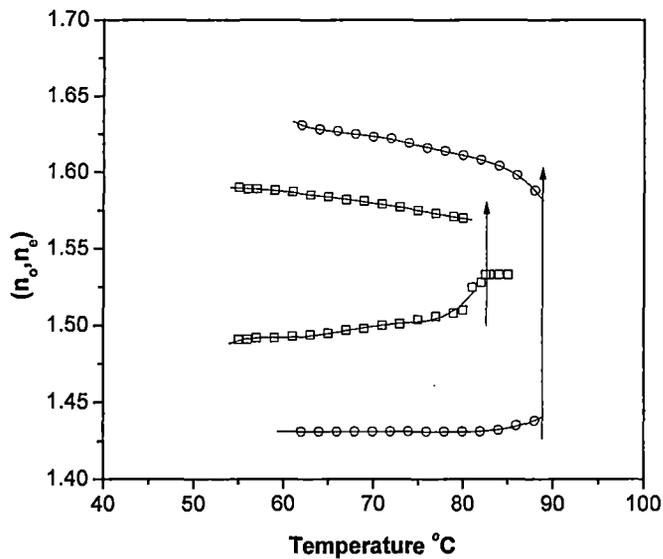
The refractive indices of the mixtures and that of the pure compounds were measured throughout the mesomorphic range for  $\lambda = 5780\text{\AA}$ , having accuracy  $\pm 0.001$  with the thin prism method ( $\angle 2^\circ$ ) [7], described in chapter 2. The variation of refractive indices ( $n_o, n_e$ ) with temperature are shown in figure 4.2 (a) – 4.2(c).



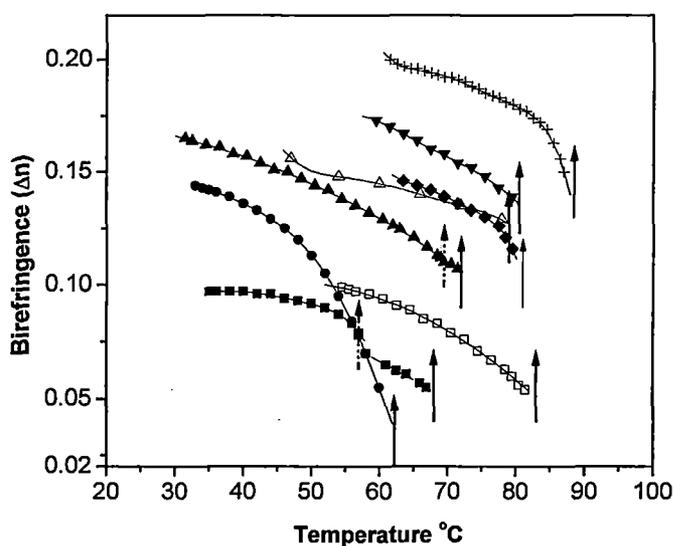
**FIGURE 4.2 (a):** Refractive indices ( $n_o, n_e$ ) as function of temperature for pure compounds. ● ME6.O5 and mixtures ■  $x = 0.08$ ;  $\triangle x = 0.18$ .  $\uparrow$  represents S-N and  $\uparrow$  N-I transition temperature.



**FIGURE 4.2 (b):** Refractive indices ( $n_o$ ,  $n_e$ ) as function of temperature for mixture  $\blacktriangledown$   $x = 0.38$ ;  $\nabla$   $x = 0.50$  and  $+$   $x = 0.78$ .  $\uparrow$  represents S-I transition temperature.



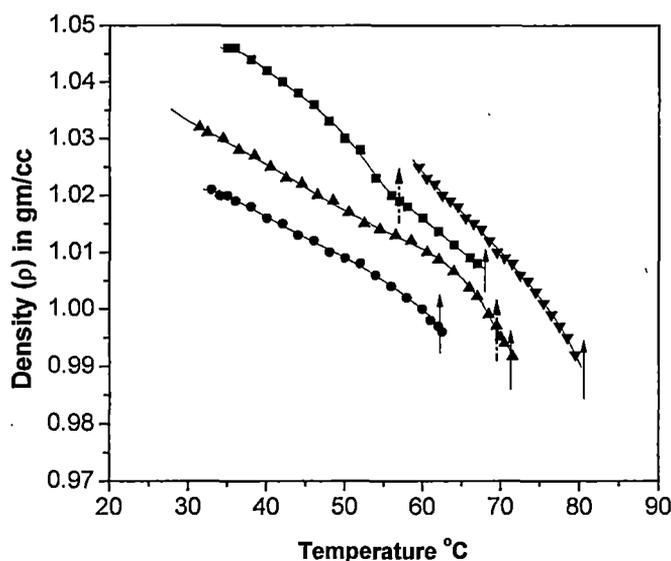
**FIGURE 4.2 (c):** Refractive indices ( $n_o$ ,  $n_e$ ) as function of temperature for mixtures pure compound  $\circ$  11OCB and for mixture  $\square$   $x = 0.86$ .  $\uparrow$  represents the S-I transition temperature.



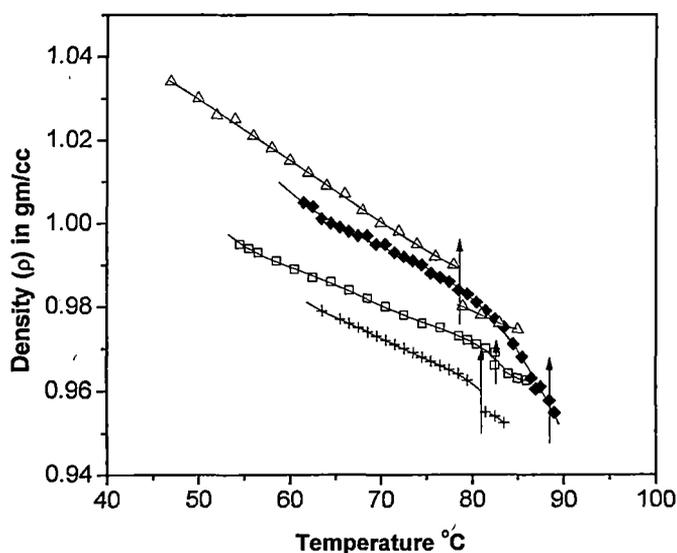
**FIGURE 4.3:** Birefringence ( $\Delta n = n_e - n_o$ ) as function of temperature for different mixtures and pure compounds. ● ME6.O5; + 11OCB; ■  $x = 0.08$ ; ▲  $x = 0.18$ ; ▼  $x = 0.38$ ; △  $x = 0.5$ ; ◆  $x = 0.78$ ; □  $x = 0.86$ . ↓ represents S-N and ↑ N-I transition temperature.

I have plotted optical birefringence ( $\Delta n = n_e - n_o$ ) as a function of temperature in figure 4.3. Birefringence values of ME6.O5 are lower than those obtained from 11OCB. This is expected because it is well known that cyanobiphenyl have greater birefringence than ester mesogens. On the other hand density values of ME6.O5 are higher than those obtained from 11OCB. A discontinuity in the density as well as  $\Delta n$  values at the smectic A to nematic phase transition is observed for mixtures having  $x = 0.08$ , indicating a first order smectic A to nematic phase transition.

The densities of the mixtures at different temperatures are determined within  $\pm 0.1\%$ , as described in chapter 2 of this thesis. The results of density measurements are presented in figures 4.4(a) and 4.4(b).

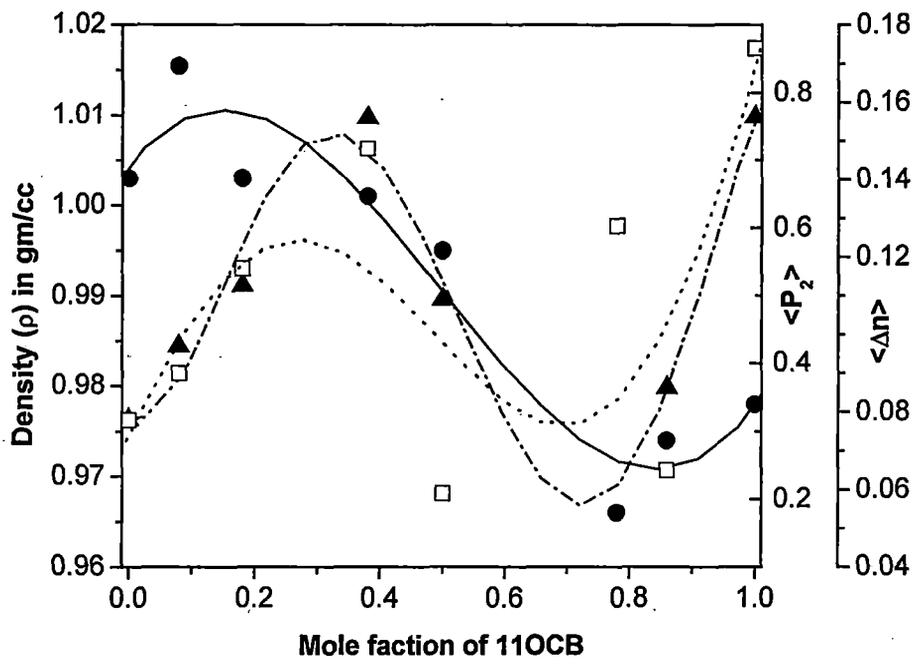


**FIGURE 4.4 (a):** Temperature variation of density ( $\rho$ ) of mixtures having mole fraction of 11OCB; ●  $x = 0.0$ (ME6.O5); ■  $x = 0.08$ ; ▲  $x = 0.18$ ; ▼  $x = 0.38$ .  
 ↑ represents S-N and ↑ N-I transition temperature.



**FIGURE 4.4 (b):** Temperature variation of density ( $\rho$ ) of mixtures having mole fraction of 11OCB;  $\Delta$   $x = 0.50$ .+  $x = 0.78$ ; □  $x = 0.86$ ; ◆  $x = 1.0$  (11OCB).

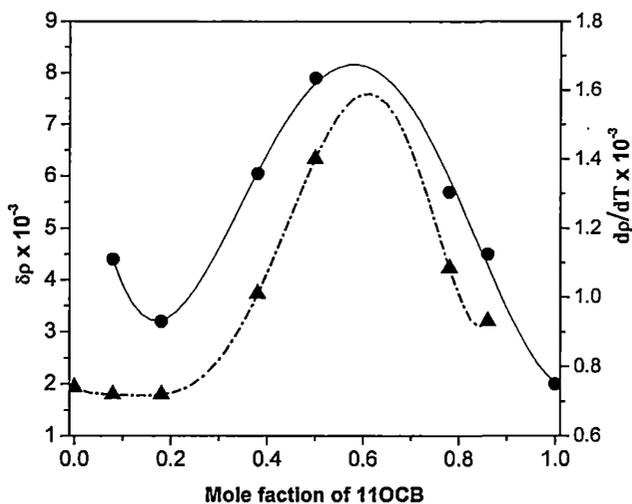
At a temperature 5°C below the isotropic transition temperature the density values increases slowly with mole fraction of 11OCB up to  $x = 0.25$  and then decreases continuously having a broad minimum near  $x \approx 0.8$  (Figure 4.5). On the other hand birefringence values increases up to  $x \approx 0.4$  and then continuously decreases creating a minimum near  $x = 0.8$ . It is to be noted that while density values of 11OCB are lower than the values obtained from ME6.O5, the birefringence values are somewhat higher.



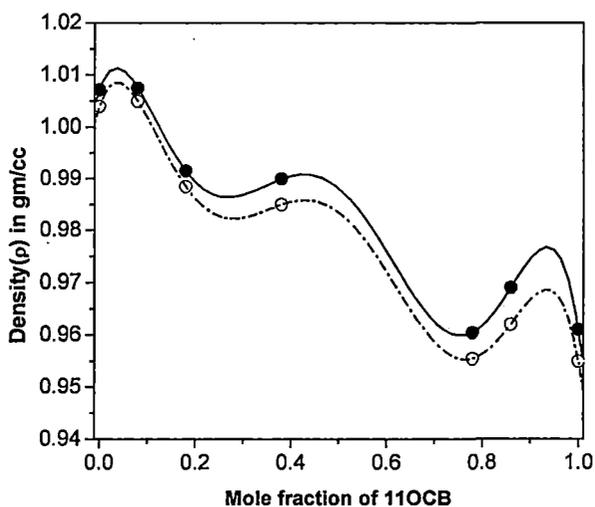
**FIGURE 4.5:** Density ( $\rho$ ),  $\langle P_2 \rangle$  and  $\Delta n$  against mole fraction of 11OCB at  $T=T_{SI}(T_{NI}) - 5^\circ\text{C}$ . ●  $\rho$ , ▲  $\langle P_2 \rangle$ , □  $\Delta n$ .

In figure 4.6, I have plotted thermal expansivity  $\beta = dp/dT$  in the smectic A phase along with the relative change of density ( $\delta\rho$ ) during Smectic A (nematic) / Isotropic phase transition. In both the cases the respective values

increases gradually with increase of  $x$  having a maximum near equimolar concentration. Similar behaviour is has also been reported by Das et al [2].



**FIGURE 4.6:** Change in density ( $\Delta\rho$ ) during smectic A or nematic to isotropic phase transition and ( $d\rho/dT$ ) in the smectic A phase with mole fraction of 11OCB. ●  $\Delta\rho$  and ▲  $d\rho/dT$ .



**FIGURE 4.7:** Density values ( $\rho$ ) just below (●) and above (○) the clearing temperature with mole fraction of 11OCB ( $x$ ).

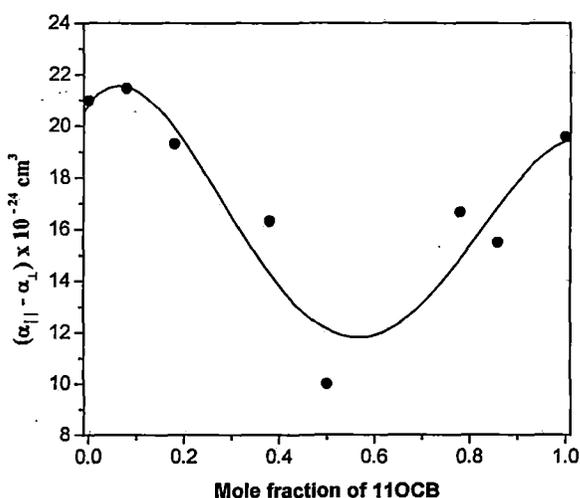
In figure 4.7, I have plotted density values in the mesomorphic and isotropic phase just below and above the mesomorphic to isotropic phase transition

against mole fraction. From this curve it has been found that for both the cases two minima are observed near  $x \approx 0.3$  and  $x \approx 0.8$ , where enhancement and depression of clearing temperature have been observed.

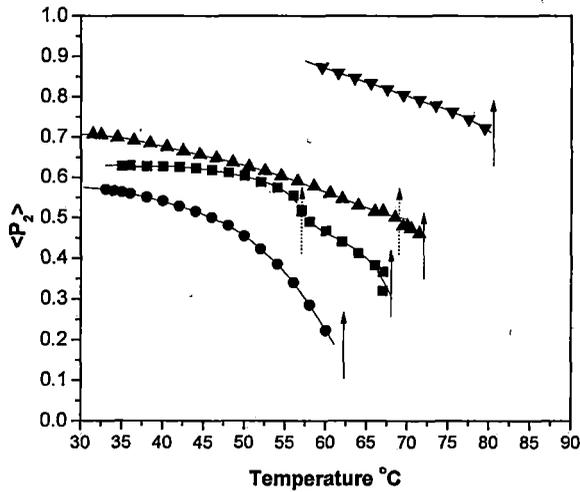
The refractive index data can be used in conjunction with density data to determine the orientational order parameter. The order parameter and optical properties of the system is connected by the relation

$$\langle P_2 \rangle = \frac{(\alpha_e - \alpha_o)}{\Delta\alpha} \quad 4.1$$

where  $\alpha_e$  and  $\alpha_o$  are the effective polarizabilities for extraordinary and ordinary rays which are calculated from refractive indices using Neugebauer's method [8].  $\Delta\alpha = (\alpha_{\parallel} - \alpha_{\perp})$  is the polarizability anisotropy, which can be estimated by applying well known Haller's extrapolation procedure [9]. In figure 4.8, I have plotted the polarizability anisotropy values for pure as well as different mixtures. Although polarizability anisotropy values obtained from Haller's procedure are somewhat scattered, a minimum of  $\Delta\alpha$  near equimolar concentration has been observed.

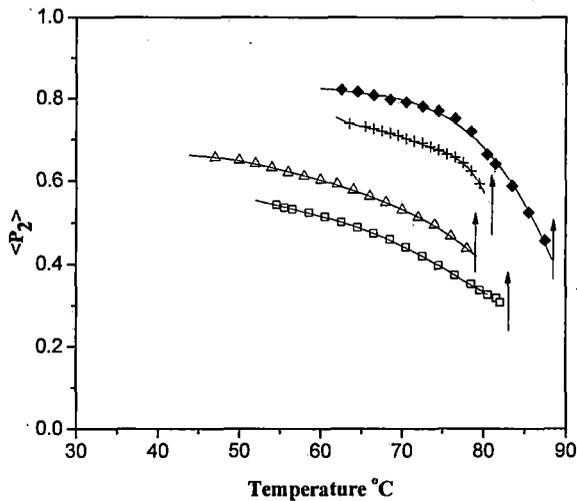


**FIGURE 4.8:** Variation of  $(\alpha_{\parallel} - \alpha_{\perp})$  against mole fraction of 11OCB. ● Neugebauer's method.



**FIGURE 4.9 (a):** Temperature variation of order parameter  $\langle P_2 \rangle$  for different mixtures and pure compound  $\bullet$  ME6.O5;  $\blacksquare$   $x=0.08$ ;  $\blacktriangle$   $x=0.18$ ;  $\blacktriangledown$   $x=0.38$ .

$\uparrow$  Represents S-N and  $\downarrow$  N-I transition temperature.



**FIGURE 4.9 (b):** Temperature variation of order parameter  $\langle P_2 \rangle$  for different mixtures and pure compound;  $\triangle$   $x = 0.50$ ;  $+$   $x = 0.78$ ;  $\square$   $x = 0.86$ ,  $\blacklozenge$  11OCB.

$\downarrow$  Represents the N-I transition temperature.

Figure 4.9(a) - 4.9(b) shows the variation of  $\langle P_2 \rangle$  values with temperature for different mixtures as well as for pure components.  $\langle P_2 \rangle$  values of ME6.O5 are lower than those obtained from 11OCB. The experimental

order parameter values at the SmA-N phase transition appears to be discontinuous for  $x = 0.08$  implying a first order phase transition. Maximum  $\langle P_2 \rangle$  values are obtained for mixtures with  $x = 0.38$  where the stability of smectic phase is maximum. Variations of  $\langle P_2 \rangle$  with mole fraction ( $x$ ) of 11OCB follow the trend as observed from birefringence and density measurements (Figure 4.5).

## References

1. B. Engelen, H. Heppke, R. Hopf and F. Schneider, *Ann. Phys.* **3**, 403 (1978).
2. M. K. Das, B. Jha and R. Paul, *Mol. Cryst. Liq. Cryst.*, **261**, 95 (1995).
3. M.K. Das and R. Paul, *Phase Transitions*, **46**, 185 (1994).
4. M.K. Das and R. Paul, *Phase Transitions*, **48**, 255 (1995).
5. D. A. Dunmur, R. G. Walker, P. Palffy Muhoray, *Mol. Cryst. Liq. Cryst.* **122**, 321 (1995).
6. R. Dabrowski, B. Wazynska and B. Sasnowska, *Liq. Cryst.*, **1**, 415 (1986).
7. A. K. Zeminder, S. Paul and R. Paul, *Mol. Cryst. Liq. Cryst.* **61**, 191, (1980).
8. H.E.J. Neugabauer, *Can. J. Phys.*, **32**, 1 (1954).
9. I. Haller, H.A. Huggins, H.R. Lilienthal, T.R. McGuire, *J. Phys. Chem.* **77**, 900 (1973).