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# Study of the physical properties of a mesogenic mixture showing induced smectic $A_d$ phase by refractive index, density and x-ray diffraction measurements

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## Abstract

The binary mixture of 4-n-pentyl phenyl 4-n'-hexyloxy benzoate (ME6O.5) and *p*-cyanophenyl trans-4-pentyl cyclohexane carboxylate (CPPCC) shows the presence of an induced smectic  $A_d$  phase in a certain concentration range  $0.03 < x_{\text{CPPCC}} < 0.6$ . The results of the differential scanning calorimetry (DSC), refractive indices, densities and x-ray diffraction measurements are reported here. In general, the change in birefringence is continuous at the smectic  $A_d$  to nematic phase transition for mixtures with  $x > 0.33$ , whereas there is a discontinuity in these values for mixtures with  $x < 0.33$ , consistent with the density and transition entropy measurements done on this system. The orientational order parameter, measured from x-ray diffraction studies, are somewhat smaller than those obtained from refractive index measurement in the induced smectic phase for all the mixtures. In the smectic phase, the OOP values initially increases with molar concentration up to  $x = 0.24$  and then decreases showing a broad minima around  $x = 0.4$ . The variation of layer thickness in the induced smectic phase with composition has been explained by assuming the formation of homo- and heterodimers. We conclude that the possible packing of molecules in the induced smectic  $A_d$  phase stabilizes the layers but increases the orientational free volume, consistent with the lower orientational order parameter.

## 1. Introduction

An induced smectic  $A_d$  phase has been observed to occur in bi-component mixtures of mesogens when none of the components of this mixture have a smectic phase [1–7]. Generally, induced smectic phases are found to form in binary mixtures of nematogenic compounds, one having a terminal polar group and the other being a terminal non-polar one and in a few cases in binary mixtures of non-polar mesogens [8, 9]. The strong induction of smectic  $A_d$  phase is also possible in binary mixtures of polar nematic compounds as well [10, 11]. A theoretical interpretation of this phenomenon has been given by considering complex formation between the two kinds of molecules [12] which imply an important influence of

the chemical structure. Although a considerable volume of work has been reported in the literature on systems involving polar–non-polar mixtures of biphenyl compounds showing induced smectic phases, not much work has been done on binary systems of cyclohexane compounds showing an induced smectic phase.

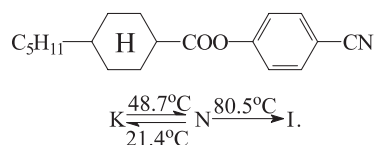
In this work, we report the existence of an induced smectic  $A_d$  phase in a binary mixture of 4-n-pentyl phenyl 4-n'-hexyloxy benzoate (ME6O.5) and *p*-cyanophenyl trans-4-pentyl cyclohexane carboxylate (CPPCC). The pure compounds show nematic phase only. For a proper understanding of the formation of an induced smectic phase and their influence on the adjacent nematic phase, the physical properties of the mixtures were studied by differential scanning

calorimetry (DSC), refractive index, density and x-ray diffraction measurements throughout the entire composition range.

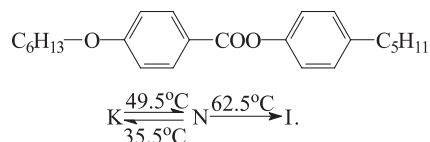
## 2. Experimental details

The compounds ME6O.5 and CPPCC were donated by E Merck, UK and were used without further purification. The transition temperatures of the pure compounds, their structural formulae and chemical names are as follows:

*Component 1.* *p*-cyanophenyl trans-4-pentyl cyclohexane carboxylate (CPPCC for short)



*Component 2.* 4-*n*-pentyl phenyl 4-*n'*-hexyloxy benzoate (ME6O.5 for short)

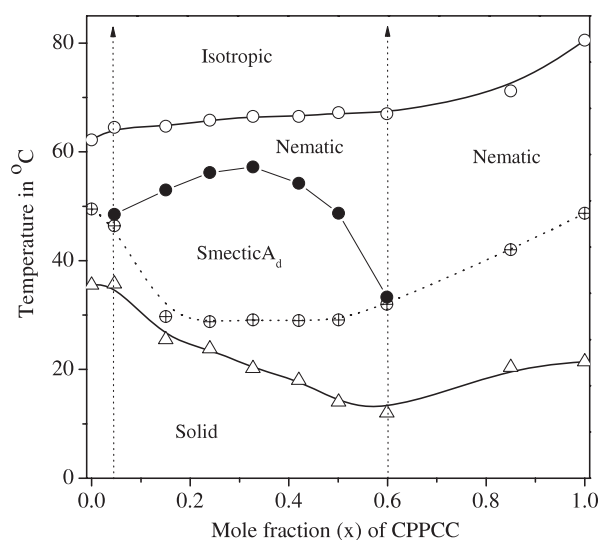


Phase transitions were studied by observing textures under a polarizing microscope equipped with a Mettler FP80/82 thermo-system. Transition entropies  $\Delta S$  ( $\text{J mol}^{-1} \text{K}^{-1}$ ) were obtained from DSC studies (at a heating rate of  $1^\circ\text{C min}^{-1}$ ) for all the mixtures and the pure compounds using a Mettler FP84HT TA Cell.

The densities of all the binary mixtures were measured with the help of a dilatometer of the capillary type. Temperature during the experiment was controlled to about  $\pm 0.5^\circ\text{C}$  by a temperature controller. Experimental uncertainty of the density measurement is 0.1%.

The ordinary ( $n_o$ ) and extraordinary refractive indices ( $n_e$ ) for wavelength  $\lambda = 5780 \text{ \AA}$  of a mercury vapour lamp were measured within  $\pm 0.001$  by the thin prism method (refracting angle  $< 2^\circ$ ). Details of the experimental technique used have been described by Zeminder *et al* [13]. From the density and refractive index values, we have calculated the principal polarizabilities  $\alpha_e$  and  $\alpha_o$ , using Neugebauer's anisotropic internal field model [14].

X-ray diffraction patterns were recorded on an x-ray film in a flat plate camera at several temperatures within the mesomorphic phase, using Ni-filtered  $\text{Cu K}\alpha$  radiation of wavelength  $\lambda = 1.542 \text{ \AA}$ . For x-ray diffraction study, the pure compounds as well as mixtures were aligned in a magnetic field of about 0.5 T. The x-ray diffraction photographs were scanned by a Mustek 1200 UB scanner. The grey mode scan was used and the resolution was set at 600 dpi. Optical densities of the pixels were calculated and then converted to x-ray intensities with the help of a calibration curve following the procedure of Klug and Alexander [15]. The Origin 7 software was used for data analysis purposes.



**Figure 1.** Phase diagram for the binary system of ME6O.5 + CPPCC.  $x$  is the mole fraction of CPPCC.  $\circ$  nematic–isotropic transition temperature,  $\bullet$  smectic  $A_d$ –nematic transition temperature,  $\oplus$  melting temperature,  $\Delta$  super-cooling temperature.

## 3. Results and discussion

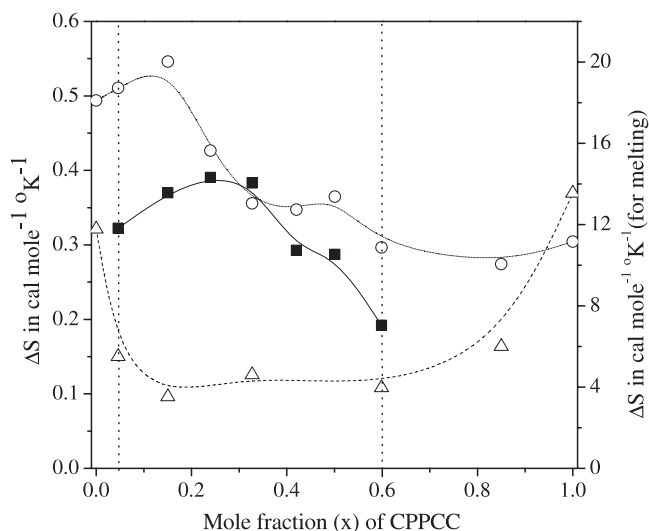
### 3.1. Phase diagram

The phase diagram of this system is shown in figure 1. A detailed study of the phase diagram by microscopic observation revealed that the transition temperatures are reproducible within  $\pm 0.5^\circ\text{C}$  between heating and cooling cycles for all the mixtures.

Of the eight mixtures prepared, one shows only a nematic phase and the rest have both nematic and induced smectic  $A_d$  phases. The nematic–isotropic and smectic  $A_d$ –nematic transition temperatures are plotted against molar concentration. The mixtures show an induced smectic  $A_d$  phase in the concentration range  $0.03 < x < 0.6$ , where  $x$  is the mole fraction of CPPCC. Maximum stability of the smectic phase occurs for mixtures having  $x \approx 0.33$ . Both the pure compounds and most of the mixtures show large super-cooling. The super-cooling temperatures show a minimum near  $x \approx 0.6$ . Textures of the pure compounds and their mixtures in nematic phases are of typical marbled type and those of the induced smectic phases are either fan-shaped or focal-conic, both typical of a smectic A phase. Homeotropic texture studies also confirmed the existence of an orthogonal phase in the induced smectic region.

### 3.2. DSC measurements

In figure 2, the results of the transition entropy are plotted as a function of molar concentration ( $x_{\text{CPPCC}}$ ). The entropy change during the smectic  $A_d$ –nematic phase transition ( $\Delta S_{\text{SN}}$ ) is largest near the maximum in the induced smectic phase. With the increase in concentration of CPPCC above  $x = 0.4$ , there is a rapid decrease in  $\Delta S_{\text{SN}}$ . This suggests that, for  $x > 0.4$ , the nature of the smectic  $A_d$  to nematic phase change



**Figure 2.** Transition entropies ( $\Delta S$ ) as a function of mole fraction of CPPCC. ■ smectic  $A_d$ –nematic transition, ○ nematic–isotropic transition,  $\Delta$  crystal–mesomorphic transition.

is different from that for  $x < 0.4$ . The increase in  $\Delta S_{SN}$  near  $x = 0.4$  is accompanied by a decrease in  $\Delta S_{NI}$ , from which it appears that the nematic phase above the induced smectic phase region is relatively disordered near  $x = 0.4$ .

It is to be noted that for all the mixtures (except  $x = 0.33$ )  $\Delta S_{NI}$  values are higher compared to  $\Delta S_{SN}$ . It appears from the figure that  $\Delta S$  values for the crystal–mesomorphic transition decreases with increasing concentration ( $x_{CPPCC}$ ), having a broad minimum near equimolar concentration.

### 3.3. Density measurements

The temperature variation of the density values for the mixtures is shown in figures 3(a) and (b).

A small discontinuity in the density values could be observed at the nematic to smectic  $A_d$  phase transition for mixtures around  $x \approx 0.33$ , consistent with the observed entropies of transition. Density values of pure ME6O.5 are

higher compared to CPPCC. However, density values in the induced  $SmA_d$  phase decrease with increase in mole fraction of CPPCC showing a minimum near  $x = 0.33$ . This indicates that the mixtures having the highest stability of the  $SmA_d$  phase are rather loosely packed.

### 3.4. Refractive index measurements

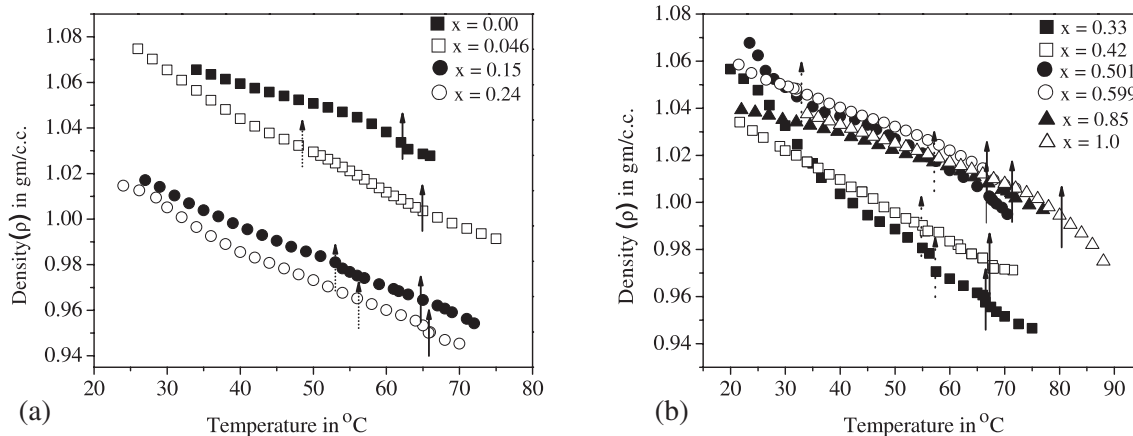
The temperature dependence of the principal refractive indices  $n_o$  and  $n_e$  and the refractive index in the isotropic phase ( $n_{iso}$ ) at wavelength  $\lambda = 5780 \text{ \AA}$  of all the mixtures and the pure components were measured, of which the temperature dependences of mixtures at  $x = 0.501, 0.599, 0.33$  and  $0.42$  are reported in figures 4(a) and (b). In general, the change in birefringence ( $\Delta n = n_e - n_o$ ) is continuous at the smectic  $A_d$ –nematic phase transition, for  $x > 0.4$ , which indicates a very weakly first-order or a second-order phase transition (figure 4(a)). On the other hand, for mixtures with  $x < 0.4$  a discontinuity in birefringence occurs at the smectic  $A_d$ –nematic phase transition which indicates a first-order phase transition (figure 4(b)). This observation is also supported from density and transition entropy measurements of these mixtures.

The variation of the refractive indices ( $n_o, n_e$ ) at temperature  $T = T_{NI} - 3.5^\circ\text{C}$  and  $n_{iso}$  with mole fraction is shown in figure 5. For mixtures with  $x < 0.24$  the  $n_o, n_e$  and  $n_{iso}$  values are more or less constant. However, for  $x > 0.24$ , these values decrease with increase in the molar concentration and show a broad minimum near  $x = 0.4$ .

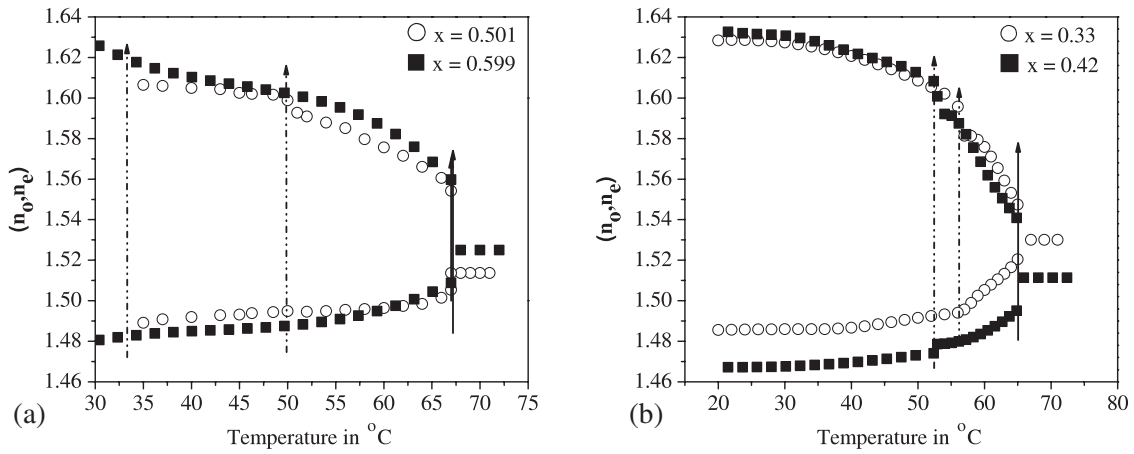
The principal molecular polarizabilities ( $\alpha_o, \alpha_e$ ) are measured from the refractive indices ( $n_o, n_e$ ) using Neugebauer’s method [14]. The orientational order parameter ( $\langle P_2 \rangle$ ) is calculated using the relation

$$\langle P_2 \rangle = \frac{\alpha_e - \alpha_o}{\alpha_{\parallel} - \alpha_{\perp}} \quad (1)$$

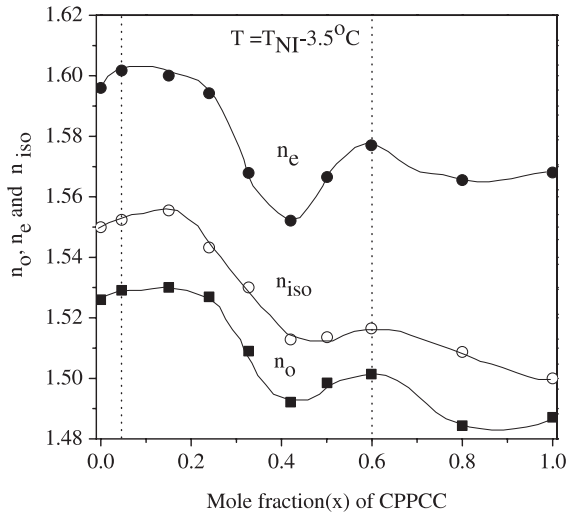
where  $\alpha_o$  and  $\alpha_e$  are the effective polarizability for the ordinary and extraordinary rays, respectively, and  $\alpha_{\parallel}$  and  $\alpha_{\perp}$  are the polarizabilities parallel and perpendicular to the long axis of the molecule in the solid state. The polarizability anisotropies in the perfectly ordered state were determined from the well-known Haller’s extrapolation method [16].



**Figure 3.** Variation of density ( $\rho$ ) as a function of temperature for (a)  $x = 0.0, 0.046, 0.15, 0.24$ , (b)  $x = 0.33, 0.42, 0.501, 0.599, 0.85, 1.0$ .  $\uparrow$  nematic–isotropic and  $\uparrow$  smectic  $A_d$ –nematic transition temperatures.



**Figure 4.** Temperature variation of refractive indices ( $n_o, n_e$ ) for (a)  $\circ x = 0.501$ ,  $\blacksquare x = 0.599$ , (b)  $\circ x = 0.33$ ,  $\blacksquare x = 0.42$ .  $\uparrow$  nematic-isotropic and  $\uparrow$  smectic  $A_d$ -nematic transition temperatures.



**Figure 5.** Variation of refractive indices  $\blacksquare n_o$ ,  $\bullet n_e$  and  $\circ n_{iso}$  with concentration.  $\uparrow$  represents the induced smectic  $A_d$  concentration range.

### 3.5. X-ray diffraction measurements

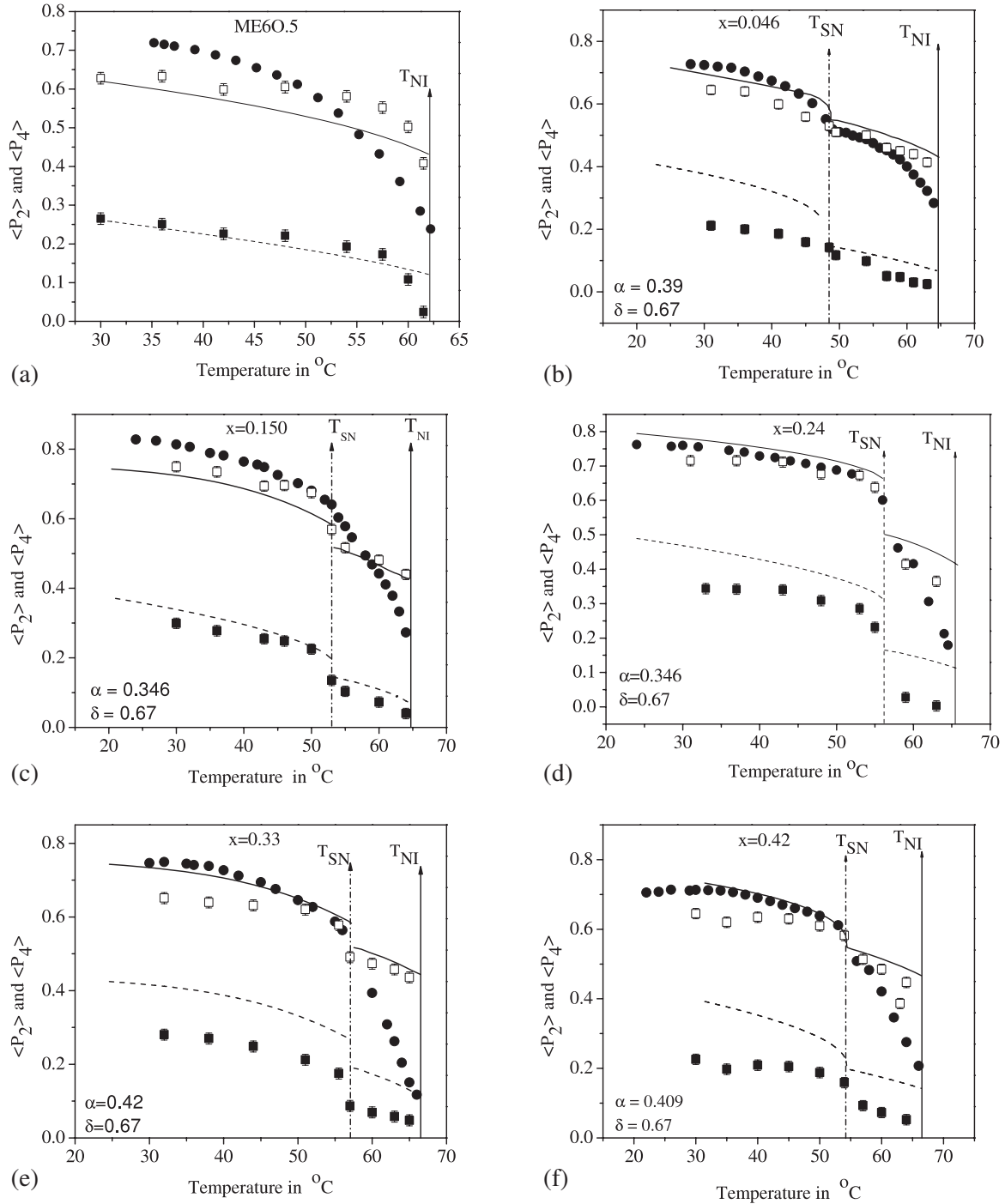
X-ray diffraction patterns were recorded throughout the mesomorphic range. A magnetic field of 0.5 T was applied to align the samples. The x-ray diffraction intensity data were analysed to evaluate order parameters following a procedure described by Bhattacharya and Paul [17]. Layer thickness and the apparent molecular length in the smectic and nematic phases were also determined from the x-ray data. The angular distribution of the x-ray intensity along the outer arc of the diffraction pattern was used to determine the orientational order parameter after necessary background correction.

Figures 6(a)–(j) show the variation of the experimentally determined orientational order parameters (OOP),  $\langle P_2 \rangle$  and  $\langle P_4 \rangle$ , with temperature for this system from x-ray diffraction measurements. In the same figures, we have also plotted the  $\langle P_2 \rangle$  values obtained from refractive index studies. The  $\langle P_2 \rangle$  values measured from x-ray diffraction studies are somewhat smaller than those obtained from refractive index

measurements for all the mixtures except near the nematic to isotropic phase transition. From the temperature dependences of the orientational order parameters for mixtures at different concentrations, it is again observed that there is an appreciable change in the order parameter values at the smectic  $A_d$  to nematic phase transition temperature for mixtures around  $x \approx 0.33$ .

We have also fitted the experimental order parameter values with McMillan's theory [18] for mixtures having a smectic  $A_d$  phase using  $\alpha$  and  $\delta$  as adjustable parameters in the McMillan potential. It may be mentioned that the order parameter values have been calculated keeping the  $\delta$  values constant over the entire composition range. This was done because the  $\alpha$  parameter depends on the molecular length, which varies with the chain length, whereas the parameter  $\delta$ , being the ratio of the translational to the orientational part of the potential, may be assumed to be almost constant with composition. The best fitted theoretical curve and the values of  $\alpha$  and  $\delta$  used for these calculations are shown in the respective figures. It is to be noted here that x-ray diffraction photographs of mixtures having 0.15 and 0.24 mole fractions of CPPCC are found to exhibit second-order meridional reflections from the smectic layers, implying rather a high degree of translational ordering. Orientational order parameter values from x-ray diffraction measurements are also found to be relatively high for these mixtures. The agreement between the experimental  $\langle P_2 \rangle$  values from x-ray diffraction measurements with those calculated from McMillan's theory is fair for  $x = 0.15$  and excellent for  $x = 0.24$  (figures 6(c) and (d)). Also, there is a discrete change in the values of  $\langle P_2 \rangle$  and  $\langle P_4 \rangle$  at the smectic  $A_d$ -nematic phase transition, indicating a first-order phase transition for these mixtures.

Mixtures having  $x = 0.33$  and 0.42 do not show second-order meridional reflection (as observed from x-ray diffraction photographs) but these mixtures exhibit a first-order smectic  $A_d$ -nematic phase transition as observed from the discontinuity in the OOP values at the transition (figures 6(e) and (f)). The best fitted theoretical curve from McMillan's theory is also indicated in these figures. For mixtures having mole fraction  $x = 0.046, 0.501$  and 0.599, the experimental



**Figure 6.** Temperature variation of  $\langle P_2 \rangle$  and  $\langle P_4 \rangle$  for (a) ME6O.5, (b)  $x = 0.046$ , (c)  $x = 0.15$ , (d)  $x = 0.24$ , (e)  $x = 0.33$ , (f)  $x = 0.42$ , (g)  $x = 0.501$ , (h)  $x = 0.599$ , (i)  $x = 0.85$ , (j) CPPCC. ● = refractive index data for  $\langle P_2 \rangle$ , □ = x-ray data for  $\langle P_2 \rangle$ , ■ = x-ray data for  $\langle P_4 \rangle$ , —  $\langle P_2 \rangle$  and - - -  $\langle P_4 \rangle$  from Maier–Saupe theory ((a), (i) and (j)), from McMillan’s theory ((b)–(h)).  $T_{NI}$  = nematic–isotropic and  $T_{SN}$  = smectic  $A_d$ –nematic transition temperatures.

order parameter values seem to change continuously at the smectic  $A_d$ –nematic phase transition and their agreement with McMillan’s theory is fair for  $x = 0.501$  and  $0.599$ ; and poor for  $x = 0.046$  (figures 6(b), (g) and (h)).  $\langle P_2 \rangle$  and  $\langle P_4 \rangle$  values for the remaining three samples (two pure components and the mixture with  $x = 0.85$ ) having a nematic phase only (figures 6(a), (i) and (j)) have been compared with the theoretical Maier–Saupe [19] values. The experimental  $\langle P_2 \rangle$

and  $\langle P_4 \rangle$  values from x-ray diffraction measurements are in fair agreement with the theoretically predicted Maier–Saupe values for ME6O.5 and are somewhat lower for the mixture with  $x = 0.85$  and the pure compound CPPCC.

In the nematic phase of the mixtures, the experimental OOP values determined from x-ray diffraction study are in closer agreement with the theoretical curve compared to that obtained from refractive index measurement. Near the

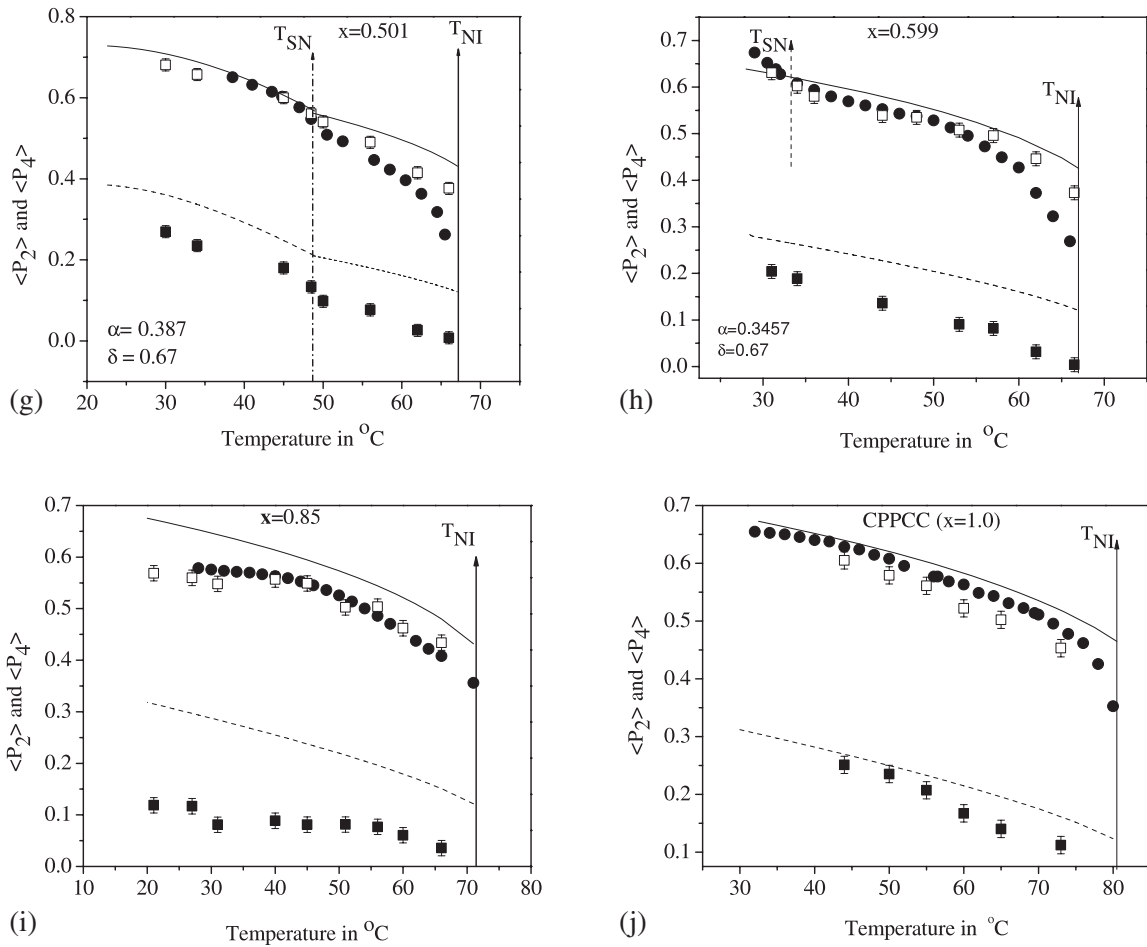


Figure 6. (Continued.)

nematic–isotropic transition temperature, we find a significant disagreement between the order parameter values determined from x-ray diffraction and refractive index measurements. This discrepancy may be due to the fact that different approximations and averaging are involved in calculating the orientational order parameter from experimental data obtained from x-ray studies on the one hand and birefringence measurements on the other [20]. The  $\langle P_4 \rangle$  values obtained from x-ray diffraction measurement, however, are always significantly less than the theoretically calculated values in both smectic and nematic phases. Such behaviour of  $\langle P_4 \rangle$  has been observed by others [20–23].

Figure 7 shows the variation of the OOP values at  $T = 35^\circ\text{C}$  against mole fraction from x-ray diffraction measurements. The birefringence ( $\Delta n$ ) values at the same temperature are also plotted in this figure. From this figure it is clear that, in the smectic phase, the OOP values initially increase with molar concentration up to  $x = 0.24$  and then decrease showing a broad minima around  $x = 0.4$ . The  $\Delta n$  values also show similar behaviour. Previously we have also observed a similar trend in the variation of  $\langle P_2 \rangle$  and birefringence with mole fraction for a binary mixture with ME6O.5 and a cyanobiphenyl (5CB) as the individual components. However, for such a system this minimum has been observed at nearly equimolar concentration [4].

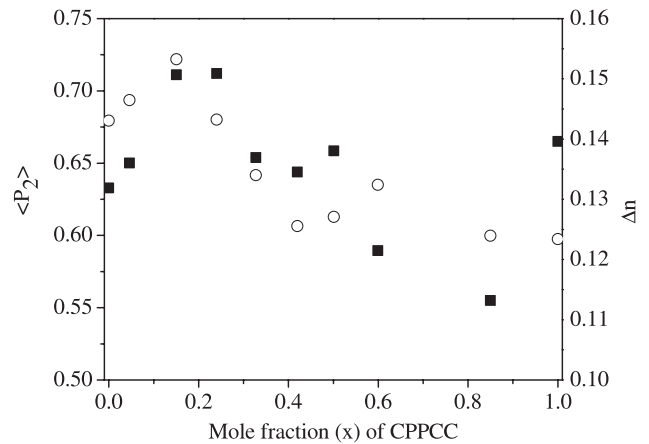
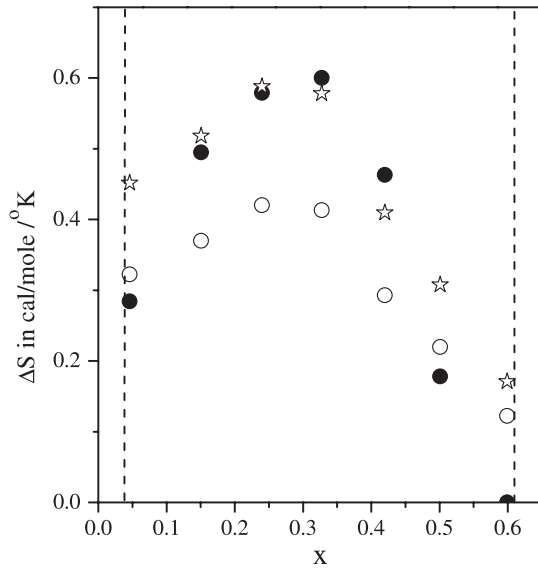


Figure 7. Concentration variation of  $\langle P_2 \rangle$  values obtained from x-ray diffraction measurements (■) and  $\Delta n$  values (○) at  $T = 35^\circ\text{C}$ .

Regarding the behaviour of the entropy change associated with the smectic  $A_d$ –nematic phase transition,  $\Delta S_{SN}$  in this system, we have calculated  $\Delta S_{SN}$  from McMillan’s theory, taking the values of  $\alpha$ ,  $\delta$ ,  $\eta$ ,  $\tau$  and  $\sigma$  at either side of the smectic–nematic transition temperature obtained from the best fit theoretical curve to the experimental x-ray  $\langle P_2 \rangle$  data. The



**Figure 8.** Entropy change associated with smectic to nematic phase transition of a mixture ME6O.5/CPPCC with mole fraction. ○ calculated values of  $\Delta S_{SN}$  from McMillan's theory. ☆ calculated values multiplied by a factor 1.4, ● experimental values.

$\Delta S_{SN} = (S_N - S_S)$  is calculated from the following well-known expressions [24]:

$$S_S = -\frac{Nk}{T^*}(\eta_S^2 + \alpha\delta\tau_S^2 + \alpha\sigma_S^2) + Nk \ln Z_S \quad (2)$$

$$S_N = -\frac{Nk}{T^*}\eta_N^2 + Nk \ln Z_N \quad (3)$$

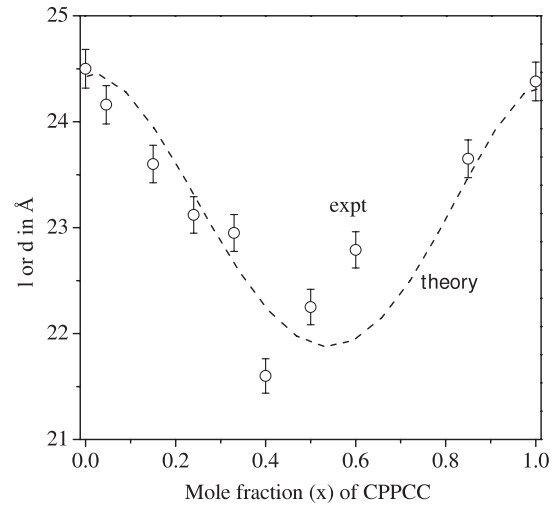
where

$$T^* = \frac{kT}{\nu}.$$

Figure 8 shows the theoretically estimated and experimentally determined entropy values. It is observed that, although the general trend of the behaviour of the entropy change at the smectic  $A_d$ -N phase transition,  $\Delta S_{SN}$ , in the region of the induced smectic phase is reproduced by the theory, the calculated values of the entropy change at the smectic  $A_d$  to nematic transition are somewhat larger, by 1.4 times. The agreement could have been better by changing the values of  $\alpha$  and  $\delta$ , but we have used only those values which give the best fit to our experimental order parameter values.

The temperature dependence of the apparent molecular length, i.e. density wave parallel to the director, in the nematic phase and layer thickness in the smectic phase have been measured from the x-ray diffraction pattern for all the mixtures. It has been found that the apparent molecular lengths ( $l$ ) in the nematic phase increase with increasing temperature. The layer thickness ( $d$ ) in the smectic phase, however, is found to be almost independent of temperature, which is quite common in the smectic A phase.

In figure 9 we have plotted the variation of layer spacing or apparent molecular lengths with mole fraction of CPPCC at  $T = 35^\circ\text{C}$ . The variation shows a broad minimum of  $\sim 21.6 \text{ \AA}$  at about  $x = 0.42$  concentration. This behaviour was



**Figure 9.** Variation of layer thickness ( $d$ ) with molar concentration. Vertical bars represent the estimated error.

also observed by us earlier [3–5], where the layer thickness shows a minimum at about equimolar concentration. In order to calculate the variation of layer thickness with molar concentration we assume that the pure CPPCC molecules (molecule A) form an association in the nematic phase. The apparent molecular length of CPPCC as determined from x-ray diffraction studies is  $24 \text{ \AA}$ , which is much larger than its model molecular length of  $17 \text{ \AA}$ . It is considered that the molecules form an association and the pure state is a mixture of predominantly associated dimers and monomers, which are in dynamic equilibrium. On the other hand, since the apparent molecular length of the ME6O.5 molecule (molecule B), as determined from x-ray studies [3], is almost equal to the model molecular length, so molecule B exists as a monomer in its pure state. In mixtures we can assume that the terminal polar molecules form homodimers (AA) as well as heterodimers (AB). The possibility of formation of such homo- and heterocomplexes was proposed earlier by others [25, 26]. Garg and Spears from their molecular modelling on a related system showed a strong interaction between two species forming a hybrid molecule [27]. Such cross-interaction is also proposed by Kyu *et al* [28, 29] from their theoretical work on induced smectic A phases.

Hence, in the mixtures we can assume that there exists A, B, AA and AB types of molecules in equilibrium. The mole fractions of different species  $x_A$ ,  $x_B$ ,  $x_{AA}$  and  $x_{AB}$  can be determined from the equilibrium constants  $K_A$  and  $K_{AB}$  for the associations  $A + A \leftrightarrow AA$  and  $A + B \leftrightarrow AB$ , respectively. Using equilibrium constants  $K_A = 1000$  and  $K_{AB} = 800$ , the percentage of different species, A, B, AA and AB as a function of the mole fraction of CPPCC have been calculated. These values of  $K_A$  and  $K_{AB}$  are typical of similar systems we have studied previously [4].

The average  $d$  value may then be written as

$$d = x_A d_A + x_{AA} d_{AA} + x_{AB} d_{AB} + x_B d_B \quad (4)$$

where  $x_A$ ,  $x_B$ ,  $x_{AA}$  and  $x_{AB}$  are mole fractions of the respective components in chemical equilibrium, and  $d_A$  and  $d_B$  are taken



to be equal to the lengths of the molecules A and B as obtained from a molecular model kit.  $d_{AB}$  is taken as the arithmetic mean  $d_A$  and  $d_B$ , while  $d_{AA}$  has been adjusted so that in the pure terminal polar compound, which has both A and AA molecules, the apparent molecular length equals ( $=x_A d_A + x_{AA} d_{AA}$ ) the experimentally observed  $d$  value. The values of  $d$  at  $T = 35^\circ\text{C}$ , calculated from equation (4), is shown in figure 9. It is to be noted that the values of  $K_A$  and  $K_{AB}$  can be varied by about 15% without much change in the calculated values of  $d$ . From figure 9 it is seen that the calculated result for the layer thickness is in good agreement with the experimental values.

#### 4. Summary and conclusions

The physical properties of a polar–non-polar binary system comprising of two nematogenic compounds, one having a biphenyl core and the other a cyclohexane-containing core have been studied extensively by different experimental techniques. The phase diagram reveals the presence of an induced smectic  $A_d$  phase in the concentration range  $0.03 < x_{CPPCC} < 0.6$ . The order of the induced smectic  $A_d$  to nematic phase transition is continuous for  $x > 0.4$  and discontinuous for  $x < 0.4$ . This observation has been supported from DSC, density, optical birefringence and x-ray diffraction studies. Measurements of the refractive indices and x-ray diffraction on mixtures at different compositions of this system have shown that there is a minimum in the birefringence as well as orientational order parameter values, corresponding to a maximum in the stability of the  $SmA_d$  phase. Further analysis of the x-ray data has revealed a minimum in the smectic layer spacing at nearly the same composition range. From this work, we now have a better understanding of the molecular association in mixtures of polar–non-polar systems. The minimum of layer spacing can be attributed to the specific molecular organization between the components of the mixture, which stabilizes the translationally ordered phase but increases the orientational free volume, resulting in lower orientational order parameter as determined from optical and x-ray methods. This result is consistent with the translationally ordered mesophases of hard particles in which translational ordering in layers can increase the orientational free volume of the particles [30]. The apparent anomalous increase in the transitional entropy for the induced smectic A phase is consistent with the predictions of mean-field theory on a qualitative basis. As the nematic range above the smectic  $A_d$  phase decreases, the entropy change at the smectic to nematic transition increases, and the nematic to isotropic transition decreases. Studies of pretransitional phenomena in the isotropic phase could provide further evidence for this.

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