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# Determination of the orientational order parameter of a binary mixture showing an induced smectic $A_d$ phase from magnetic susceptibility measurements

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## Abstract

The diamagnetic susceptibility anisotropy ( $\Delta\chi$ ) measurement of a binary mixture comprising of a strongly polar mesogen (CPPCC) and a weakly polar mesogen (ME6O.5) showing an induced smectic  $A_d$  phase is reported here. Assuming an axially symmetric molecule, the temperature dependence of the orientational order parameter ( $\langle P_2 \rangle$ ) has been investigated from the anisotropy of the susceptibility at different temperatures throughout the entire composition range. The results are compared with x-ray and optical birefringence measurements along with the mean-field theory of the smectic A phase. The maximum in the stability of the smectic  $A_d$  phase (at  $x_{\text{CPPCC}} = 0.33$ ) corresponds to the minimum in the order parameter values. The order of the smectic to nematic phase transition has also been discussed.

## 1. Introduction

The order parameter, which relates the anisotropic physical properties to its macroscopic and microscopic ordering, is one of the most important material parameters in the study of liquid crystals. To determine this parameter, several methods have been developed. Although all anisotropic properties of liquid crystals are related to the orientational order parameter,  $\langle P_2 \rangle$ , in a more or less complicated way, magnetic susceptibility anisotropy measurements provide a direct method for the evaluation of orientational order [1–8]. It is widely accepted to be one of the best methods for studying the variation of order parameter with temperature [9, 10]. Also, the absolute values of the magnetic susceptibility anisotropy are essential for the determination of elastic constants of liquid crystals from the Freedericksz transition [1] and for the understanding of magnetic field effects. Since magnetic susceptibility measurements are quite difficult to perform, not much work has been done to determine the orientational order parameter from such measurements. Moreover, we are not aware of any order parameter measurement from magnetic susceptibility studies in binary systems of polar–non-polar mixtures showing

an induced smectic  $A_d$  phase. In this work, we report the temperature variation of the orientational order parameter ( $\langle P_2 \rangle$ ), as obtained from magnetic susceptibility measurements, for a series of mixtures of a binary liquid crystalline system, which shows the presence of an induced smectic  $A_d$  phase.

We have earlier extensively studied the binary system of two nematogenic mesogens, 4-n-pentyl phenyl 4-n'-hexyloxy benzoate (ME6O.5 in short) and p-cyanophenyl trans-4-pentyl cyclohexane carboxylate (CPPCC in short) showing an induced smectic  $A_d$  phase from DSC, refractive index, density, x-ray diffraction and dielectric permittivity measurements [11, 12]. Eight mixtures having molar concentrations of CPPCC,  $x = 0.046, 0.15, 0.24, 0.33, 0.42, 0.51, 0.599$  and  $0.81$ , were studied, of which one shows only a nematic phase ( $x = 0.85$ ) while all others have both nematic and induced smectic  $A_d$  phases. The orientational order parameter ( $\langle P_2 \rangle$ ) as obtained from refractive index and x-ray diffraction studies of these mixtures exhibits a minimum near  $x = 0.4$ . The birefringence and layer thickness also show a minimum at this concentration. Thus, it is of interest to investigate whether the magnetic susceptibility anisotropy and the order parameter as

determined from magnetic susceptibility studies also follow a similar trend.

## 2. Experimental details

### 2.1. Magnetic susceptibility measurements

The magnetization  $\mathbf{M}$  induced by the applied magnetic field  $\mathbf{H}$  is given by

$$\mathbf{M}_0 = \chi_{\alpha\beta} \mathbf{H}_\beta \quad \alpha, \beta = x, y, z \quad (1)$$

where  $\chi_{\alpha\beta}$  is an element of the magnetic susceptibility tensor  $\bar{\chi}$  and the summation convention over repeated indices is followed. For a uniaxial phase like nematic or smectic A phase, choosing the director  $\mathbf{n}$  along the  $z$  axis, we have

$$\bar{\chi} = \begin{bmatrix} \chi_\perp & 0 & 0 \\ 0 & \chi_\perp & 0 \\ 0 & 0 & \chi_\parallel \end{bmatrix}. \quad (2)$$

The subscripts  $\chi_\parallel$  and  $\chi_\perp$  refer to the components of the mass susceptibility parallel and perpendicular to the director, respectively. The average susceptibility is given by

$$\begin{aligned} \bar{\chi} &= \frac{1}{3} \sum_\gamma \chi_{\gamma\gamma} \\ &= \frac{1}{3} (\chi_\parallel + 2\chi_\perp). \end{aligned} \quad (3)$$

The magnetic susceptibility anisotropy is defined as

$$\Delta\chi = (\chi_\parallel - \chi_\perp). \quad (4)$$

In most cases  $\Delta\chi$  is positive. Since we cannot measure  $\chi_\perp$  directly we replace equation (4) by the following:

$$\Delta\chi = \frac{3}{2} (\chi_\parallel - \bar{\chi}) \quad (5)$$

$\bar{\chi} = \frac{1}{3} (\chi_\parallel + 2\chi_\perp)$  being the mass susceptibility in the isotropic phase.

The order parameter  $\langle P_2 \rangle$  is defined by

$$\langle P_2 \rangle = \frac{\Delta\chi}{\Delta\chi_0}. \quad (6)$$

$\Delta\chi_0$  being the diamagnetic susceptibility anisotropy in the completely ordered solid phase. To determine the order parameter, we need the value of  $\Delta\chi_0$  which can be obtained from solid single-crystal measurements. Since we could not measure  $\Delta\chi_0$  from the completely ordered crystalline phase, in the present case  $\Delta\chi_0$  has been determined from the well-known Haller extrapolation method [13].

According to the classical Faraday–Curie method, the force ( $F$ ) experienced by a sample in an inhomogeneous magnetic field with a gradient ( $dH^2/dx$ ) along the horizontal  $x$  direction is given by

$$F = \frac{1}{2} (m_r \chi_r - m_o \chi_o) \left( \frac{dH^2}{dx} \right)_{\text{avg}} \quad (7)$$

where  $\chi$  and  $m$  are the mass susceptibility and mass of the sample and  $\chi_o$  and  $m_o$  are those of the air driven out of the sample. When the sample is replaced by almost the same volume of the reference sample (subscript ‘r’ stands for

reference sample) and is placed at nearly the same position between the pole pieces of the magnet, then ( $dH^2/dx$ ) will be same for both cases. Then the magnetic susceptibility as a function of temperature can be written as

$$\chi(t) = \frac{F m_r}{F_r m} \left[ \chi_r - \frac{\rho_o(t_o)}{\rho_r(t_o)} \chi_o(t_o) \right] + \frac{\rho_o(t)}{\rho(t)} \chi_o(t) \quad (8)$$

where  $\rho$ ,  $\rho_r$  and  $\rho_o$  are the densities of the experimental sample, reference sample, air and  $t$  and  $t_o$  are the temperatures at which the measurement of the experimental sample and reference sample are made, respectively.

The diamagnetic susceptibility anisotropy ( $\Delta\chi$ ) was determined by a Curie balance, the movement of the arms being restricted to the horizontal plane. The sample was put in a cylindrical quartz container (volume  $\sim 0.1 \text{ cm}^3$ ) and hung by a glass capillary between the pole pieces of an inhomogeneous magnetic field of gradient  $\sim 1.5 \text{ kG}^2 \text{ cm}^{-1}$ . The temperature of the sample was controlled by a temperature controller, Indotherm-457, having accuracy of  $\pm 0.25^\circ\text{C}$ . The whole system was evacuated to avoid disturbance to the balance due to convectional air currents. About 30 min were allowed for the sample to reach thermal equilibrium. The accuracy of the measurement using this balance is  $\sim 1\%$ .

Trans-decaline, a non-volatile liquid at room temperature, having  $\chi = 0.779 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1} \text{ m}^{-1}$  [14] and density  $\rho = 0.869 \text{ g}^{-1} \text{ m cm}^{-3}$  [15] was used as a reference sample. The necessary correction term for  $\chi_o(t)$  in equation (8) was calculated by using the tabulated density of air [15], the magnetic susceptibility of air ( $\chi_o = 106.3 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1} \text{ m}^{-1}$  at  $20^\circ\text{C}$ ) [16] and using the Curie law ( $\chi_o \sim 1/T$ ). Here we have neglected the influence of dissolved oxygen as discussed and ignored by de Jue *et al* [8].

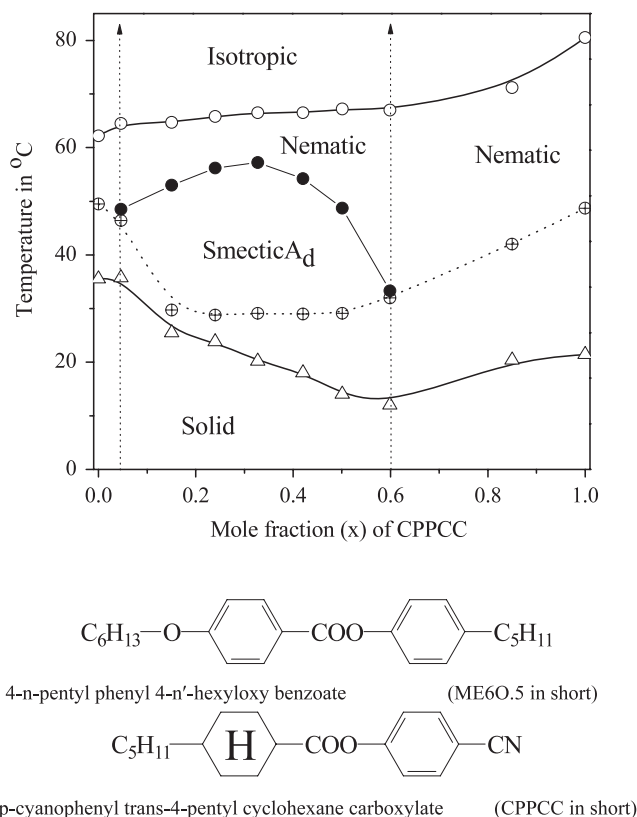
In our experimental set-up, the force experienced by the sample due to an inhomogeneous magnetic field is exactly balanced by the force exerted on the horizontal coil rigidly attached to the beam balance, placed inside a hollow permanent magnet with a uniform radial field and carrying a suitable current  $i$  ( $= F/2\pi r n H$ , where  $n$  = number of turns in the coil,  $r$  = radius of the coil and  $H$  = magnetic field). In general, the suspended system experiences a force even in the absence of any sample due to the diamagnetism of the sample holder. To compensate for this pull, an initial current ( $i_o$ ) is passed through the coil. In this case, instead of current we measure the potential drop across a standard resistance ( $\sim 10 \text{ k}\Omega$ ) with the help of a precision digital voltmeter and the final expression for the susceptibility becomes

$$\chi(t) = \frac{(V - V_o) m_r}{(V_r - V_o) m} \left[ \chi_r - \frac{\rho_o(t_o)}{\rho_r(t_o)} \chi_o(t_o) \right] + \frac{\rho_o(t)}{\rho(t)} \chi_o(t). \quad (9)$$

We have verified the accuracy of our data by measuring the susceptibility of pure compound CPPCC as a function of temperature and these values are within 1% of the values reported by Mitra *et al* [10].

## 3. Results and discussion

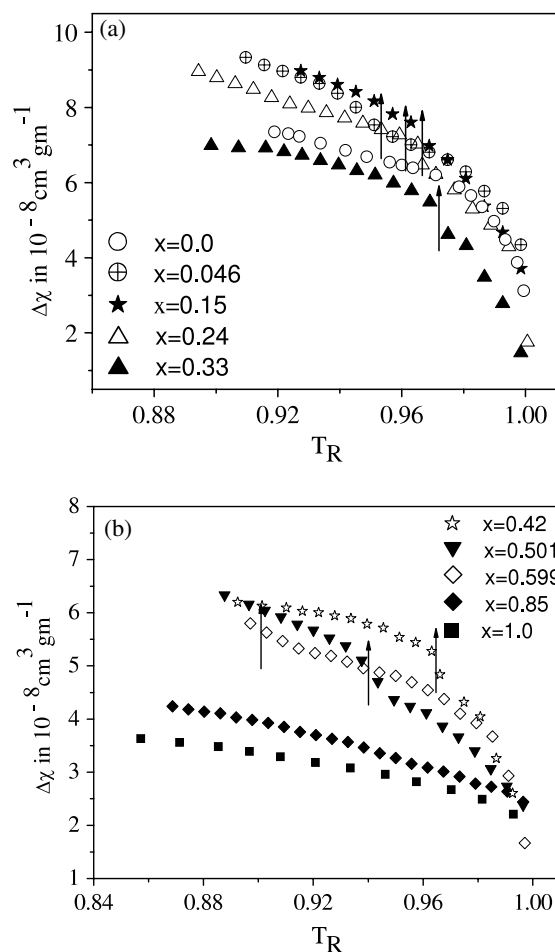
The phase diagram of this system as reported earlier by us [11] is shown in figure 1. The mixtures show an induced smectic  $A_d$



**Figure 1.** Phase diagram of ME6O.5/CPPCC as a function of mole fraction ( $x$ ) of CPPCC.

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  $x \approx 0.3$ .

The mass diamagnetic susceptibility as a function of temperature for eight different compositions of this mixture has been measured along with two pure compounds. Both the pure compounds and their mixtures are found to be diamagnetic in nature. Our experiment gives, therefore, the principal susceptibility parallel to the director. The diamagnetic susceptibility anisotropy as a function of reduced temperature ( $T_R = T/T_{NI}$ ) for all eight mixtures as well as pure compounds are shown in figures 2(a) and (b). For all the mixtures as well as pure compounds,  $\chi_{||}$  and hence  $\Delta\chi$  increases with decrease in temperature in nematic as well as smectic phases. The anisotropy of diamagnetic susceptibility values of ME6O.5 are higher than those obtained from CPPCC. This is expected because ME6O.5 contains two phenyl rings with terminal alkyl chains and hence gives large diamagnetic anisotropy. On the other hand, CPPCC molecules contain one cyclohexane ring and one benzene ring in its core. The replacement of one aromatic benzene ring by a cyclohexane ring therefore leads to a decrease in anisotropy. Also, the presence of a terminal CN group in CPPCC with a negative magnetic anisotropy reduces the anisotropy further [7]. The change in  $\Delta\chi$  values at the smectic  $A_d$  to nematic transition are more pronounced for mixtures  $x = 0.24, 0.33$  and  $0.42$ , which was also observed in the case of birefringence as well as density values of these mixtures [11]. The experimental data for  $\Delta\chi$  was used to



**Figure 2.** Variation of magnetic susceptibility anisotropy ( $\Delta\chi$ ) with reduced temperature for different mixtures and a pure compound.  $\uparrow$  indicates nematic–smectic  $A_d$  phase transition.

calculate the temperature dependence of the order parameters for different concentrations of mixtures of this binary system. For all the samples studied, Haller’s extrapolation method [13] was used to get the value of  $\Delta\chi_0$ . The variation of absolute susceptibility anisotropy ( $\Delta\chi_0$ ) values estimated from Haller’s method in the most ordered crystalline phase against mole fraction of CPPCC shows a decreasing trend and there appears to be a minimum around  $x = 0.3$  (figure 3).

The variation of magnetic susceptibility in the isotropic phase is almost independent of temperature, similar to that of an ordinary substance, and in the solid phase the susceptibility also remains independent of temperature and its value is nearly equal to that in the isotropic phase [7].

It has also been found that the  $\Delta\chi_{iso}$  values decrease with molar concentration and deviate from linearity (shown by the dotted straight line connecting those of the pure compounds, figure 4) and the deviation is maximum near  $x \approx 0.6$ .

The variation of the magnetic susceptibility anisotropy values ( $\Delta\chi$ ) as a function of molar concentration is shown in figure 5. It is observed that, within the smectic  $A_d$  phase, the  $\Delta\chi$  values show a pronounced depression around  $x = 0.4$  in accordance with our previously observed birefringence ( $\Delta n$ ) values [11].

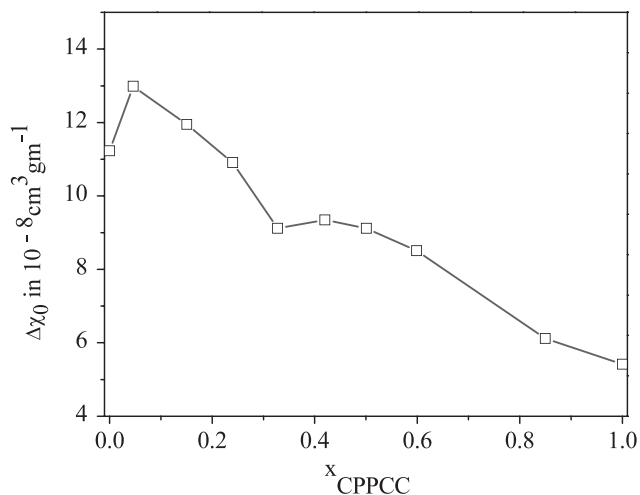


Figure 3. Variation of  $\Delta\chi_0$  with molar concentration ( $x$ ) of CPPCC.

The temperature variation of the order parameter values for all eight mixtures and the pure components, obtained from magnetic susceptibility measurements, x-ray diffraction studies [11] and refractive index measurements [11], are shown in figures 6(a)–(j). We have also fitted the theoretical McMillan order parameter values with our experimental values by varying the  $\alpha$  and  $\delta$  parameters of the McMillan potential [11]. The continuous curves correspond to the Maier–Saupe mean-field theory [17] in the case of the two pure compounds and the mixture with  $x = 0.85$ , possessing a nematic phase only. For other mixtures, the continuous curve corresponds to McMillan’s theory [18, 19]. From all figures 6(a)–(j), it is observed that, near the isotropic temperature, the experimental order parameter values from magnetic susceptibility measurements are lower than the theoretically predicted values. This trend has also been observed in the  $\langle P_2 \rangle$  values obtained from optical birefringence measurements of these mesogens. The rapid decrease in the order parameter values obtained from refractive index and magnetic susceptibility measurements, close to the nematic isotropic transition temperature, has been observed by many workers as well [10, 11, 20–22].

However, our x-ray diffraction studies on these compounds show higher  $\langle P_2 \rangle$  values near the nematic to isotropic transition in comparison to those determined from magnetic susceptibility and refractive index measurements. This is due to the fact that in x-ray studies we essentially measure short range order, whereas in magnetic susceptibility and refractive index measurements we measure long range order. It is well known that the long range order parameter decreases rapidly near the transition temperature  $T_{NI}$  and vanishes at  $T = T_{NI}$ . On the other hand, short range order is expected to decrease less rapidly near  $T_{NI}$  and should persist even above  $T_{NI}$ . This explains the apparent contradiction between the experimentally determined order parameters found from x-ray diffraction measurements on the one hand and those obtained from refractive index and magnetic susceptibility anisotropy on the other. For mixtures with  $x = 0.046, 0.24, 0.33$  and  $0.5$  (figures 6(b), (d), (e) and (g), respectively) the experimental orientational order parameter values determined from magnetic susceptibility

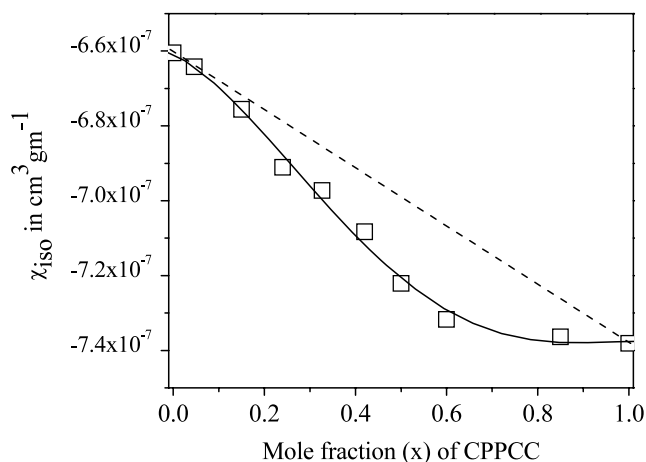


Figure 4. Variation of  $\chi_{iso}$  for the binary mixture of ME6O.5 + CPPCC with mole fraction. The dotted line represents the average value.

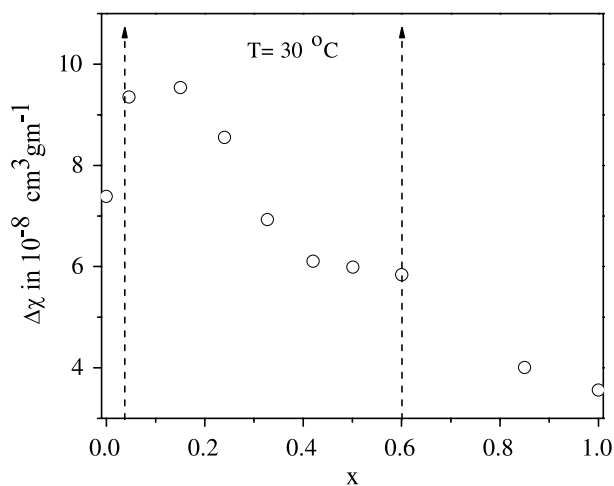
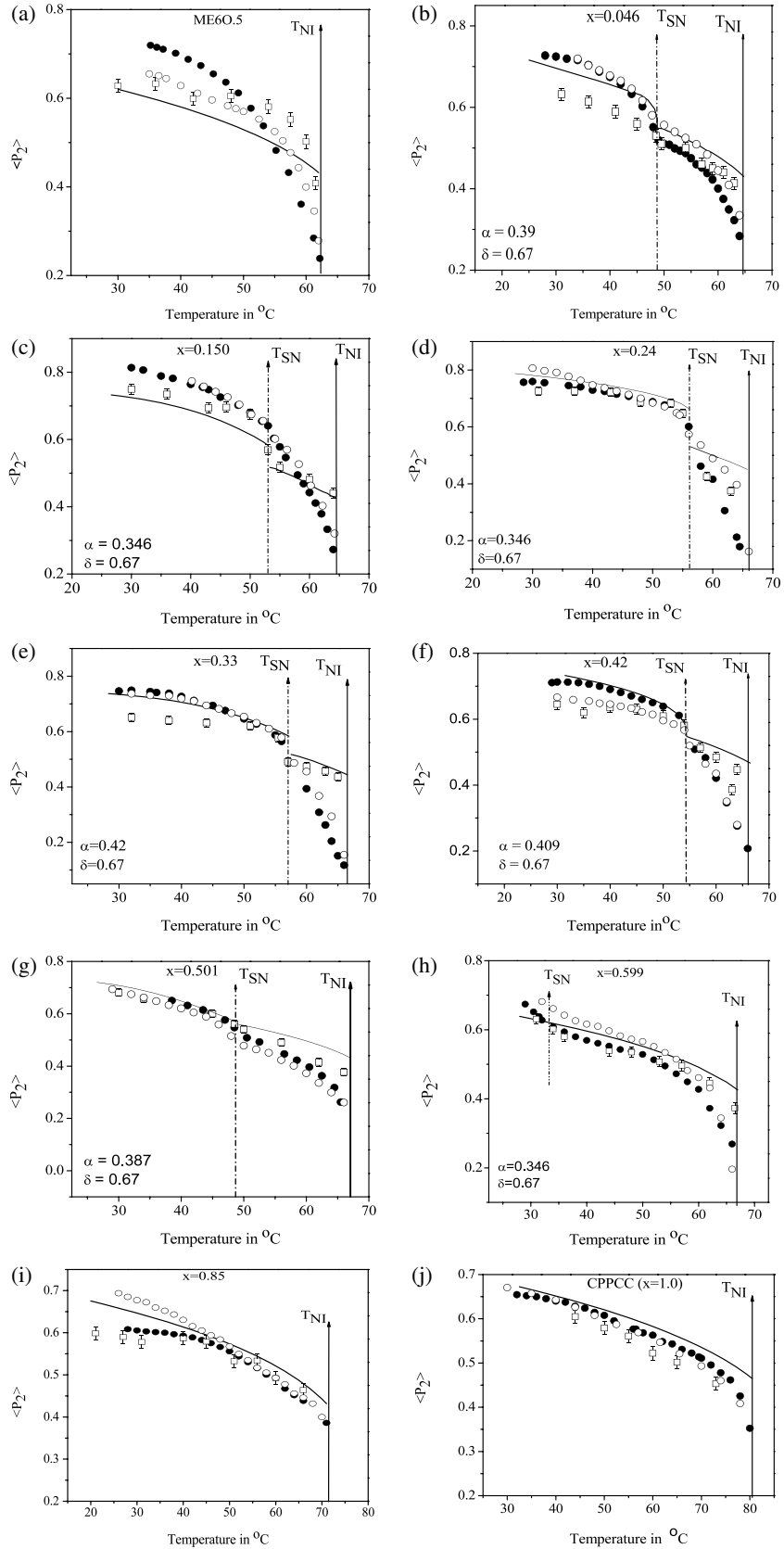


Figure 5. Variation of magnetic susceptibility anisotropy ( $\Delta\chi$ ) with a mole fraction of CPPCC at a fixed temperature  $T = 30^\circ\text{C}$ . Vertical dotted arrows indicate the region of induced smectic  $A_d$  phase.

measurements agree quite well with the theoretical values except near the nematic to isotropic transition temperature. Mixtures with  $x = 0.85$  and the two pure compounds (figure 6(a), (i) and (j), respectively) have only a nematic phase; hence the experimental  $\langle P_2 \rangle$  values have been compared with the theoretical Maier–Saupe values. In this case, agreement is fairly good except near the nematic–isotropic transition temperature. However, agreement between the experimental order parameter values for mixtures  $x = 0.15, 0.42$  and  $0.59$  (figures 6(c), (f) and (h), respectively) is not good with McMillan’s values for any combination of  $\alpha$  and  $\delta$ .

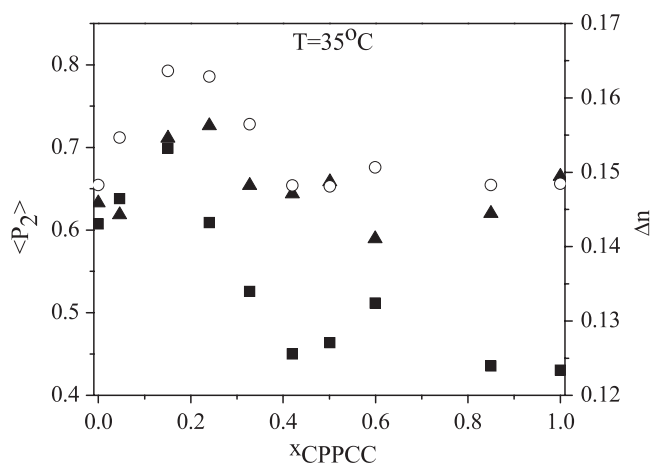
There is an appreciable change in the  $\langle P_2 \rangle$  values at the smectic  $A_d$ –nematic phase transition for mixtures in the concentration range  $0.15 < x < 0.42$  (figures 6(c)–(f)), indicating a first-order phase transition for these mixtures.

In the smectic phase, the  $\langle P_2 \rangle$  values initially increase with molar concentration up to  $x = 0.24$  and then decrease and show a broad a minima around  $x = 0.4$  (figure 7). The birefringence also shows a minimum in the same composition



**Figure 6.** (a) Temperature variation of  $\langle P_2 \rangle$  for (a) ME60.5, (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)  $x = 0.85$  and (j) CPPCC, determined from ● refractive index, ○ magnetic susceptibility, □ x-ray diffraction measurements.  $\langle P_2 \rangle$  from Maier–Saupe theory ((a), (i) and (j)) and McMillan’s theory (b)–(h).  $T_{NI}$  = nematic–isotropic and  $T_{SN}$  = smectic  $A_d$ –nematic transition temperatures.





**Figure 7.** Variation of the order parameter  $\langle P_2 \rangle$  with a mole fraction of CPPCC at a fixed temperature  $T = 35^\circ\text{C}$ .  $\circ$   $\langle P_2 \rangle$  from magnetic susceptibility,  $\blacktriangle$   $\langle P_2 \rangle$  from x-ray diffraction and  $\blacksquare$   $\Delta n$  from refractive index measurements.

range. The magnetic susceptibility data therefore is found to agree quite well with the findings from refractive index as well as x-ray diffraction studies on this system. The maximum in the stability of the smectic  $A_d$  phases ( $x = 0.33$ ) corresponds to the minimum of the order parameter. This lowering in the order parameter values has also been confirmed from the present magnetic susceptibility studies.

#### 4. Summary and conclusions

Magnetic susceptibility anisotropy measurements have been undertaken on a binary system of nematogenic compounds exhibiting an induced smectic  $A_d$  phase. This method provides a relatively straightforward way for the determination of the orientational order parameter,  $\langle P_2 \rangle$ , values. The  $\langle P_2 \rangle$  values at different compositions of this mixture have also been previously investigated by us using x-ray diffraction and optical birefringence measurements [11].

The diamagnetic susceptibility anisotropy values were determined by the classical Faraday–Curie method. As expected, the  $\Delta\chi$  values for all the mixtures as well as pure compounds increases with a decrease in temperature in the nematic as well as smectic phases. CPPCC exhibits lower magnetic susceptibility anisotropy in comparison to ME6O.5 due to the presence of the cyclohexane ring at the core and the cyano group at the terminal end. The variation of the absolute susceptibility anisotropy ( $\Delta\chi_o$ ) values as estimated from Haller’s method show a decreasing trend and there appears to be a minimum around  $x = 0.3$ .

The orientational order parameter values  $\langle P_2 \rangle$  as determined from magnetic susceptibility anisotropy measurements are observed to decrease rapidly at the nematic–isotropic phase transition for all the mixtures as well as the pure compounds in agreement with the  $\langle P_2 \rangle$  values obtained from optical birefringence measurements of these mesogens. However,  $\langle P_2 \rangle$  val-

ues determined from x-ray diffraction measurements are higher near the nematic–isotropic transition temperature. This is due to the fact that, in the x-ray measurements, one essentially determines the short range order which decreases gradually and is found to persist even in the isotropic phase [10]. This is in contradiction to magnetic anisotropy and refractive index measurements, where the long range order of the molecules is measured, which is expected to fall off rapidly as the nematic–isotropic phase transition is approached. The experimentally determined  $\langle P_2 \rangle$  values have been fitted with McMillan’s theory in the smectic  $A$  phase and Maier–Saupe theory in the nematic phase. The  $\langle P_2 \rangle$  values show broad minima around  $x = 0.4$ , which corroborates the findings of the x-ray diffraction and refractive index measurements done on this system. As mentioned earlier [11], this minimum in the order parameter values is attributed to specific interactions between the molecules, which in trying to pack the different molecules within the layers of the smectic  $A_d$  phase in effect reduces the orientational order within the layers. This lowering in the order parameter values has been confirmed by our present magnetic susceptibility studies.

#### Acknowledgments

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