

Chapter **6**

Physical Properties Of A Mesogenic Mixture Showing Induce Smectic A_d Phase II: Diamagnetic Susceptibility Anisotropy And Splay And Bend Elastic Constants

6.1 Introduction:

In chapter 5, I have reported some physical properties of a binary system (ME6O.5 + CPPCC) showing induced smectic phase from x-ray diffraction, refractive index and dielectric anisotropy measurements. In this chapter the results of magnetic susceptibility anisotropy measurements on the same mixture, throughout their mesomorphic and concentration range is reported. The splay (K_{11}) and bend (K_{33}) elastic constants, for this binary system have also been determined by observing Fredericksz transition [1] in magnetic field. It is to be noted that, although the formation of induced smectic phase is undesirable in LCD materials, its presence at a lower temperature than the working temperature of the LCD may be helpful under certain conditions [2-4]. The performance of liquid crystal materials in LCD's depends critically on the temperature dependence of the dielectric, optical, elastic constants and the viscosity coefficients of the materials to be used. Measurements of Frank elastic constants [5] play an important role in characterizing liquid crystal display devices and this information is important from display manufacturing point of view [6-8]. Again, precise determination of the elastic constant requires knowledge of the corresponding diamagnetic anisotropy of the material.

6.2 Magnetic susceptibility measurement:

The details of the experimental techniques involved have already been described in chapter 2 of this thesis. The experimental data for magnetic susceptibility anisotropy have been analysed to calculate the order parameter of the system.

The phase diagram of this mixture has been reported and discussed in chapter 5. As observed earlier, this mixture shows an induced smectic A_d

phase in the concentration range $0.03 < x < 0.6$, where x is the mole fraction of CPPCC. Refractive indices (n_o , n_e) as well as birefringence (Δn) show a minimum near $x=0.4$. The orientational order parameters as calculated from refractive index and x-ray diffraction studies of this mixture, when plotted against composition, show a minimum near the $x=0.3$. The layer thicknesses also show a minimum near $x=0.4$. It is of interest to investigate whether the magnetic susceptibility anisotropy $\Delta\chi$ and orientational order parameter $\langle P_2 \rangle$ as determined from magnetic susceptibility studies, also follow a similar trend. Moreover, the experimental magnetic susceptibility anisotropy $\Delta\chi$ data, which has been analyzed to calculate the temperature variation of the order parameter [9-10] of the system, is widely accepted to be one of the best methods.

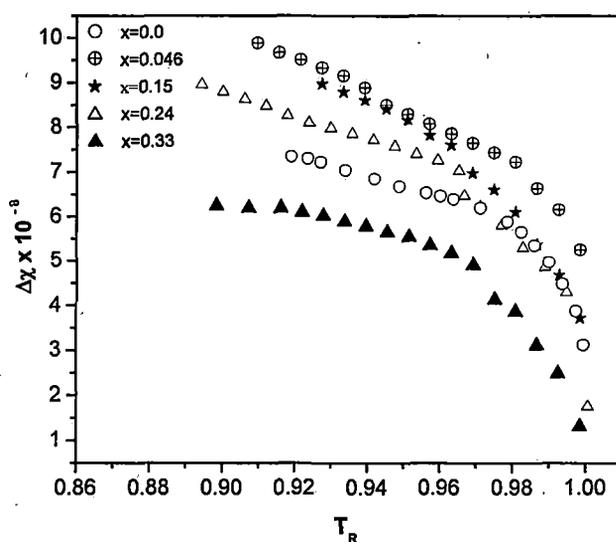


FIGURE 6.1: Variation of magnetic susceptibility ($\Delta\chi$) with reduced temperature for different mixtures and pure compounds.

The mass diamagnetic susceptibility as a function of temperature for eight different concentrations of this mixture has been measured. 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 for all the eight mixtures as well as pure compounds are shown in figure 6.1 – 6.2.

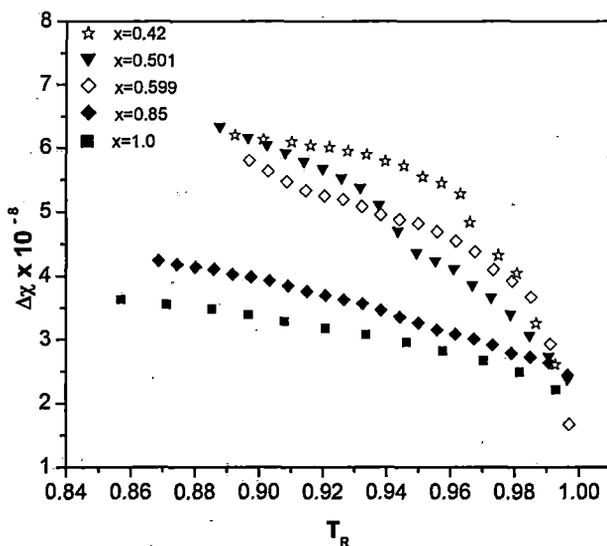


FIGURE 6.2: Variation of magnetic susceptibility ($\Delta\chi$) with reduced temperature for different mixtures and pure compounds.

For all the mixtures as well as pure compounds, χ_{\parallel} and hence $\Delta\chi$ increases with decrease in temperature in nematic and smectic phases. 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 molecule contains one cyclohexane ring and one benzene ring in its core. As expected, the replacement of one aromatic benzene ring by cyclohexane leads to a decrease in anisotropy. Presence of the terminal CN group in CPPCC with a negative magnetic anisotropy reduces the anisotropy further [11]. Since this system exhibits induced smectic phase and the behaviour of physical parameters is more or less

complex compared to the pure compounds, additional interactions between the constituent molecules may play an important role on the physical properties of the mixtures.

In the isotropic state, χ_{iso} remains practically independent of temperature similar to the ordinary diamagnetic substances. In the solid phase the susceptibility χ also remains independent of temperature and its value is nearly equal to that in the isotropic phase. This happens due to the fact that during this transition a large amount of energy is released in the form of latent heat, which overcomes the magnetic energy. Hence in going through this, the completely oriented ensemble of molecules is broken into almost randomly oriented crystallites in the solid phase. This loss of alignment may be regarded as the cause of observed decrease in χ and hence $\Delta\chi$ [12]. The changes in $\Delta\chi$ values at the SmA_d - N transition are more pronounced for mixtures with $x = 0.24$ and 0.33 . Similar behaviour is also observed in birefringence (Δn) as well as in the density values of these mixtures [13].

The experimental data for $\Delta\chi$ have been analyzed to calculate the order parameter of the system. As discussed in chapter 2, the determination of order parameter from equation 2.48 requires knowledge of the absolute susceptibility anisotropy values ($\Delta\chi_0$). Since the experimental data on $\Delta\chi_0$ are not available, one can derive from equation 2.37 only the relative temperature dependence of $\langle P_2 \rangle$. However, $\Delta\chi_0$ can be estimated using well-known Haller's extrapolation method [14].

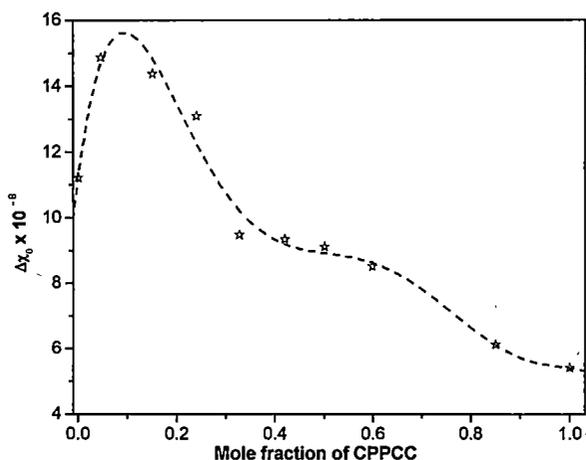


FIGURE 6.3: Variation of $\Delta\chi_0$ with reduced temperature for different mixtures and pure compounds.

In figure 6.3 I have plotted the absolute susceptibility anisotropy values estimated from Haller's method in the most ordered crystalline phase against mole fraction of CPPCC. The $\Delta\chi_0$ values decreases with increase in mole fraction of CPPCC. From the figure it is clear that inspite of the inaccuracies involved in this calculation and the arbitrariness of the Haller's procedure, there appears to be a minimum of $\Delta\chi_0$ values near $x=0.4$.

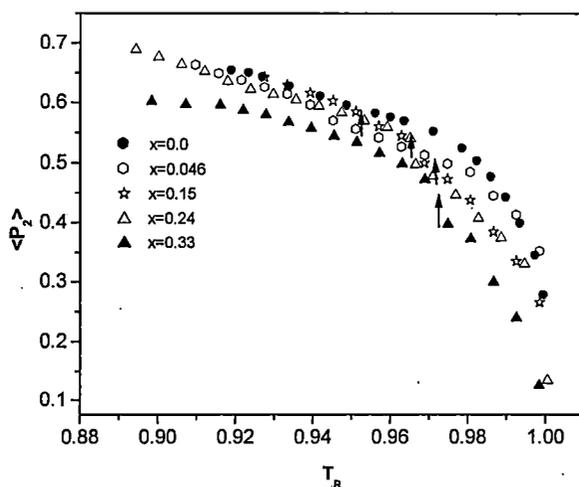


FIGURE 6.4: Temperature variation of order parameter $\langle P_2 \rangle$ with reduced temperature for different mixtures and pure compounds. \uparrow $\text{SmA}_d\text{-N}$ transition.

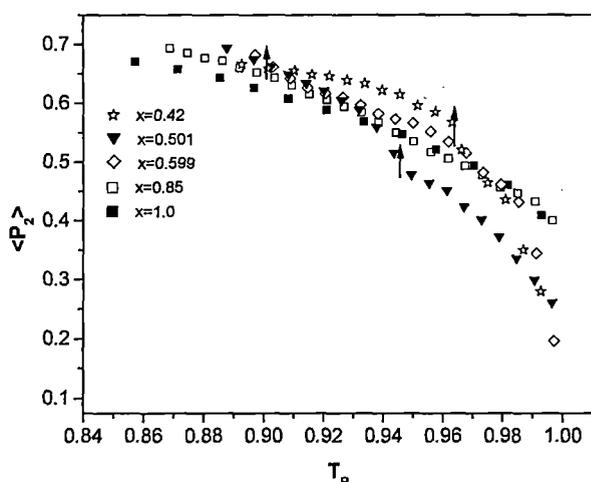


FIGURE 6.5: Temperature variation of order parameter $\langle P_2 \rangle$ with reduced temperature for different mixtures and pure compounds. \uparrow SmA_d -N transition.

The temperature variations of order parameter values for all the eight mixtures and pure components are shown in figures 6.4 – 6.5. From the temperature dependences of the orientational order parameters for mixtures at different concentration it is again observed that there is an appreciable change in the order parameter value at the smectic A_d to nematic phase transition temperature for mixtures in the range $0.15 < x < 0.42$.

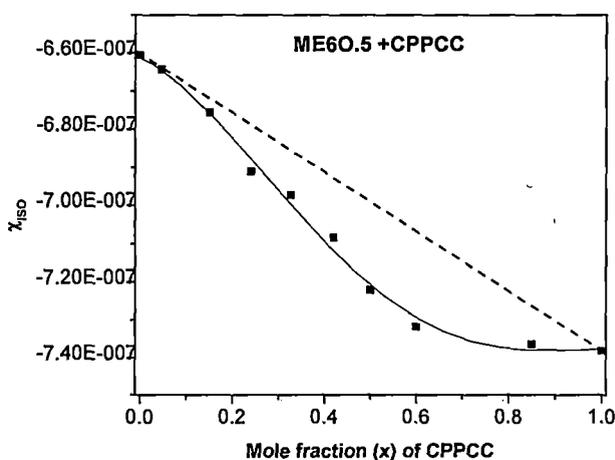


FIGURE 6.6: Variation of χ_{iso} for binary mixture of ME6O.5+CPPCC with mole fraction. Dotted line represents the average value.

The composition variation of the magnetic susceptibility in the isotropic phase, χ_{iso} , of all the mixtures is shown in figure 6.6. The experimental values of the pure components ME6O.5 and CPPCC are also plotted in the same figure. It has been found that the χ_{iso} values decreases with molar concentration and deviates from linearity (shown by straight line connecting those of the pure compounds). This deviation is maximum near $x \approx 0.6$.

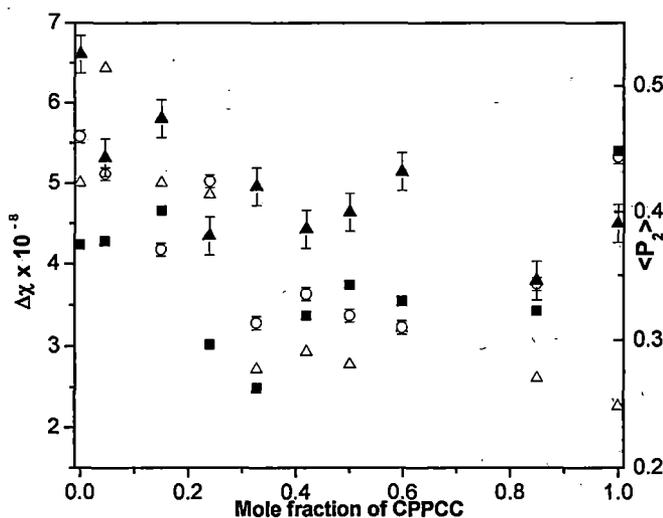


FIGURE 6.7: Variation of $\Delta\chi$ and order $\langle P_2 \rangle$ of CPPCC + ME6O.5 mixture with mole fraction of CPPCC at a fixed reduced temperature $T_R = 0.99 T_{NI}$. Δ $\Delta\chi$ values, \circ $\langle P_2 \rangle$ from magnetic susceptibility, \blacktriangle $\langle P_2 \rangle$ from x-ray diffraction and \blacksquare $\langle P_2 \rangle$ from refractive index measurements.

Figure 6.7 shows the composition variation of $\Delta\chi$ in the mixture CPPCC + ME6O.5 at a reduced temperature of $T_R = 0.99 T_{NI}$. The order parameter values from magnetic susceptibility measurement are also shown in this figure. The $\Delta\chi$ values are higher for mixtures having mole fraction $x < 0.3$ in comparison to the both the pure compounds. In the concentration range $x > 0.04$, $\Delta\chi$ values decreases with increase in molar concentration and shows a broad minimum near $x = 0.3$. The orientational order parameter $\langle P_2 \rangle$ also shows a minimum there. 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 smectic A_d phases ($x=0.33$) corresponds to the minimum of the order parameter. The birefringence shows a minimum nearly the same composition range [13]. This lowering in the order parameter values has also been confirmed from the present magnetic susceptibility studies done on this system.

6.3 Elastic constants measurement:

In this section, I present the results of the splay and bend elastic constants measurement of this mixture. The experimental set up and the techniques adopted have been given in detail in chapter 2. The values of splay (K_{11}) and bend (K_{33}) elastic constants as functions of reduced temperature ($T_R=T/T_{NI}$) are given in figures 6.8 and 6.9 respectively.

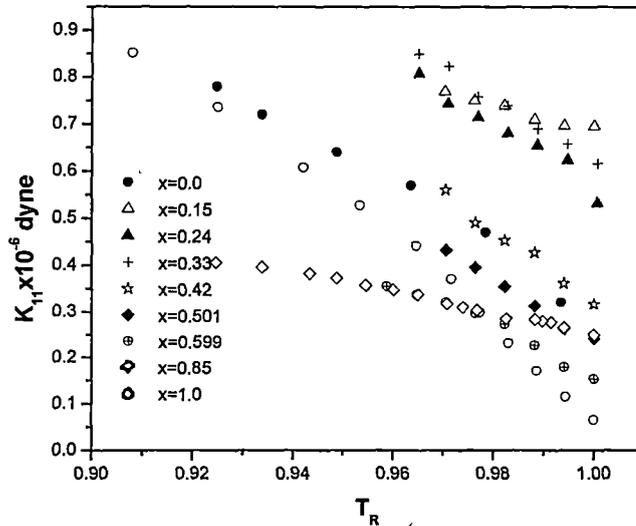


FIGURE 6.8: The splay (K_{11}) elastic constant as a function of reduced temperature ($T_R=T/T_{NI}$).

Figure 6.10 shows the K_{33}/K_{11} ratios for the pure compounds as well as their mixtures as a function of reduced temperature. It is observed that the K_{33}/K_{11} values decreases with increasing temperature as is expected. For mixtures exhibiting the induced smectic phase, the K_{33}/K_{11} values in the nematic shows a sharp increase particularly near the SmA-N transition. This increase of the bend to splay has also been reported by Bradshaw et al [2] in hybrid mixtures containing phenyl benzoate esters. Possible reason for this may be formation of smectic clusters as pre-transitional effects. Whereas such rapid increase is not found in the mixture ($x=0.85$), possibly because this mixture was studied in the concentration range which is far away from the induced phase region.

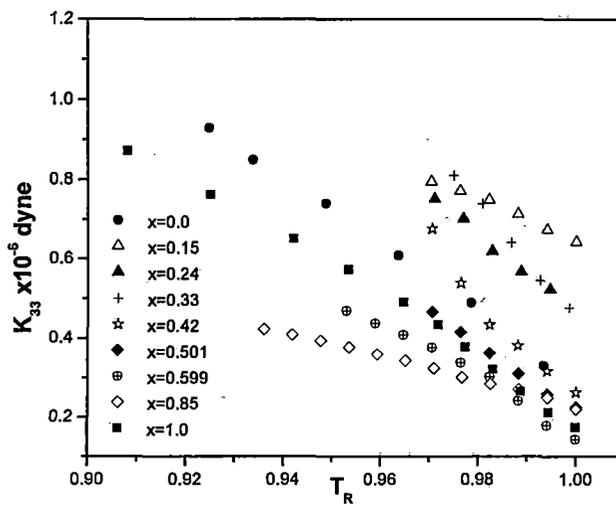


FIGURE 6.9: The bend (K_{33}) elastic constant as a function of reduced temperature ($T_R=T/T_{NI}$).

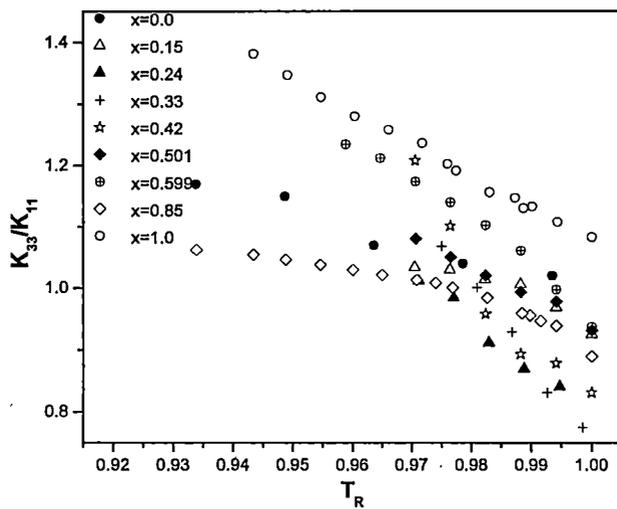


FIGURE 6.10: The splay to bend elastic constant ratios (K_{33}/K_{11}) as a function of reduced temperature ($T_R=T/T_{NI}=0.99T_{NI}$).

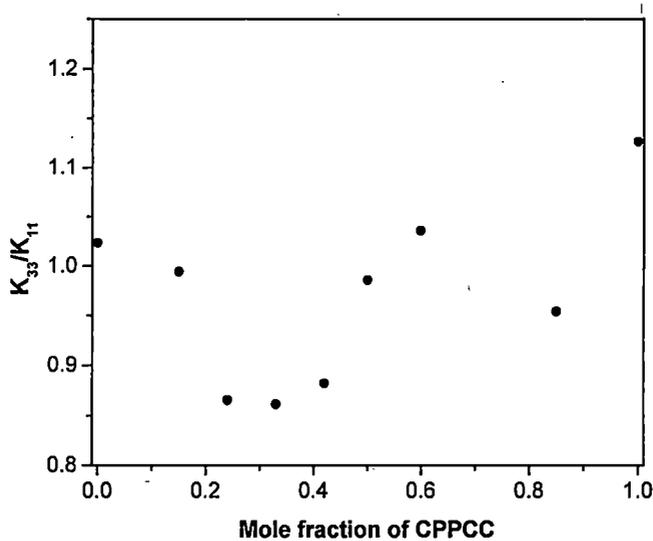


FIGURE 6.11: The splay to bend elastic constant ratios $\bullet K_{33}/K_{11}$ as a function of mole fraction of CPPCC at reduced temperature ($T_R=T/T_{NI}=0.99T_{NI}$).

In Figure 6.11, I have plotted the K_{33}/K_{11} values at $T=0.99T_{NI}$ against mole fraction of CPPCC. The variation of K_{33}/K_{11} shows a minimum near $x=0.33$ where the maximum stability of induced smectic A_d is observed in the mixtures.

The values of (K_{33}/K_{11}) for all the mixtures are lower than those of the pure compounds. Low values of (K_{33}/K_{11}) were observed in the binary mixtures [15-17] of strongly polar compounds containing terminal cyano groups together with weakly polar or non-polar esters [2]. This may be a consequence of the reduction in anti-parallel ordering of the cyano molecules (CPPCC) as the non-polar esters (ME6O.5) are added.

References:

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