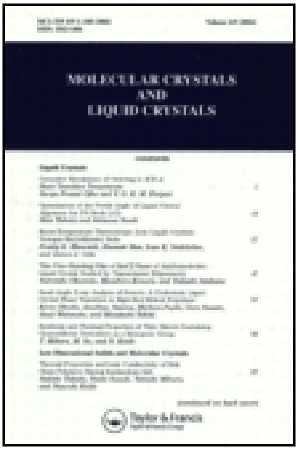

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Orientational Order Parameter of a Binary Liquid Crystal Mixture Showing Induced Smectic Phase

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Binary mixture of 4 – pentyl 4′ – cyanobiphenyl (5CB) and 4-n-pentyl phenyl 4 – n′- pentyloxy benzoate (ME5O.5) shows the presence of an induced smectic A phase. In the present work we report the density and refractive indices on this system in the entire composition range. The density and refractive indices are used to calculate molecular polarizability values parallel and perpendicular to the molecular long axes using Neugebauer's method. Orientational order parameters (OOP's) as a function of temperature and concentration are determined. The relative change in density at the smectic A-nematic phase transition shows a maximum near equimolar concentration. The orientational order parameter values and calculated packing fraction show a minimum around $x \approx 0.4$ at a temperature T=35°C. Similar behaviour is also observed at a temperature $T = 0.98T_C$, in the nematic phase where the induced smectic A phase is the precursor of the nematic phase. Average lateral distance (D) between the molecules is measured from the analysis of x-ray diffraction data. The variation of D with molar concentration in smectic A phase shows a maximum near equimolar concentration.

Keywords: Induced smectic phase; density; refractive index; orientational order parameter; x-ray diffraction

INTRODUCTION

One of the unexpected behaviour of liquid crystal mixtures is the formation of so-called induced smectic A phases from the components which show only nematic phases in their pure states [1-3]. The formation of induced smectic phase is accompanied by a significant deviation from the linear dependence on composition of the nematic to isotropic transition temperature for the mixtures. Induced smectic phases are mostly formed in binary mixtures, in which at least one component has a strong terminal polar group. The dipole-dipole or dipole-induced dipole interaction play a major role in stabilization of these phases. However, it has been shown that steric effects are also quite important for phase stabilization. Hence, it is desirable to know the conditions for the formation of induced smectic phases, since such knowledge would help us in producing better materials for display devices. Binary mixture of 4-n-pentyl 4′ - cyanobiphenyl (5CB) and 4-n-pentyl phenyl 4 - n′- pentyloxy benzoate (ME5O.5) shows the presence of an induced smectic A phase where the pure compounds show only nematic phase. Phase diagram of this system has been reported by Dunmur et al [4]. They have measured transition enthalpies, refractive indices and electric permittivities of a series of mixtures of these compounds. Using an empirical scaling procedure they have calculated the orientational order parameter only in the nematic phase above the induced smectic phase. Using an extension of Maier-Saupe theory, Palffy-Muhoray et. al [5] have determined the nematic-isotropic co-existence region for the entire range of concentrations of this system and they have proposed a relation between the refractive index of the binary mixture and order parameters of its components in the nematic phase. We have earlier reported [6] the orientational order parameters, layer thickness and apparent molecular length for a series of mixtures at different temperature and concentrations of this system. Hence, it is of interest to determine order parameters from refractive index and density studies in both induced smectic and nematic phases and compare these with those found from x-ray studies.

In the present work we report density and refractive indices (n_o, n_e) of this system in the entire composition range. The refractive index and density data have been analyzed to measure orientational order parameters. We have also fitted these experimental order parameters with the theoretical values from McMillan's theory[7] for mixtures having smectic A phase, and Maier-Saupe theory[8] for others having nematic phase only. Since layer thickness as observed by us previously[6] and density values reported in this work, both show a definite minimum near equimolar concentration, it is of interest to know how the molecules are arranged perpendicular to their long axis. Hence we have analysed our x-ray diffraction photographs to calculate the average lateral distance between the molecules, which has not been reported in our previous x-ray work[6].

EXPERIMENTAL

The chemicals ME 5O.5 and 5CB were donated by E. Merck, U.K. Ten mixtures with mole fractions (x) of 5CB equal to 0.15, 0.207, 0.305, 0.4, 0.465, 0.501, 0.59, 0.645, 0.702, 0.812 were prepared. The measured transition temperature values agree well with the values obtained from the phase diagram of this system given by Dunmur et.al [4]. Refractive indeces (n_o, n_e) for λ=5780 Å have been measured within ±0.001 by the thin prism method. Experimental set up and the procedure for order parameter determination from refractive indices studies have been described in detail in our earlier publication [9]. The experimental technique employed to obtain x-ray diffraction data and subsequent analysis have been described earlier by Bhattacharjee et al [10]

RESULTS AND DISCUSSIONS

Phase diagram of this system which is similar to that obtained by Dunmur et. al. is shown in figure 1. Figure 2 shows the variation of density values with temperature. The density as a function of temperature for x=0.4 only have been reported in our earlier publication [6]. In figure 3 we have plotted optical birefringence ($\Delta n = n_e - n_o$) values for different mixtures as a function of temperature. Δn and density values of 5CB have already been reported [10,11] earlier. The change in density as well as birefringence (Δn) values at the smectic A to nematic phase transition is discontinuous near x = 0.4 and the discontinuity decreases gradually above and below this concentration, in agreement with the transition entropy and refractive index measurements by Dunmur et al [5].

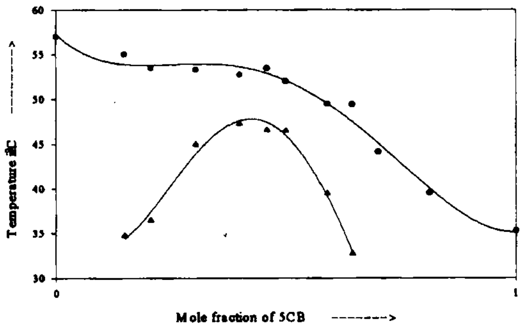

FIGURE 1. Phase diagram of 5CB/ME5O.5 as a function of mole fraction (x) of 5CB. ● T_{NI};; ▲ T_{SN}

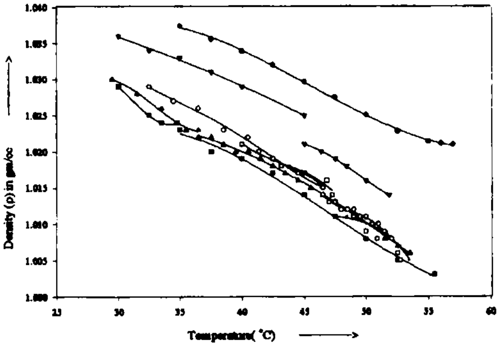

FIGURE 2A Temperature dependence of density values for 5CB/ME 5O.5 mixtures at different compositions, x = mole fraction of 5CB. ● x=0.0 ■ x=0.15; ▲ x=0.207; ▼ x=0.305; □ x=0.40

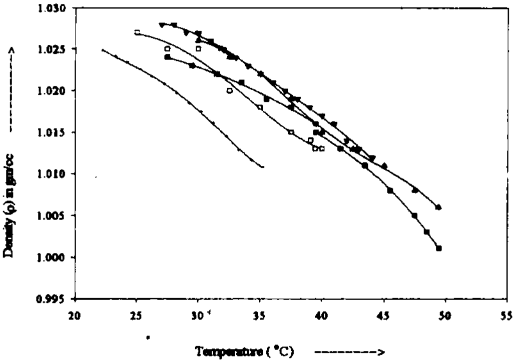

Figure 2B. Temperature dependence of density values for 5CB/ME 5O.5 mixtures at different compositions, x = mole fraction of 5CB. ■ x=0.59; ▲ x=0.645; ▼ x=0.702; □ x=0.812; ✚ x=1.0.

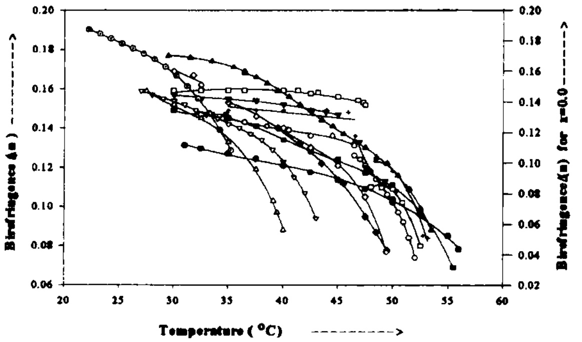

Figure 3. Birefringence (Δn) values as a function of temperature for different mixtures . • x=0.0; ■ x=0.15; ▲ x=0.207; ▼ x=0.305; □ 0.4; ✚ x=0.465; o x=0.501;◆ x=0.59; ‹› x=0.645; ∇ x=0.702; Δ x=0.812; ⊕ x=1.0 (from Karat et al. [11])

This indicate that a first order Sm A - N phase transition occurs near the center of the phase diagram. This first order phase transition changes to second order for mixtures of higher and lower concentration of 5CB. The refractive index data have been analyzed to determine the polarizability values (α_e and α_o) using Neugebauer's[12] method. The polarizability anisotropy for a perfectly ordered sample, i.e., at $<P_2> = 1$ was obtained from these data using extrapolation procedure given by Haller et. al. [13]. Since most of the mixtures studied in this system have two phases, and temperature variation of α_e and α_o are different for two phases, we have plotted Haller's extrapolation by taking the values of α_e and α_o in only nematic phase. Again the temperature variation of $\Delta\alpha$ is large in nematic phase, but in most of the smectic A phase this variation is very small. The order parameter $<P_2>$ is calculated from the well-known relation,

$$<P_2> = (\alpha_e - \alpha_o)/(\alpha_{\parallel} - \alpha_{\perp})$$

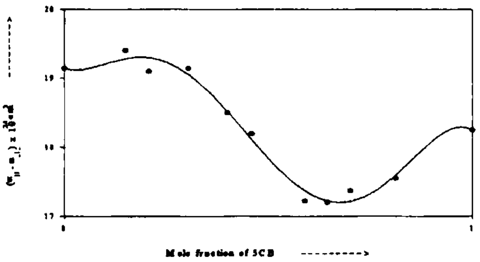

FIGURE 4 $(\alpha_{\parallel} - \alpha_{\perp})$ against mole fraction of 5CB. ● Neugebauer's method.

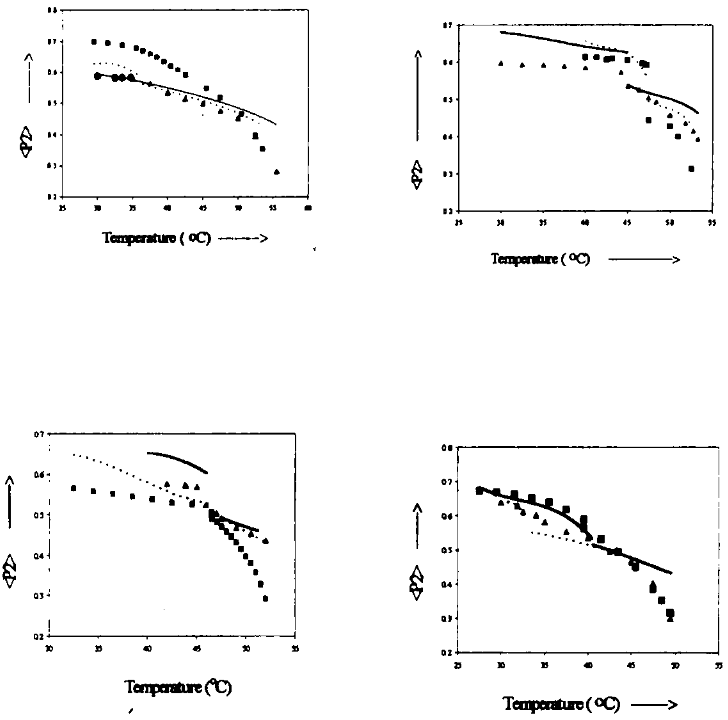

FIGURE 5(a) - 5(d). Variation of <P2> with temperature for different mixtures having induced smectic A phase. ▲Experimental <P_2> for x = 0.15, 0.305, .465, .59; ■ experimental <P2> for x = 0.207, 0.4, 0.501, 0.65; — calculated from McMillan's theory for x = 0.15 (α= 0.346, δ=0.67), 0.305 (α= 0.424, δ=0.67), 0.465 (α= 0.46, δ=0.67), 0.59 (α=0.46, δ= 0.67); and ... calculated from McMillan's theory for x = 0.207(α=0.39, δ=0.67), 0.4 (α=0.433, δ=0.67),0.501(α=0.433,δ=0.67), 0.65 (α=0.39,δ=0.67).

We have also fitted experimental order parameter values with McMillan's theory for the mixtures having induced smectic A phase and Maier-Saupe theory for others having nematic phase only. In figure 4, we have found that $\alpha_a = (\alpha_{\parallel} - \alpha_{\perp})$ decreases near equimolar concentration. From x-ray diffraction studies, we have found a definite minimum in layer spacing or apparent molecular length near equimolar concentration. Since anisotropy is proportional to the apparent molecular length, our x-ray result do support the variation of the polarizability anisotropy values with molar concentration. In figure 5(a) to 5(f), we have plotted the variation of $<P_2>$ values with temperature. Our experimental order parameter values at the smectic A to nematic phase transition appears to be of the first order in the mixtures for $x \approx 0.45$. Whereas, a second order phase transition is observed for mixtures with $x >> 0.4$ and $x << 0.4$. In the middle of the phase diagram change in $<P_2>$ is very large at Sm A - N phase transition. We have also fitted the experimentally determined orientational order parameters having an induced smectic phase to McMillan's theory using the mean field potential,

$$V_M(\cos\theta) = -\nu[\alpha\tau\delta\cos(2\pi z/d) + (\eta + \alpha\sigma\cos(2\pi z/d))P_2(\cos\theta)]$$

where α and δ are adjustable parameters. In fitting $<P_2>$ values to the McMillan's model, it is difficult to vary α and δ independently. We assumed that intermolecular pair potential do not change with composition and have taken constant δ values over the entire composition range (δ=0.67). The α values show a broad maximum near $x = 0.4$. This is expected since near x=0.4 smectic phases occurs at a relatively higher temperature and is separated from the isotropic phase by a narrow temperature range nematic phase.

Our order parameter values calculated using Neugebauer's relation do not agree well with Maier-Saupe theory for the pure compounds ME5O.5. But, in case of 5CB and mixtures with x=0.702 and 0.812, where only nematic phases are present, the agreement with the theory is good (Fig 5f). However, in all the mixtures as well as in pure compounds the experimental OOP values near N - I transition are significantly lower than the theoretical values. This may be due to the fluctuations of director, which is more pronounced near the clearing point.

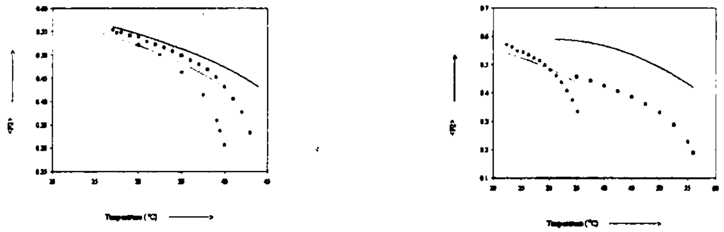

FIGURE 5(e) - 5(f). Variation of $<P_2>$ with temperature for different mixtures having nematic phase only.

● Experimental $<P_2>$ for x = 0.00, 0.702 ; ▪ experimental $<P_2>$ for x = 0.812, 1.0 ; — calculated from Maier -Saupe theory for x = 0.0, 0.702, and ... calculated from Maier- Saupe theory for x = 0.812, 1.0 .

Figure 6, shows the variation of orientational order parameters (both from x-ray and refractive index measurements) and packing fractions at 35 °C.

Our experimental OOP values in the smectic A phase agree well with those calculated from McMillan's theory for mixtures having x = 0.15, 0.645, in the region of the phase diagram where the $<P_2>$ values changes continuously across the Sm A - N phase transition. However, the agreement between the calculated and the experimentally determined OOP values is rather poor for mixtures having x = 0.207, 0.305, 0.465, 0.501, 0.59, where it has been found that there is a discontinuous change of $<P_2>$ values at the smectic A to nematic transition, except for x = 0.207. In order to obtain a better idea about orientational order parameter values we have calculated the molecular packing fraction. The packing fraction is defined as the ratio of the geometrical volume (Vanderwaal's volume) to the volume occupied per molecule in the mesophases. Following Kitaigordsky[14], we have calculated geometrical volume of the pure components V_A and V_B, where A,B refers to 5CB and ME5O.5 molecules respectively. Now, if ρ be the density of a mixture at any temperature and N be the Avogadro's number, then packing fraction

$$=(\rho N V')/M'$$

$$=\rho N(x_A V_A + x_B V_B)/(x_A M_A + x_B M_B)$$

where x_A, x_B and M_A, M_B are the mole fractions and molecular weights of the respective molecules in the mixture.

Our OOP values from refractive index measurements agree quite well with the values obtained from x-ray diffraction measurements. The lower values of $<P_2>$ from refractive index measurements near x = 1 may be due to the fact that the temperature T =35 °C is very near to the clearing temperature. Director fluctuations, which is more pronounced in case of refractive index measurements where surface alignment technique has been employed, could account for such

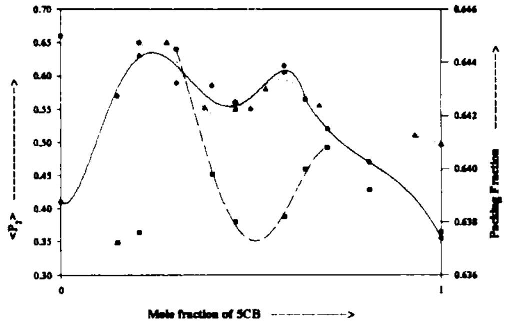

FIGURE 6 Variation of $<P_2>$ values obtained from refractive index measurements and that of from X-ray measurements and packing fraction at a temperature T = 35 °C • — $<P_2>$ from refractive index measurements, ▲ … $<P_2>$ from x-ray measurements ▴ packing fraction.

discrepancy as compared with those from magnetically aligned samples used in x-ray diffraction measurements. From figure 6 it is clear that the OOP's in the smectic phase and the packing fraction values show definite minimum around x=0.4. The birefringence (Δn), density (ρ) also follow the same trend indicating that the

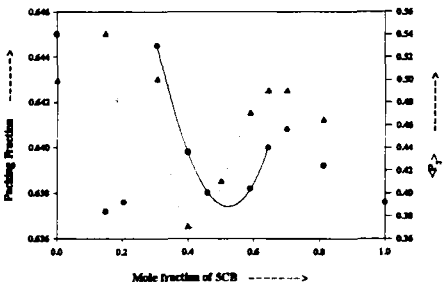

FIGURE 7 Variation of orientational order parameter $<P_2>$ and the packing fraction values in the nematic phase at a temperature T = 0.98 T_{NI}. ● $<P_2>$ values ▲ packing fraction

packing in nearly equimolar mixtures is rather loose. Similar behaviour is also observed in the nematic phase where the smectic A phase is the precursor of the nematic phase (Figure 7) . This may due to the smectic fluctuations present in the nematic phase.

To investigate the minimum in the OOP, packing fraction and other physical properties observed for mixtures around x = 0.4, we have analysed our x-ray diffraction data to calculate the average lateral distance between the molecules. The average lateral intermolecular distance D between the molecules can be obtained from the diffraction angle of the outer ring of x-ray pattern by the formula,

$$2D \sin\theta = 1.117\,\lambda$$

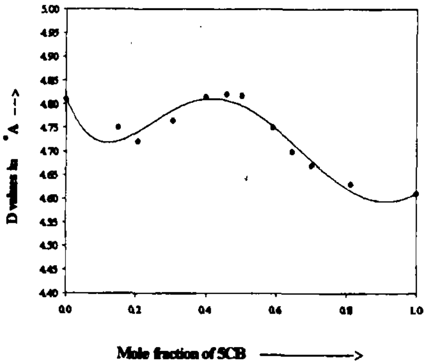

FIGURE 8 Variation of D with mole fraction of 5CB at T=35 °C.

From figure 8, it is clear that the experimental D values, within the smectic phase shows an enhancement in their magnitudes near equimolar concentration, whereas the density and layer thickness show a reverse trend i.e, minimum near $x \approx 0.4$. This implies that the packing of the molecules in the smectic layers is poor near $x \approx 0.4$. This variation of D with molar concentration clearly explains why the density of the mesogen decreases even when layer thickness is also decreasing near $x \approx 0.4$.

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