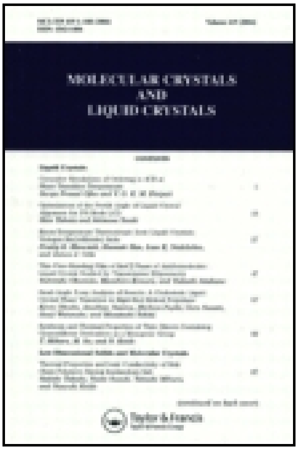

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Refractive Index, Density and Order Parameter of Two Binary Mixtures Showing Reentrant Nematic Phase

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Refractive Index, Density and Order Parameter of Two Binary Mixtures Showing Reentrant Nematic Phase

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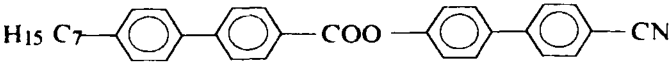
Binary mixtures of 4-cyanobiphenyl-4'-yl-4-heptylbiphenyl-4-carboxylates (7CBB) with alkyloxycyanobiphenyl (nOCB) show both reentrant nematic and induced (or enhanced) smectic A_d phases in certain composition range. The temperature dependence of density and refractive indices, both ordinary and extraordinary, have been determined for two such mixtures of 7CBB with 7OCB or 12OCB in their reentrant nematic and smectic A_d phases. The absence of discontinuity in density and refractive index values at the N_{re} - SmA_d transition temperatures indicate that for both the mixtures studied, these phase transitions are of second order. The order parameter values have been calculated from the refractive index data. These $<P_2>$ have been compared with those obtained from x-ray diffraction studies and from McMillan's theory. Discrepancies have been explained qualitatively.

Keywords: reentrant nematic; refractive index; density; order parameter; induced (enhanced) smectic A_d phase

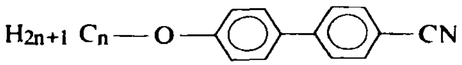
INTRODUCTION

Dabrowski and his co-workers[1-3] have recently investigated the phase diagrams of binary mixtures of 4-cyanobiphenyl-4'-yl-4-alkylbiphenyl-4-

carboxylates (nCBB) with alkyl or alkoxy cyanobiphenyls (nCB or nOCB). They have reported very interesting and unusual phase diagram with strongly induced smectic A_d phase in the form of an 'island' or 'semi island' surrounded by nematic 'sea' for mixtures with lower homologues ($n \leq 7$) of nCB or nOCB. The mixtures with higher homologues ($n \geq 8$) show strongly enhanced smectic A_d phases. Some of these mixtures have very interesting property of showing induced (or enhanced) smectic A_d phase as well as reentrant nematic phase over a particular composition range. Hence these mixtures are well suited for the study of physical properties, which may elucidate the formation of smectic A_d and reentrant nematic phases. We have already reported[4] x-ray diffraction studies on two of the mixtures, namely, 7CBB + 7OCB and 7CBB + 12OCB. The structural formulae of the compounds are given below.



7CBB



n = 7, **7OCB**
n = 12, **12OCB**

In the present paper we are reporting the experimental temperature variation of density and refractive indices, both ordinary and extraordinary, of these two mixtures at a certain composition where both reentrant nematic and smectic A_d phases exist. The experimental data have been analysed to calculate the order parameters in the reentrant nematic and smectic A_d phases. The continuous change of density and refractive index values at the reentrant nematic to smectic A_d phase transition seems to indicate that these phase transitions are of second order for both the mixtures.

EXPERIMENTAL

The pure compounds 7CBB (Cr 123 SmA$_1$ 136 N 350 I), 7OCB (Cr 54 N 75.5 I) and 12OCB (Cr 69 SmA$_d$ 88.5 I) were prepared at the Institute of Chemistry, Military University of Technology, Warsaw, Poland. The mixtures were prepared at Physics Department, University of North Bengal, India. The transition temperatures (in °C) of the mixtures as determined with Mettler

FP80/82 thermosystem by observing the textures under a polarising microscope are shown below:

Mixture A, 7CBB + 7OCB, mole fraction of 7CBB = 0.8495
Cr 116 $\mathbf{N_{re}}$ 154 $\mathbf{SmA_d}$ 241.3 **N** ~ 320 **I**
Mixture B, 7CBB + 12OCB, mole fraction of 7CBB = 0.9170
Cr 120 $\mathbf{N_{re}}$ 161.5 $\mathbf{SmA_d}$ 261 **N** ~ 320 **I**

The phase diagrams of these two systems have been given previously by Brodzik et al[1].

Both these mixtures show sign of decomposition at higher temperatures, so density and refractive index values in the normal nematic phase could not be obtained. The experimental methods for density and refractive index measurements have been reported earlier[5].

RESULTS AND DISCUSSIONS

The temperature variation of the density of Mixture A, from its melting point to 170 °C, is shown in Fig. 1. It is seen that the density changes smoothly at the reentrant nematic to smectic A_d phase transition. The variation of ordinary and extraordinary refractive indices at wavelength 5780Å with temperature is given in Fig. 2. Again, there is no discontinuity in these values at the N_{re} to SmA_d transition temperature. These observations indicate that the reentrant nematic to induced smectic A_d phase transition in this mixture is of second order. Fig. 3 shows the temperature variation of density of Mixture B from its melting point to 175 °C. Once again, it can be seen from the figure that density values vary continuously across the reentrant nematic to smectic A_d phase transition temperature. Ordinary and extraordinary refractive indices for three different wavelengths (5461Å, 5780Å and 6907Å) as a function of temperature are plotted in Fig. 4. The refractive indices curves also change smoothly at the N_{re} to SmA_d phase transition. Hence, for both the mixtures studied, the reentrant nematic to smectic A_d transitions are of second order. This is in accordance with our earlier x-ray studies on these mixtures[4]. Both the mixtures show large birefringence (~ 0.3) in the reentrant nematic phase.

The refractive index data have been analysed to determine the polarisability values (α_e and α_o) using Neugebauer's procedure[6,7]. The polarisability anisotropy ($\Delta\alpha_o$) for a perfectly ordered sample, i.e., at $\langle P_2 \rangle = 1$, was obtained from these data using an extrapolation procedure given by Haller et al[8]. The order parameter $\langle P_2 \rangle$ is calculated from the well-known relation[9]

$$\langle P_2 \rangle = (\alpha_e - \alpha_o) / \Delta\alpha_o.$$

Fig. 5 shows these temperature variations of $\langle P_2 \rangle$ values for Mixture A together with $\langle P_2 \rangle$ values obtained from our x-ray studies[4]. In x-ray studies

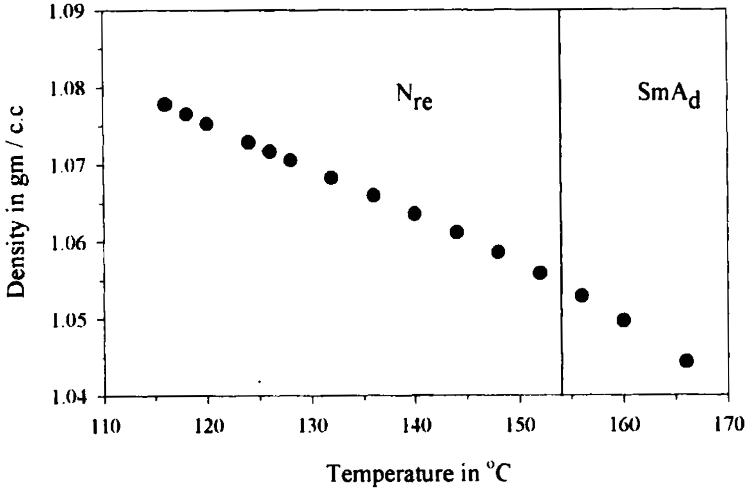


FIGURE 1 Variation of density with temperature for Mixture A

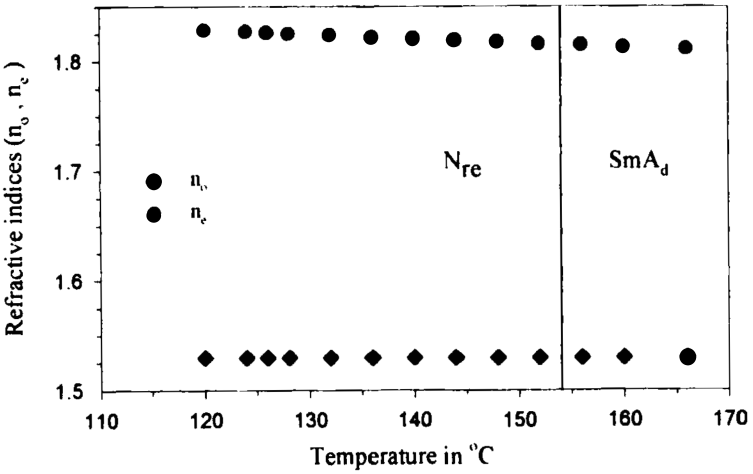


FIGURE 2 Variation of refractive index with temperature for Mixture A

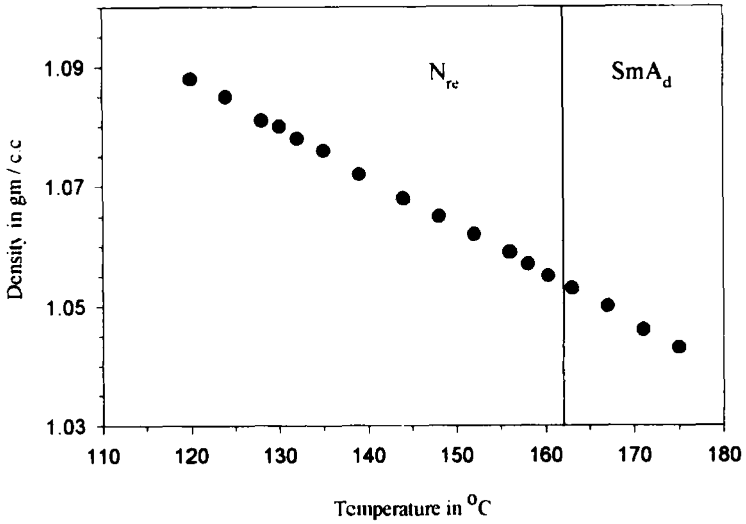


FIGURE 3 Variation of density with temperature for Mixture B

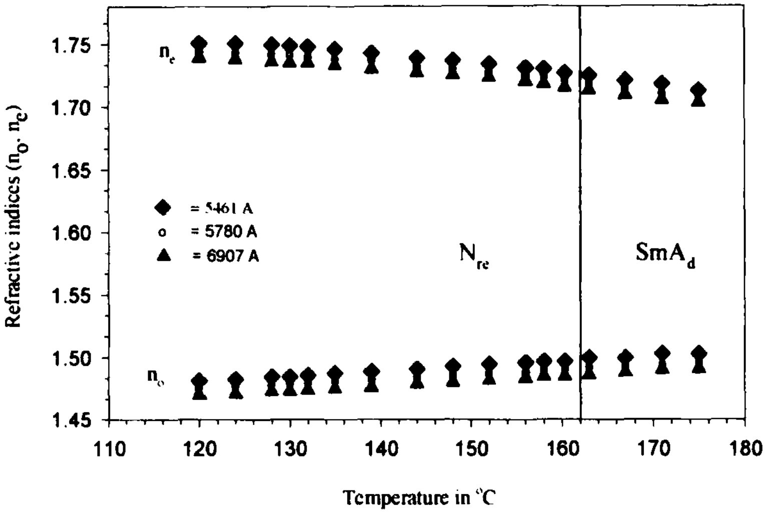


FIGURE 4 Variation of refractive indices with temperature for Mixture B

the sample could be taken upto 260 °C without decomposition since the sample was in a sealed capillary where atmospheric oxygen could not get in to react with the chemicals. In case of refractive index and density measurements, our systems were nor sealed, hence decomposition set in at a lower temperature. The $< P_2 >$ values from the x-ray data could be obtained upto 260 °C in the normal nematic phase, while the refractive index and density data are only upto 170 °C. Above 260 °C the sample could not be aligned well in the magnetic field, hence $<P_2>$ values from x-ray diffraction data were not calculated above that temperature. We have also tried to fit our experimental data for Mixture A with those calculated from McMillan's theory[10] with $\alpha=0.58$, $\delta = 0.14$. It can be seen that the order parameter values obtained from refractive index data are much larger than those obtained from our x-ray studies, though they agree quite well with the theoretical values. Fig. 6 shows the corresponding temperature variation of order parameter for Mixture B. The theoretical McMillan curve ($\alpha = 0.24$, $\delta = 0.56$) which fits the data best is also drawn in the same figure. The order parameters from refractive index, x-ray diffraction and McMillan's theory all disagree with each other. This is not surprising since even in pure 12OCB the agreement between McMillan's theory and experimental $< P_2 >$ values from x-ray diffraction is not good[11]. The discrepancy between the order parameter values obtained from x-ray data on one hand and refractive index or magnetic susceptibilities data on the other hand has been reported earlier by many authors[7,11,12]. They have also discussed probable causes for such disagreement among experimental order parameter values obtained by using different techniques. Another cause may be worth noting here. All the constituent molecules of the mixtures studied have rather long end chains. Hence, this discrepancy may be, in part, due to the fact that the rigid part and the chain part of the molecules are not collinear and hence, the x-ray diffraction pattern from an assembly of such molecules has broader outer halo than that from a linear molecular assembly. The polarisability and magnetic susceptibility anisotropies on the other hand depend mostly on the aromatic rigid part of the molecules and vary little on the orientation of the aliphatic chain part. So, the order parameter values calculated from x-ray diffraction intensities are smaller than those obtained from the other two experimental techniques. This deviation, in the case of refractive index and x-ray $<P_2>$ values caused by the chain ordering, has been successfully calculated by Gupta et al[13] for a few pure compounds having long end chains. However, such calculations for mixtures are much more difficult and have not been tried as yet.

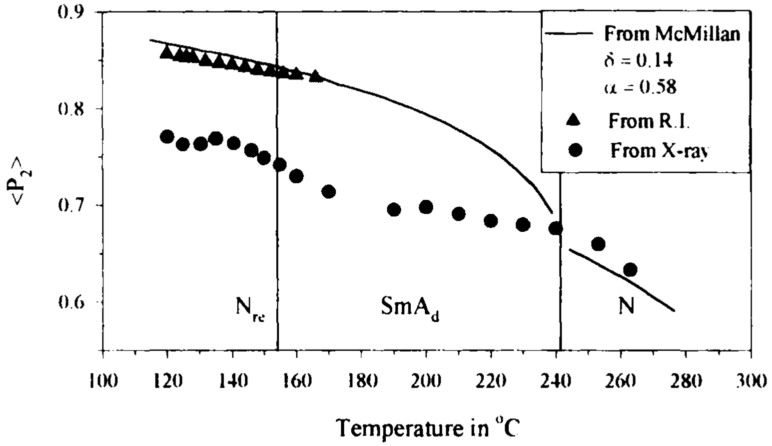


FIGURE 5 Temperature variation of order parameter of Mixture A

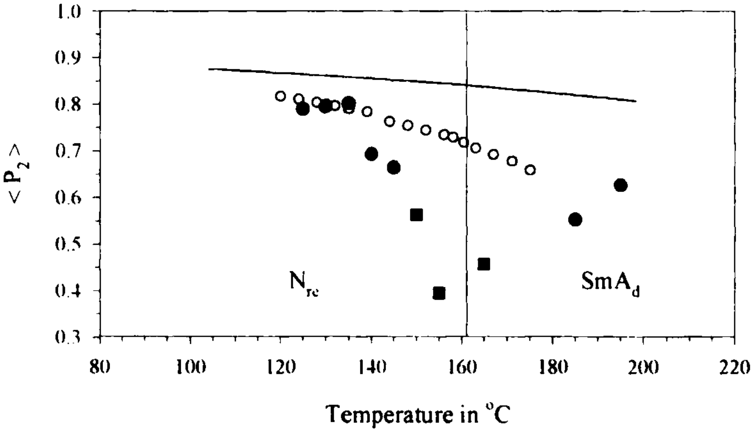


FIGURE 6 Temperature variation of order parameter of Mixture B

○ From R.I data
—— McMillan theoretical value. δ = 0.56, α = 0.24
● From x-ray data. aligned sample
■ From x-ray data. partially aligned sample

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References

[1] M. Brodzik and R. Dabrowski, *Liq. Cryst.*, **18,** 61 (1995).
[2] M. Brodzik and R. Dabrowski, *Liq. Cryst.*, **20,** 99 (1996).
[3] M. Brodzik and R. Dabrowski, *J. Phy II France,* **5,** 1805 (1995).
[4] S.K. Giri, N.K. Pradhan, R. Paul, S. Paul, P. Mandal, R. Dabrowski, M. Brodzik and K. Czuprynski, *SPIE,* **3319,** 149 (1998).
[5] A.K. Zeminder, S. Paul and R. Paul, *Mol. Cryst. Liq. Cryst.*, **61,** 191 (1980).
[6] H.E.J. Neugebauer, *Can. J. Phys.*, **32,** 1 (1954).
[7] M. Mitra, S. Paul and R. Paul, *Pramana – J. Phys.*, **29,** 409 1987.
[8] I. Haller, H.A. Higgin, H.R. Lilienthal and T.R. McGuire, *J. Phys. Chem.*, **77,** 950 (1973).
[9] P.G. de Gennes, *Mol. Cryst. Liq. Cryst.*, **12,** 193 (1971).
[10] W.L. McMillan, *Phys. Rev.* **A6,** 936 (1972), *Phys. Rev.* **A4,** 1238 (1971).
[11] M.K. Das, R. Paul and S. Paul, *Mol. Cryst. Liq. Cryst.*, **258,** 239 (1995).
[12] M. Mitra, R. Paul and S. Paul, *Mol. Cryst. Liq. Cryst.*, **177,** 71 (1989).
[13] S. Gupta, R. Paul and S. Paul, *Mol. Cryst. Liq. Cryst.*, **262,** 485 (1995).