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

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Small Angle X-Ray Diffraction Studies of an Ester/Biphenyl Mixture (5CB/ME 50.5) Showing an Injected Smectic Phase

M. K. Das [a], R. Paul [a] & D. A. Dunmur [b]

[a] Department of Physics, University of North Bengal, Siliguri, West Bengal, India, 734430

[b] Department of Chemistry and Centre for Molecular Materials, University of Sheffield, Sheffield, S3 7HF, United Kingdom

Version of record first published: 23 Sep 2006.

To cite this article: M. K. Das , R. Paul & D. A. Dunmur (1995): Small Angle X-Ray Diffraction Studies of an Ester/Biphenyl Mixture (5CB/ME 50.5) Showing an Injected Smectic Phase, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 258:1, 239-252

To link to this article: http://dx.doi.org/10.1080/10587259508034564

Mol. Cryst. Liq. Cryst., 1995, Vol. 258, pp. 239–252
Reprints available directly from the publisher
Photocopying permitted by license only

Small Angle X-Ray Diffraction Studies of an Ester/Biphenyl Mixture (5CB/ME 50.5) Showing an Injected Smectic Phase

M. K. DAS*, R. PAUL* and D. A. DUNMUR†

*Department of Physics, University of North Bengal, Siliguri, West Bengal, India, PIN-734430
†Department of Chemistry and Centre for Molecular Materials, University of Sheffield, Sheffield, S3 7HF, United Kingdom

(Received March 14, 1994)

The molecular organisation in a binary mixture of a strongly polar mesogen (5CB) and a weakly-polar mesogen (ME50.5) is investigated using results of X-ray scattering and density studies.. Analysis of the intensity distribution of X-ray scattering has yielded results for orientational order parameters in addition to smectic layer spacings and effective molecular lengths. The results are compared with a mean field theory of the smectic phase. Previously unexplained results for mixtures showing a minimum in the anisotropy of physical properties coincident with a maximum in the nematic/smectic A transition entropy are shown to be consistent with the theory. We conclude that favourable packing of molecules in the injected smectic A phase stabilises the layers but increases the orientational free volume, consistent with a lower orientational order parameter.

Keywords: injected smectic phase, order parameters, layer thickness, X-ray diffraction.

INTRODUCTION

The study of the physical properties of mixtures of liquid crystalline compounds has been the subject of considerable interest in the past in order to produce room temperature mesophases for applications in display devices. There is also special interest in understanding the behaviour of the mixtures, so that better materials may be produced for applications. One of the unusual aspects of binary liquid crystal mixtures of strongly dipolar and weakly dipolar mesogens is the formation of smectic phases, called injected smectic phases, from components which do not show smectic properties in their pure state.[1–4] The formation of injected phases is also observed with discotic liquid crystals[16] where addition of a strongly dipolar solute (4,5-dibromo-o-xylene) to a non-polar discotic nematic (hexakis (4-nonylphenylethynyl) naphthalene results in the appearance of rectangular and hexagonal columnar phases. It is believed that specific solute-solvent interactions are responsible for the formation of both injected smectic and injected columnar phases. In an injected smectic phase, the stabilization of a translationally ordered phase must imply more efficient packing of dissimilar molecules in layers or specific interactions between the mixture components. The formation of injected smectic phases can be a problem for mixtures used in electro-optical devices. However, existence of injected smectic phases at a lower temperature may improve the performance of a device.[5]

One system, which shows an injected smectic phase, is the mixture of 4-pentyl-4'-cyanobiphenyl (5CB) and 4-pentylphenyl-4'-pentyloxybenzoate (ME50.5) which has an injected smectic A phase. The phase diagram of this system has been reported earlier by Dunmur *et al.*[4] who measured transition enthalpies, refractive indices, and electric permittivities of a series of mixtures of these two compounds, and observed an increase in the entropy change at the smectic–nematic transition for mixtures having mole-fraction of 5CB around 0.4 which was not explained. Using an extension of Maier–Saupe theory, Palffy–Muhoray *et al.*[6] have determined the nematic-isotropic coexistence region for the entire range of concentrations of this mixture, and they proposed a relation between the refractive index of the binary mixture and order parameters of its components. Measurements of the birefringence and the dielectric anisotropy in the nematic phase showed a negative deviation from a simple additivity relation for mixtures having mole fractions of 5CB ~ 0.4, coincident with the increase in the smectic/nematic transitional entropy.

The present work on the same system was undertaken to try to explain these experimental observations, and reports small angle X-ray diffraction measurements of orientational order parameters, layer thickness and apparent molecular length for a series of mixtures having different compositions.

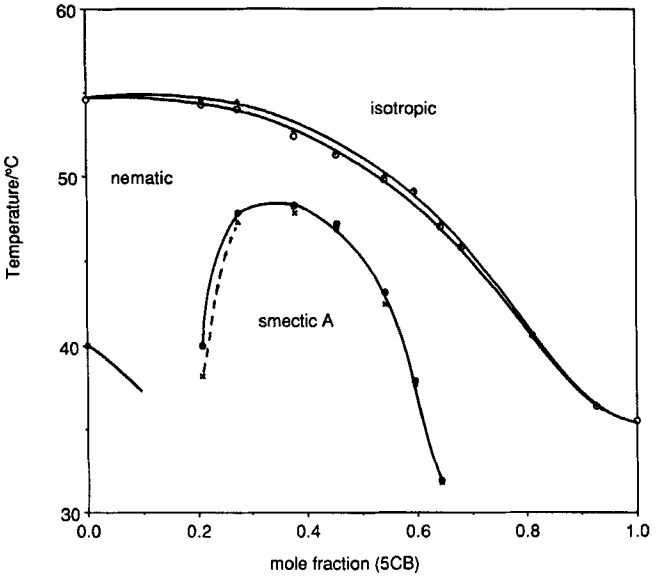
EXPERIMENTAL METHODS

The experimental work was performed at the Department of Physics, University of North Bengal, using an experimental set up which has been described earlier.[7] X-Ray diffraction patterns were recorded photographically on a flat plate camera using Ni filtered CuK_α radiation of wavelength $\lambda = 1.5418$ Å. The sample was sealed in a 0.5mm diameter thin walled Lindemann glass capillary, and the temperature during the experiment was maintained at 0.5°C by using a temperature regulator. The sample was aligned using a 0.1 T magnetic field. Photographs for order parameter measurements were taken with sample to film distance of about 6 cm. To obtain better accuracy in the measurement of layer thickness, X-ray diffraction photographs of inner spots were taken with sample to film distance increased to about 9 cm to 12 cm.

X-Ray photographs of the aligned samples were scanned to obtain X-ray diffraction intensities, the angular distribution of which were utilised to obtain the orientational distribution function and hence orientational order parameters, $\langle P_2 \rangle$ and $\langle P_4 \rangle$, following the procedure given by Bhattacharjee *et al.*.[8] The apparent molecular length in the case of nematics (l) and layer thickness in the case of smectics (d) were also determined from the diffraction pattern. Densities for the particular mixture corresponding to a maximum in the temperature of the smectic A phase were made at Sheffield using an Anton PAAR Digital Densimeter model No DMA60.

RESULTS AND DISCUSSION

Figure 1 shows the phase diagram of this binary system which is similar to that obtained by Dunmur *et al.*.[4] There is a narrow biphasic region associated with the



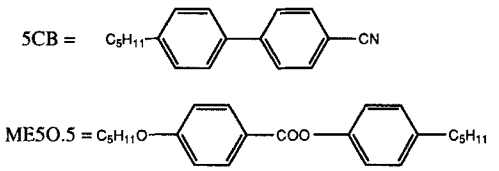


FIGURE 1 Phase diagram of 5CB/ME50.5 as a function of mole fraction (x) of 5CB.

nematic/isotropic transition, but the two-phase coexistence region for the smectic/nematic transition was more difficult to identify. As the entropy of this transition decreased away from the maximum of the phase stability region, the transition became close to second order and the two-phase coexistence region disappears. In our earlier work[4] we correlated the extent of the two phase coexistence region with the size of the discontinuity in birefringence and dielectric anisotropy at the smectic/nematic transition. As the transition approached second order, the birefringence and dielectric anisotropy, and hence order parameter became continuous.

The angular distribution of the diffuse scattering was used to determine the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ defined below:[8,17]

$$\langle P_2 \rangle = \langle \tfrac{1}{2}(3\cos^2\theta - 1) \rangle$$

$$\langle P_4 \rangle = \langle \tfrac{1}{8}(35\cos^4\theta - 30\cos^2\theta + 3) \rangle$$

The procedure is described in previous publications, but relies on a number of approximations. It is assumed that the molecules are parallel over a local region, and that smectic-like molecular organisation persists over a short range even in the nematic

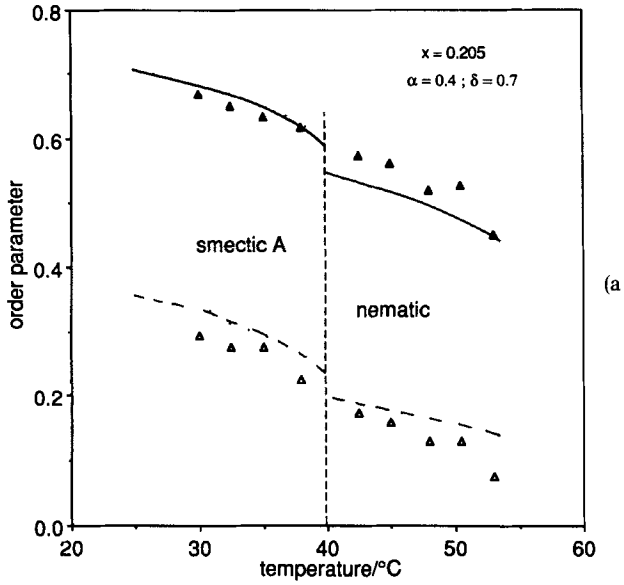
phase. Both these assumptions are necessary to analyse the data but their influence on the accuracy of the results is not known. We have also assumed that the molecules are rigid, and that the two components have the same order parameter in the binary mixtures. The theory for the orientational order in binary mixtures has been reported,[6] and it was shown that the order parameters of components in a binary mixture depended on the ratio of the transition temperatures and molar volumes of the pure components. In this paper, we neglect this refinement.

The variation of the orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ with temperature for different compositions of the mixture are shown in Figures 2(a)–2(i). We have fitted experimental order parameters for the mixtures having an injected smectic A phase to McMillan's theory [9] using the mean field potential,

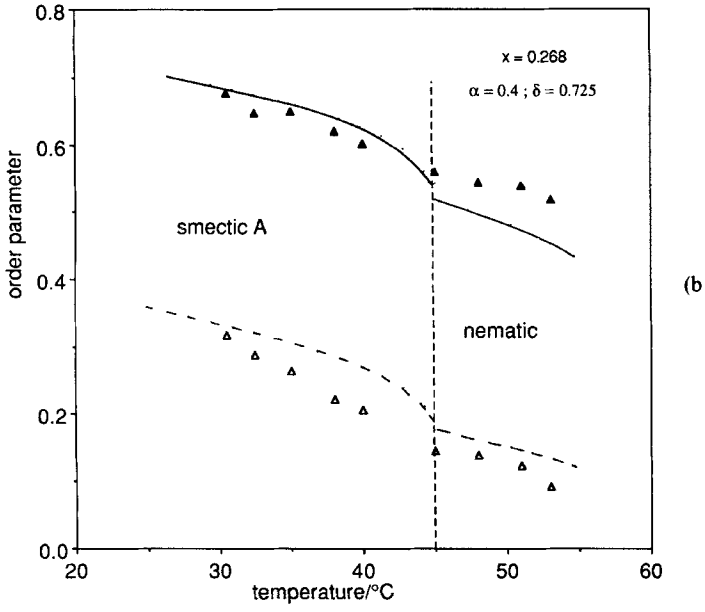
$$V_M(\cos\theta) = -v[\alpha\tau\delta\cos(2\pi z/d) + (\eta + \alpha\sigma\cos(2\pi z/d))P_2(\cos\theta)] \quad (1)$$

treating α and δ as the adjustable parameters. The quantity z is the displacement along the layer normal, d is the layer thickness, $\eta = \langle P_2(\cos\theta) \rangle$, the orientational order parameter; $\tau = \langle \cos(2\pi z/d) \rangle$, the translational order parameter and $\sigma = \langle P_2(\cos\theta)\cos(2\pi z/d) \rangle$, the mixed order parameter. The parameter v is obtained from the nematic/isotropic transition temperature, assuming the simple mean field theory result ($kT_{NI}/v = 0.22019$). Values for η, τ and σ are calculated using the self-consistency relationships as a function of temperature for various values of the parameters α and δ. The latter are adjusted to give agreement between the experimental and calculated smectic/nematic transition temperature, at which τ and σ became zero, and to give the best fit between the experimental and calculated values for $\langle P_2 \rangle$. The theoretical values of order parameters are also shown in respective figures. The values of δ and α which produce the best agreement with our experimental data are noted on each figure.

The mixtures can be divided into three groups. The first group consisting of mixtures with mole fractions of 5CB (x) < 0.27. The orientational order parameters are large and the agreement between the experimental values with those calculated from McMillan's theory is fair (Figures 2a–2b). The second group consisting of mixtures having $x > 0.45$, also show large $\langle P_2 \rangle$ and $\langle P_4 \rangle$ large values. The experimental orientational order parameters change continuously from smectic to nematic phase and their agreement with McMillan's theory is fair (Figures 2e–2g). It may not be out of place to mention that Dunmur *et al.* [4] also observed a second order smectic-to-nematic phase transition in this mixture for $x > 0.45$, from refractive index measurements. The mixtures with x = 0.34 and 0.447 constitute the third group. The meridional reflections from smectic layers are diffuse for these mixtures indicating that the smectic layers are also not well defined. Like the mixtures studies previously by us (5CB/ME 60.5),[10] the X-ray diffraction pattern in the co-existing smectic-nematic phase is more like that from a smectic than from a nematic. The $\langle P_2 \rangle$ values in this phase are also closer to the smectic phase values than to those from nematic phase. Agreement between the calculated and the experimental values is rather poor, particularly in the lower temperature region (Figures 2c–2d). As the experimental orientational order parameters in the smectic phase of this mixture do not change with temperature, except near to the smectic-nematic transition temperature, no combination of δ and α values

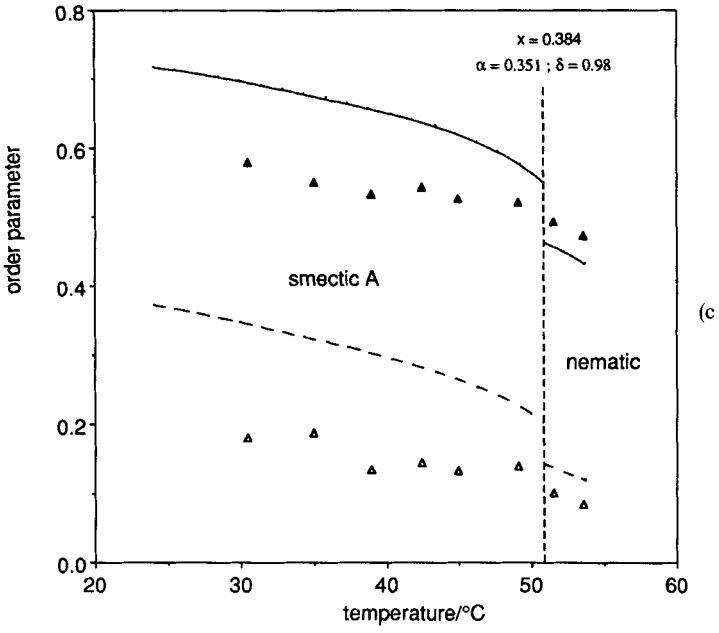


(a

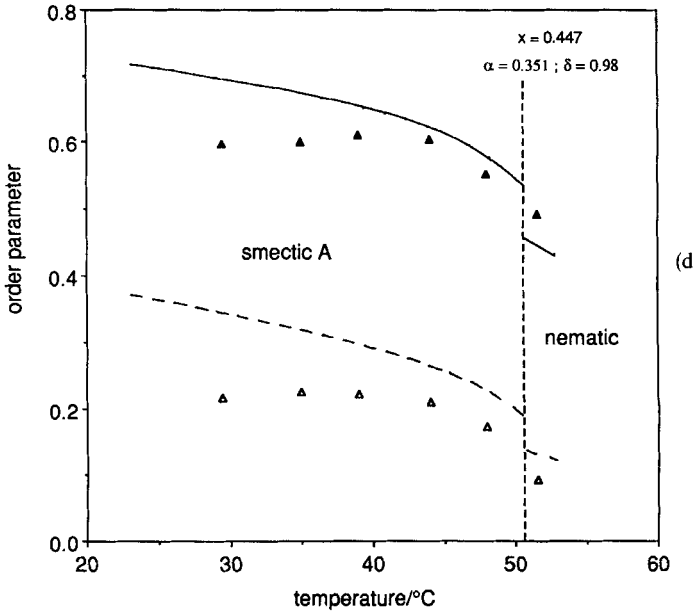


(b

FIGURE 2(a)–2(i) Temperature dependences of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ 5CB/ME50.5 mixtures at different compositions, x = mole fraction of 5CB, δ and α, are McMillan potential parameters. Full line McMillan = $\langle P_2 \rangle$ values; dashed line = McMillan $\langle P_4 \rangle$ values; ▲ = experimental data for $\langle P_2 \rangle$; Δ = experimental data for $\langle P_4 \rangle$.

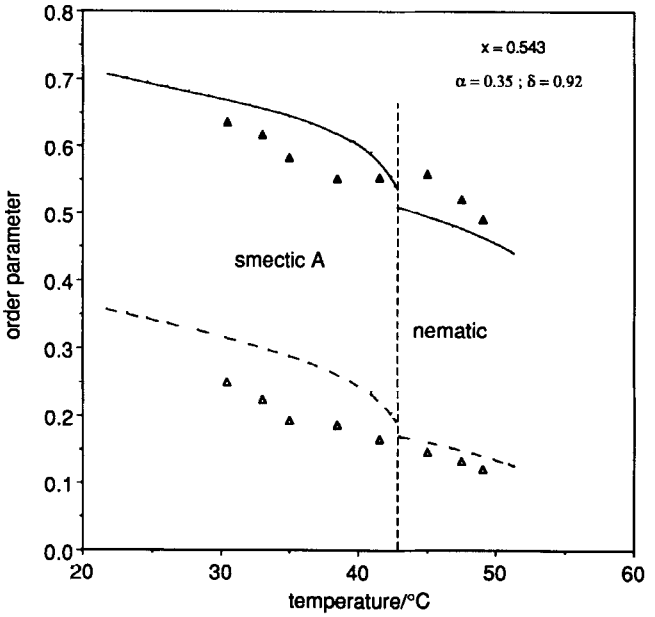


(c

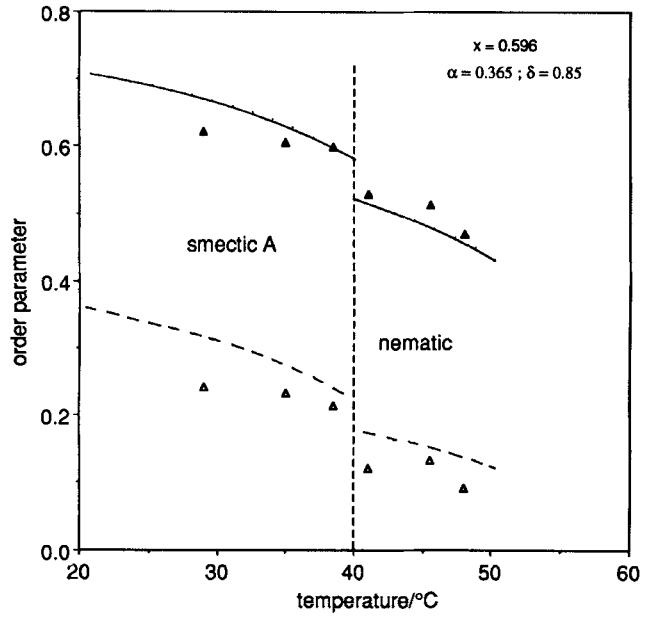


(d

FIGURE 2 (*Continued.*)

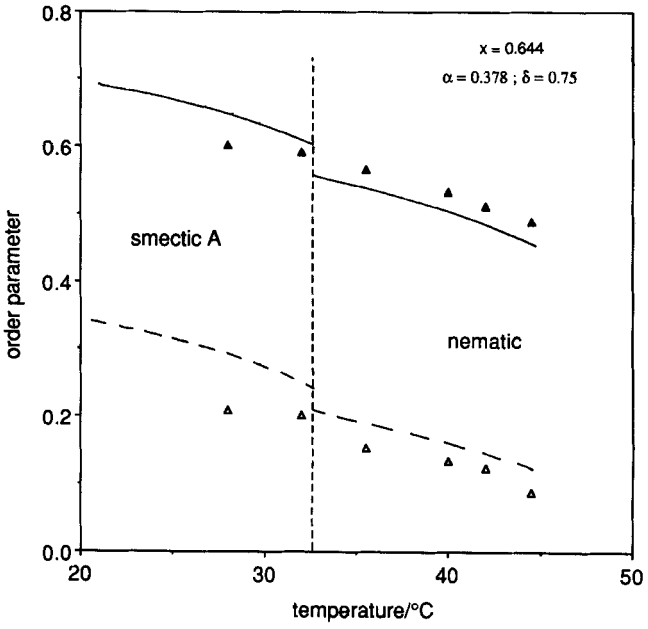


(e

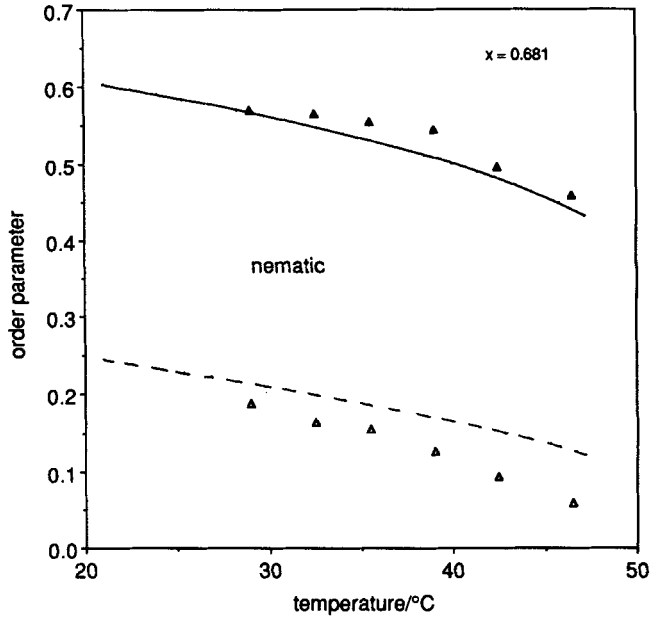


(f

FIGURE 2 (*Continued.*)

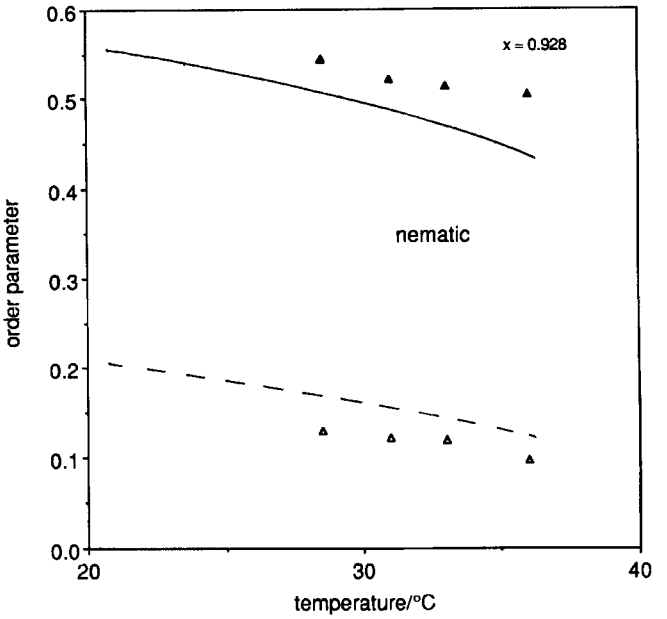


(g



(h

FIGURE 2 (*Continued.*)



(i

FIGURE 2 (*Continued.*)

in the McMillan theory can be fitted satisfactorily to the experimental orientational order parameters. Hence we have tried to fit only the data near to the smectic-nematic transition temperature. As mentioned in our earlier paper[10] the cause of this problem is possibly due to poor packing of molecules having different shape and length. For the other two mixtures, which have been studied only in the nematic phase, the experimental values agree well with Maier-Saupe[11] theoretical values (Figures 2(h)–2(i)).

Figure 3 shows the variations of $\langle P_2 \rangle$ and $\langle P_4 \rangle$ with mole fraction of 5CB at $T = 30°C$. Like the mixture 5CB/ME 60.5, we also observe a minimum which is near to $x \approx 0.4$. The $\langle P_2 \rangle$ values outside the smectic region decrease with increase in mole fraction of 5CB. As mentioned in our earlier publication[10] the same behaviour for $\langle P_2 \rangle$ was also found by Palffy-Muhoray *et al.*,[6] though they did not comment on it.

To investigate the minimum in the order parameter and other physical properties observed for mixtures around a mole fraction of 0.4, we measured the density as a function of temperature for a mixture corresponding as closely as possible to the maximum for T_{SN} in the phase diagram, and the results are presented in Figure 4. It is immediately apparent that the relative change in density at the S_A/N transition is much greater than that at the N/I transition, consistent with the anomaly observed in the entropies of transition. Furthermore the behaviour of the density at the N/I transition is more reminiscent of a second order phase change.

Results for the temperature dependence of the apparent molecular length i.e. density wave parallel to the director in nematic phase (l) and layer thickness in smectic phase (d)

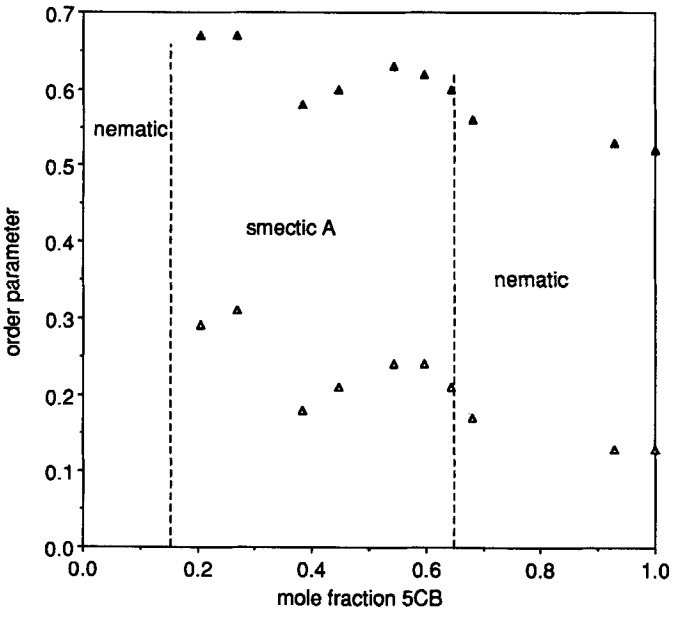


FIGURE 3 Orientational order parameters $\langle P_2 \rangle$ (▲) and $\langle P_4 \rangle$ (Δ) plotted against mole fraction of 5CB at a fixed temperature $T = 35°C$. The dotted vertical lines indicate the extent of the injected smectic phase.

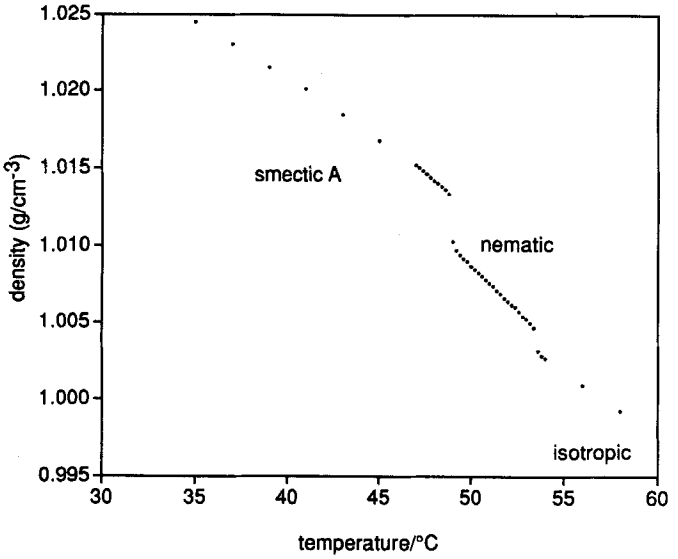


FIGURE 4 Density of 5CB/ME50.5 mixture ($x = 0.4$) as a function of temperature, indicating a strong first order smectic A-nematic transition at $T_{SN} = 48.2°C$ and an almost second order nematic-isotropic transition at $T_{NI} = 53.4°C$.

TABLE I

Smectic layer thickness (d/Å) or apparent molecular length (l/Å) in the nematic phase for mixtures of 5CB (mole fraction x) and ME50.5; measurements in the nematic phase are in bold

x =	.205	.268	.384	.447	.543	.596	.644	.681	.81	.928
temp/°C										
20.5					21.2					
21			21.35							
21.5				21.34						
23.5		21.78								
25							20.98			
26.5		21.78								
29			21.29		21.2	20.98				**24.87**
29.5				21.19			20.98		**22.9**	
30		21.78			21.2	20.98		**21.51**		
31.5	22.03									
35	22.03	21.78	21.35	21.19	21.08		**21.08**			
35.5								**21.51**		
36						20.84			**23.07**	**25.01**
38.5	22.03									
39			21.35	21.2						
40		21.78			21.08		**21.19**	**21.6**	**23.23**	
40.5			21.35			**21.08**				
42			21.32							
43.5		21.78								
44				21.19						
44.5					**21.2**					
45	**22.03**						**21.32**			
46.5								**21.83**		
47		**21.78**								
48				**21.29**		**21.2**				
49.5			**21.32**		**21.2**					
50		**21.72**								
50.5	**22.15**									
51.5				**20.92**						
53		**21.72**								
53.5			**21.32**							

are given in the table. It is seen that the layer thicknesses in the smectic phases for all the mixtures are almost temperature independent. However, the apparent molecular lengths in the nematic phase increase with increasing temperature. In Figure 5 we have plotted the variation of layer spacing or apparent molecular lengths with mole fraction of 5CB at $T = 30\,°C$. The layer spacing shows a minimum at about equimolar concentration. Assuming the formation of two types of dimers in a mixture of 5CB (A molecules) and ME50.5 (B molecules), namely AA and AB dimers, we have tried to calculate layer spacing or apparent molecular length for different concentrations. We have already shown in our previous publication[10] on a related mixture that there is no experimental evidence of BB type dimer formation. Hence in this case we will also have A, B, AA and AB type of molecules in equilibrium. The mole fractions of different species, x_A, x_B, x_{AA} and x_{AB} are determined from the equilibrium constants K_A and K_{AB} for the associations:

$$A + A \rightleftharpoons AA \text{ and } A + B \rightleftharpoons AB \text{ respectively.}$$

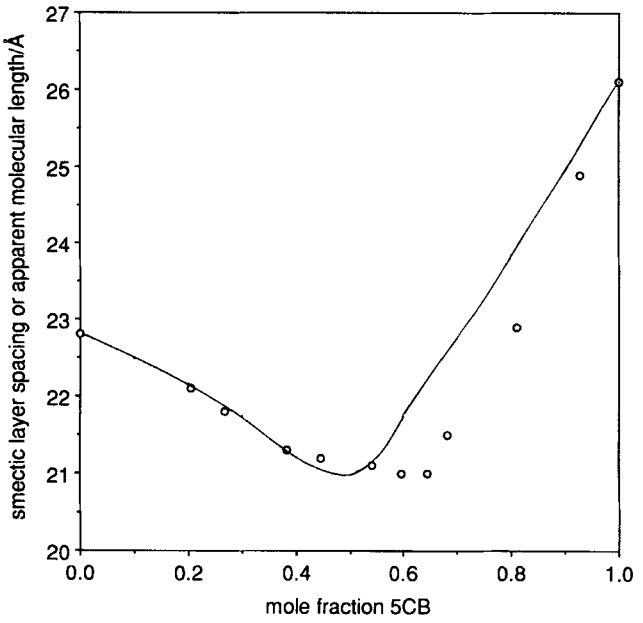


FIGURE 5 Variation of layer spacing (d) or apparent molecular length (l) at T = 30°C with mole fraction of 5CB. O = experimental data, full line is from theoretical calculations.

The mean layer thickness d of the smectic phase may be written as

$$d = x_A d_A + x_{AA} d_{AA} + x_{AB} d_{AB} \tag{2}$$

where d_A and d_B are taken to be equal to the lengths of the molecules, i.e., 18.1 $A°$ and 22.8$A°$ respectively. The quantity d_{AB} is taken as arithmetic mean of d_A and d_B, i.e., 20.5 $A°$, while d_{AA} has been adjusted so that in pure 5CB, which has both A and AA molecules, the apparent molecular length ($= x_A d_A + x_{AA} d_{AA}$) equals the experimental value 26.1$A°$. We have calculated values of d or l (Eq. 2) using the equilibrium constants $K_A = 1000$, $K_{AB} = 900$ as shown in Figure 5. The agreement is fair in this case also, however, the values of K_A and K_{AB} can be varied rather widely without much change in the values of d. This explains the invariance of layer thickness of any particular mixture with temperature.

Regarding the behaviour of ΔS_{SN} in the 5CB/ME50.5 mixture, we have calculated ΔS_{SN} from McMillian's theory, taking the values of δ, α, η, τ and σ, 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. ΔS_{SN} ($S_N - S_S$) is calculated from the following well known expressions [13].

$$S_S = -\frac{Nk}{T^*}(\eta_S^2 + \alpha\delta\tau_S^2 + \alpha\sigma_s^2) + Nkln\, Z_S, \tag{3}$$

$$S_N = -\frac{Nk}{T^*}\eta_N^2 + Nkln\, Z_N, \tag{4}$$

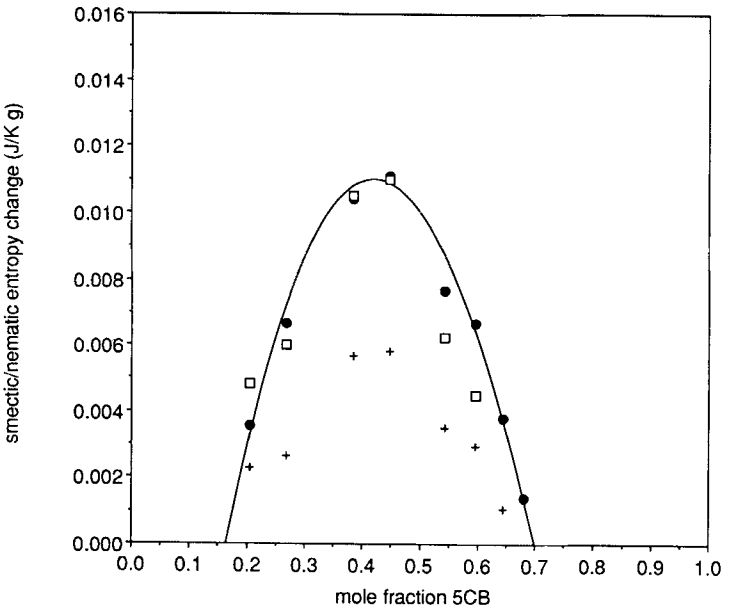


FIGURE 6 Entropy change associated with smectic to nematic phase transition of mixture 5CB/ME50.5 with mole fraction; + = calculated values of ΔS_{SN} from McMillan's theory with δ obtained from X-ray fitting: ● = calculated values using a fixed $\delta = 0.65$ (see text); □ = experimental values (ref. 4).

where $T^* = kT/v$. S_S, the entropy in the smectic phase, is calculated at a temperature just below the smectic-nematic transition temperature, while S_N, entropy in the nematic phase, is calculated at a temperature just above the transition temperature. Figure 6 shows both theoretical and experimental values for the entropy change.[4] It is clear that the behaviour of ΔS_{SN} in the region of the injected smectic phase is reproduced by the theory, but the calculations of the entropy change at the smectic to nematic transition depend critically on the value chosen for the parameter δ, which is a measure of the purely translational contribution to the pair potential. In fitting X-ray intensities to the McMillan model, it is difficult to vary α and δ independently, and the results obtained for δ in the region of the maximum in T_{SN} are close to unity. These values contrast with $\delta \sim 0.7$ obtained from the better defined X-ray pictures for mixtures outside the region of the maximum in the phase diagram. It is unlikely that the intermolecular pair potential will change with composition, and the values of $\delta \sim 0.7$ are much more in accord with the value assumed by Lee of $\delta = 0.65$. Recalculating ΔS_{SN} with this value gives the full line in Figure 7, which is very close to our experimental results.

CONCLUSIONS

New measurements of the X-ray diffraction from mixtures of a polar and non-polar mesogen which exhibit an injected smectic A phase have shown that there is a minimum in the orientational order parameter corresponding to a maximum in the stability of the

S_A phase. This surprising result explains a previously reported minimum in the birefringence and dielectric anisotropy for such mixtures. Further analysis of the X-ray data has revealed a minimum in the smectic layer spacing in the same composition range. As a result of this work we now have a clearer picture of the molecular organisation in mixtures of polar and non-polar mesogens. The minimum in the layer spacing can be attributed to specific interactions between the components of the mixture, which stabilise the translationally ordered phase, but with a lower orientational order parameter as determined by optical, dielectric and X-ray methods. This result is consistent with the reported behaviour in translationally-ordered mesophases of hard particles,[15] in which translational ordering in layers can increase the orientational free volume for the particles. The apparent anomalous increase in the transitional entropy for the injected smectic A phase is consistent with the predictions of mean field theory. As the extent of the nematic range above the smectic A phase decreases, the entropy change at the smectic to nematic transition increases, and the nematic to isotropic transition becomes more like a second order transition. Studies of pretransitional phenomena in the isotropic phase could provide further evidence for this.

Acknowledgements

The authors are grateful to E Merck (formerly BDH, U. K.) for gift of the chemicals used in this work. One of the authors (MKD) thanks the University Grants Commission, New Delhi for award of Research Fellowship and another author (RP) gratefully acknowledges financial support from Department of Chemistry, University of Sheffield for his stay in U. K. during which this paper was written. The assistance of Jo McCahy and Robert Hanson in making the density measurements is gratefully acknowledged.

References

1. J. S. Dave, P. R. Patel and K. L. Vasant, *Mol. Cryst Liq. Cryst.*, **8**, 93 (1969).
2. B. Engelen and F. Schneider, *Z Naturforsch.*, **33a**, 1077 (1978).
3. C. S. Oh, *Mol. Cryst. Liq. Cryst.*, **42**, 1 (1977).
4. D.A Dunmur, R. G. Walker and P. Palffy-Muhoray, *Mol. Cryst. Liq Cryst.*, **122**, 321 (1985)
5. M. Bradshaw and E. P. Raynes, *Mol. Cryst. Liq. Cryst.*, **91**, 145 (1983).
6. P. Palffy-Muhoray, D. A. Dunmur, W. H. Miller and D. A. Balzarini, *Liquid Crystals and Ordered Fluids*, **vol 4**, Ed. A. C. Griffin and J. F. Johonson Plenum, N. Y., p. 615 (1984).
7. B. Jha and R. Paul, *Proc. Nucl. Phys. & Solid State Phys Symp.*, (India), **19C**, 491 (1976).
8. B. Bhattacharjee, S. Paul and R. Paul, *Mol. Phys.*, **44**, 1391 (1981).
9. W. L. McMillan, *Phys. Rev.*,**A6**, 936, (1972).
10. M. K. Das and R. Paul, *Phase Transitions*, (1994), accepted for publication
11. W. Maier and A. Saupe, *Z. Naturforsch*,**15a**, 287 (1960).
12. P. E Cladis, *Mol. Cryst. Liq. Cryst.*, **67**, 177 (1981).
13. P. J. Wojtowicz, Introduction to Liquid Crystals, Eds. Eds. E. B. Priestely, P. J. Wojtwicz and P Sheng, (Plenum Press, New York, 1947) p. 95.
14. F. T. Lee, H. T. Tan, Yu Ming Shih & Chia-Wei Woo, *Phys. Rev Lett.*, **31**, 1117 (1973)
15. T. Koda, H. Kimura and M. Doi, *J. Phys. Soc. Jpn.*, **62**, 170 (1993)
16. K. Praefcke, D. Singer and B. Kohne, *Liq. Cryst.*, **13**, 445 (1993).
17. A. J. Leadbetter and P. G. Wrighton, *J. de Phys., Paris*, **C40**, 234 (1979).