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

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To cite this article: M. K. Das & R. Paul (1997): Analysis of X-Ray Diffraction Intensities of a Mesogenic Mixture Exhibiting Induced Smectic Phase, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 299:1, 477-482

To link to this article: http://dx.doi.org/10.1080/10587259708042030

Mol. Cryst. Liq. Cryst., 1997, Vol. 299, pp. 477–482
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ANALYSIS OF X-RAY DIFFRACTION INTENSITIES OF A MESOGENIC MIXTURE EXHIBITING INDUCED SMECTIC PHASE.

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Abstract We have analysed x-ray diffraction data of binary mixtures of a terminal polar (A) and a terminal non-polar (B) mesogens to calculate the average lateral distance (D) between the molecules. The variation of D with molar concentration in the smectic phase shows a definite maximum near equimolar concentration. Using a simple model, density of mixtures in the smectic phase have been calculated. The agreement with experimental values seems to be quite good.

INTRODUCTION

In our earlier papers[1,2], we have reported the phase diagram and some physical properties of a binary mixture of 4-n-pentyl phenyl-4′-cyanobiphenyl(5CB) and 4-n-pentyl phenyl 4-n′hexyloxy benzoate(ME 60.5), which shows the presence of an injected or induced smectic phase, by small angle x-ray diffraction, density and refractive indices measurements. Orientational order parameters have been measured from both x-ray diffraction and optical measurements and have been compared with a mean field theory of the smectic phase.

In the smectic phase birefringence, orientational order parameters, layer thickness, density and packing fraction all exhibit minimum at about 50% molar concentration of 5CB. We have successfully explained layer spacing minimum by considering the formation of both homo dimers and hetero-dimers in a previous paper[2].

Since both layer thickness and density follow the same trend i.e. minimum near equimolar concentration, it is of great interest to know how the molecules are arranged in the lateral direction i.e. perpendicular to their long molecular axis. In the present paper we have analysed our x-ray diffraction data to calculate the average lateral distance between the molecules. We have also calculated densities for different compositions using a very simple model.

RESULTS AND DISCUSSIONS

Experimental procedure has been given in our earlier publication[2]. Average lateral intermolecular distance D between the molecules can be obtained from the diffracting angle of the outer ring of x-ray pattern by the formula[3]

$$2D \sin\theta = 1.117\lambda \qquad (1)$$

Figure 1 shows the variation of D with mole fraction of 5CB at 35°C. From the figure it is clear that the experimental D values, within the smectic phase show an enhancement in their magnitudes near equimolar concentration whereas both density and layer thickness show a reverse trend i.e. minimum near equimolar concentration. This implies that the packing of the molecules in the smectic layer is poor for equimolar mixture. This variation of D with molar concentration clearly explains why the density of mesogen decreases even when layer thickness is also decreasing near equimolar concentration.

In an attempt to calculate density of a mixture in the smectic phase we have assumed molecules in the mesophase have cylindrical shape and are arranged in a tetragonal lattice with the length of the molecule (l) as the longest axis and intermolecular distance (D) between the molecules as the other two axes, using the expression,

$$\text{density } (\rho) = \frac{M}{N_A l D^2} \qquad (1),$$

where N_A is the Avogadro's number, M be the molecular weight.

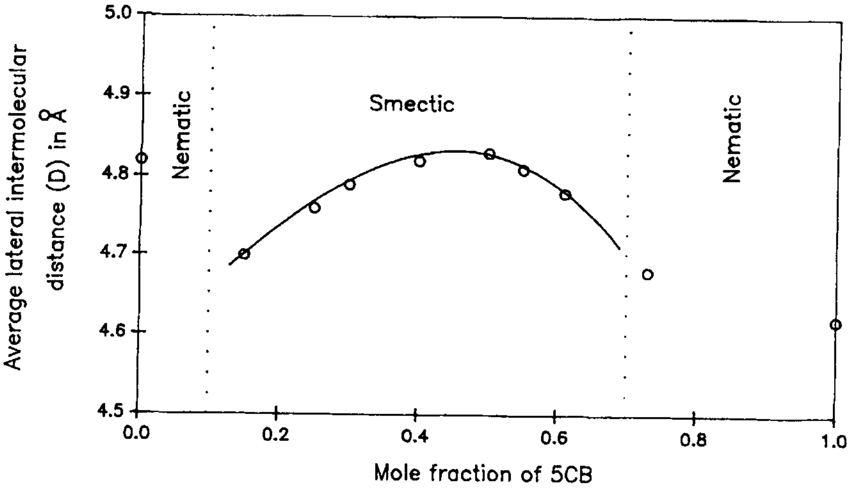

FIGURE 1 Variation of lateral intermolecular distances (D) between the molecules with mole fraction of 5CB.

From our earlier studies[2,4-5] we know that in any mixture of this binary system, there exist 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} can be calculated from the equilibrium of the following reaction $A + A \rightleftharpoons AA$ and $A + B \rightleftharpoons AB$, where K_A and K_{AB} are the respective equilibrium constants.

The mean layer thickness d in the smectic phase can be obtained as[4]

$$d = x_A d_A + x_B d_B + x_{AA} d_{AA} + x_{AB} d_{AB} \qquad (1)$$

In our case d_A = 18.1Å, d_B=24.5Å are the lengths of the molecule A and B, which have been obtained from model molecular length and x-ray diffraction data respectively. d_{AB} is the mean of d_A and d_B and d_{AA} can be calculated so that $x_A d_A + x_{AA} d_{AA}$ is equal to 26.1Å which is the value of apparent molecular length in the pure 5CB as determined from x-ray diffraction.

The best fitted layer thickness values can be obtained using $K_A=1000$ and $K_{AB}=900$.

The percentage of different species A, B, AB and AA as a function of mole fraction of 5CB are shown in figure 2.

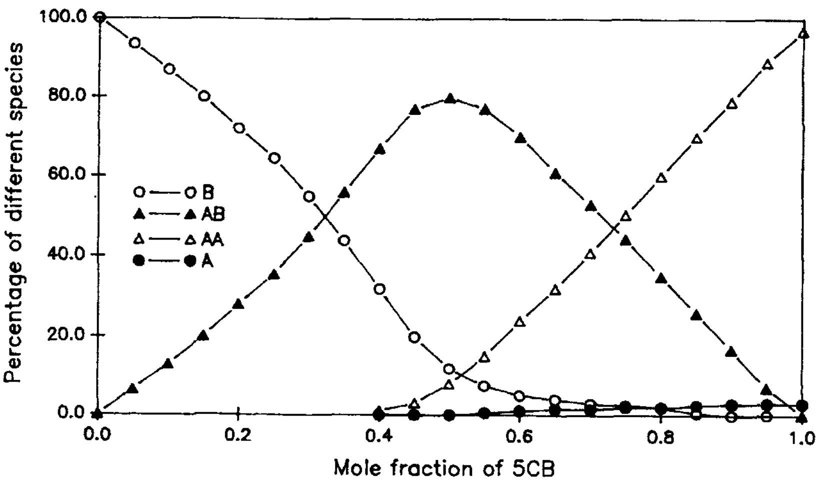

FIGURE 2 Percentage of different species A, B, AB and AA as a function of mole fraction of 5CB.

In order to calculate density values of a mixture we first calculate density values due to different components of this mixture using equation (1). We are only interested in the region where injected smectic phase exists. In this concentration range i.e., where the mole fraction of 5CB is between 0.1 and 0.7, monomer of 5CB (A molecule) is practically absent, as can be seen from figure 2. Thus we need only density values due to B monomers, AA homo-dimers and AB hetero-dimers to calculate that of the mixture.

Since ME60.5 molecules in the mesophase of pure ME60.5 are monomers, we can calculate density of B molecule (ρ_B) using equation (1), taking l as the experimentally observed molecular length and D as the experimentally observed average lateral intermolecular distance in the pure compound. The molecules of 5CB have an aliphatic chain at one end of biphenyl core, the cyano group being at the other end. The apparent molecular length as observed from x-ray diffraction studies, is significantly larger than the molecular length i.e. apparent molecular length being 26.1Å and the molecular length estimated from model being 18.1Å. This large value of apparent molecular length can be understood if one assumes that the nematic phase is made of pair of two associated molecules, the length of which is equal to one core length plus two chain length . However the density of the nematic phase is similar to that of other nematic compounds and therefore the molecular pairs are staked in a compact manner. In 5CB molecule the chain length is nearly half of the core length. Hence we can assume that in forming a pair of two associated molecules, the available void spaces will be occupied by cores or chains coming from adjacent molecules. If we consider this type of molecular arrangement we can simply calculate density of 5CB (ρ_{AA}) assuming l and D as the actual molecular length and experimental average intermolecular distance respectively. Our calculated value for 5CB differs from experimental values by about 4%. In order to calculate density of hetero dimers (AB) we first look at figure 1. In this figure we see that for mixture with x=0.5, about 80% of the molecules are forming AB dimer.The averageintermolecular distance is maximum (4.81Å). To calculate ρ_{AB} we first calculate density values due to molecule A (ρ_A') having l and D values 18.1Å and 4.81Å respectively and molecule B (ρ_B') having l and D values 24.5Å and 4.81Å respectively. Then we assume that ρ_{AB} is mean of ρ_A' and ρ_B', i.e., $\rho_{AB} = 0.5\rho_A' + 0.5\,\rho_B'$.

Finally, the effective density value for a mixture is assumed to be the weighted average of the components, viz,

$$\rho = x_A\rho_A + x_B\rho_B + x_{AB}\rho_{AB} \qquad (2)$$

Figure 3 shows the variation of calculated density values, using equation (2), along with the experimental values. It is apparent that our calculated density values also follow a definite minimum at about equimolar concentration. Considering the crudeness of the model, the agreement with experimental values seems to be quite good.

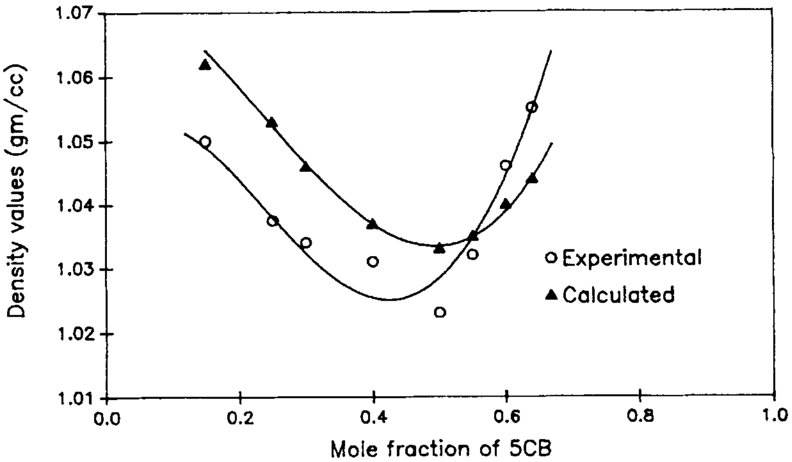

FIGURE 3 Calculated and experimental density values with mole fraction of 5CB.

ACKNOWLEDGEMENT

The authors are grateful to E. Merck, U.K. for the gift of the chemicals used in this work.

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