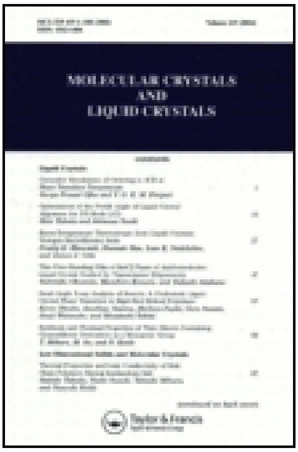

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Phase Behawour and Birefringence Studies of a Liquid Crystal Binary Mixture

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To cite this article: M. Mitra, S. Sinha Roy, T. Pal Majumder & S. K. Roy (1997): Phase Behawour and Birefringence Studies of a Liquid Crystal Binary Mixture, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 301:1, 363-369

To link to this article: http://dx.doi.org/10.1080/10587259708041789

Mol. Cryst. Liq. Cryst., 1997, Vol. 301, pp. 363–369
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PHASE BEHAVIOUR AND BIREFRINGENCE STUDIES OF A LIQUID CRYSTAL BINARY MIXTURE

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Abstract The phase diagram of binary system of 4-n-pentyl 4′-cyanobiphenyl (5CB) and 4 -pentyl phenyl trans-4 pentyl cyclohexane carboxylate (D55) is presented, which shows the presence of an injected smectic-A phase and a higher order smectic phase (SmG). Refractive indices (n_o,n_e) and densities for different compositions of this mixture and for one pure compound (D55) are measured. The orientational order parameters $<P_2>$ are determined from the polarizability values (α_o,α_e) which are calculated using both Vuks' as well as Neugebauer's internal field models. The experimental order parameter values for the samples having smectic A phase have been compared with McMillan's theory and with Maier-Saupe theory for the nematic cases.

INTRODUCTION

The importance of understanding the behavior of the mixtures is to produce better materials for applications. One of the unusual aspects of liquid crystal binary mixtures of strongly dipolar and weakly dipolar mesogens is the formation of injected smectic phases, from the components which do not possess smectic properties.[1-4] The existence of injected smectic phases at a lower temperature may help the device technology.[5] Here we have studied the phase behavior of the binary mixtures of 4-n-pentyl 4′-cyanobiphenyl (5CB) and 4-pentyl phenyl trans-4-pentyl cyclohexyl carboxylate (D55). Densities and refractive indices (n_o,n_e) are measured for the mixtures and for the second compound in its pure state. Density[6] and refractive index[7] measurements for the first compound have already been reported. The experimental data have been analyzed to obtain the orientational order parameter <P2>. Here we have used both Vuks' and Neugebauer's internal field models to calculate the polarizabilities (α_o,α_e). Finally we have tried to compare our experimental $<P_2>$ values with McMillan's theory[8] for the mixtures having smectic A phase, and with Maier-Saupe (MS) theory[9] for the nematic phase.

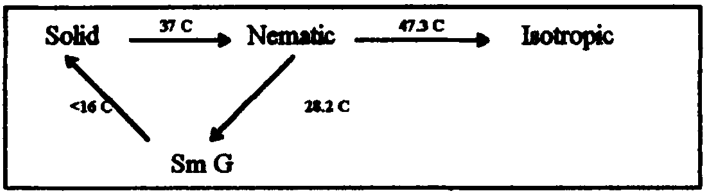
EXPERIMENTAL

Texture Study

The phase transitions of the pure samples as well as their mixtures were studied by observing the textures under crossed polarizers with a polarizing microscope (Leitz Polarizing Microscope) equipped with a hot stage (Mettler FP52). According to the literature[10] the compound 4-pentyl phenyl trans-4-pentyl cyclohexyl carboxylate (D55) possesses nematic phase only in its mesophase. The phase sequence as obtained from the literature are given below :

Solid (37^{0}C) Nematic (47^{0}C) Isotropic

According to our texture studies we have found that during heating from the solid phase it exhibits only nematic phase in the mesophase, but during cooling from the isotropic state it shows a higher order smectic phase (smectic G phase, mosaic texture) in addition to the nematic phase. X-ray diffraction studies[11] also support the presence of the smectic G phase in this compound. The transition temperatures as obtained by us for this compound are as follows :



This higher order smectic phase exists in the binary mixtures of the two compounds upto mole fraction of 5CB less than 0.07. In addition to the smectic G phase, the mixtures having mole fraction (x) of 5CB, 0.07<x<0.54, show the presence of induced smectic A phase (focal conic fan texture).

<u>Optical Studies</u>

Refractive indices (n_o,n_e) were measured using the thin prism method. The experimental details of this procedure have been given by Mitra et al.[12] We have measured the refractive indices (n_o,n_e) within ± 0.001 for wavelength λ = 5780 Å. The experimental uncertainty of measuring density values is 0.1%. We have used the Vuks' isotropic internal field model[13] and Neugebauer's anisotropic internal field model[14] to calculate the polarizabilities (α_o,α_e).

The relation[15] we used to calculate the orientational order parameter $\langle P_2 \rangle$ is as follow

$$\langle P_2 \rangle = (\alpha_e - \alpha_o)/(\alpha_\parallel - \alpha_\perp) \tag{1}$$

where $\alpha_\parallel$ and $\alpha_\perp$ are the molecular polarizabilities parallel and perpendicular to the molecular long axes respectively.

RESULTS AND DISCUSSION

Figure 1 shows the phase diagram of this binary system. There is a sharp biphasic region associated with the nematic/isotropic transition, but there exists a narrow region for the two-phase coexistence for the smectic/nematic transition. From the density (ρ) and refractive index data of the different mixtures as well as pure compounds we have calcu-

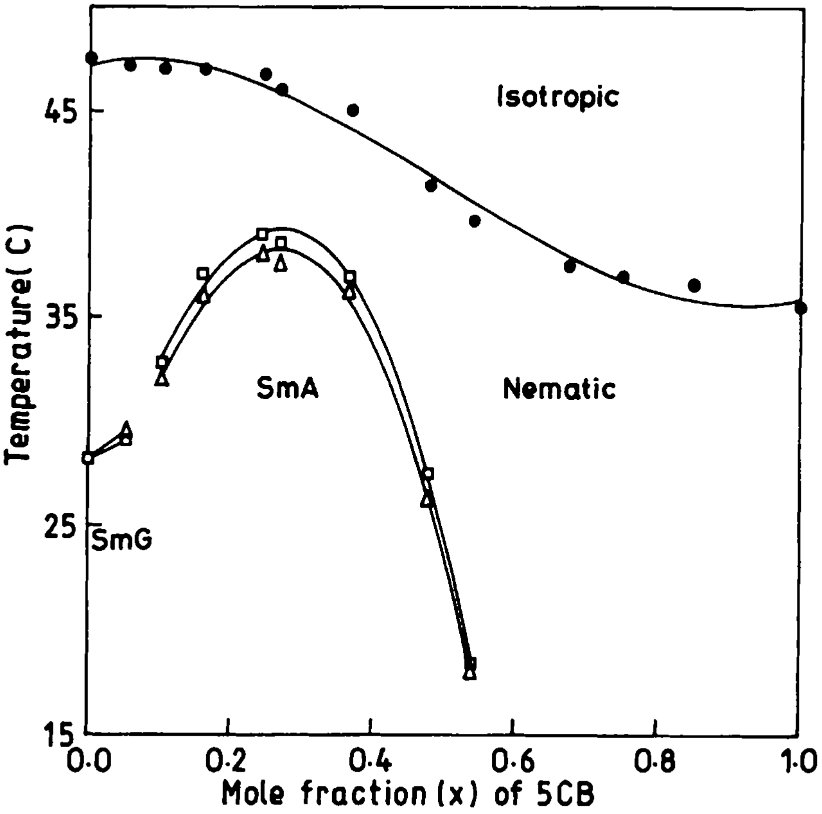


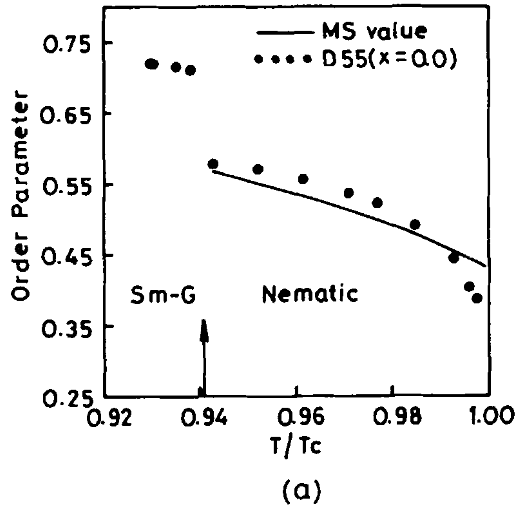
FIGURE 1 Phase diagram of 5CB/D55 as a function of mole fraction (x) of 5CB.

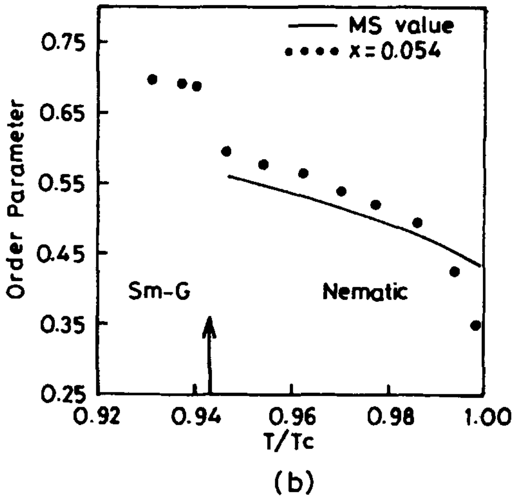
lated the polarizability values (α_e,α_o) following both Vuks' and Neugebauer's approximations. The order parameter $\langle P_2 \rangle$ has been calculated by using Equation (1). We could not calculate directly the values of $\alpha_\parallel$ and $\alpha_\perp$ since solid phase data were not available and we adopted the well-known Haller's extrapolation procedure for this purpose.[16] We have found that both Vuks' and Neugebauer's models give different absolute values of polarizabilities but the variation of order parameter with temperature is in reasonable agreement with both the models. Figures 2(a)-2(f) are given to show the variation of order parameter $\langle P_2 \rangle$ with reduced temperature (T/T_c), T_c being the nematic/isotropic transition temperature.

We have fitted our experimental order parameters for the mixtures having smectic A phase to McMillan's theory.[8] According to McMillan the mean field potential for the smectic A phase is of the form,

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

where d is the layer spacing along the z-direction; θ is the angle made by the molecular long axis with the director, assumed to be in the z-direction; δ and α are two constants which depend on the characteristics of the molecules. $\eta = \langle P_2(\cos\theta) \rangle$ is the orientational





FIGURES 2(a)-2(f) Temperature dependence of $<P_2>$ for 5CB/D55 mixtures at different compositions, x = mole fraction of 5CB, δ and α, are McMillan potential parameters. Dashed line → McMillan $<P_2>$ values; Solid line → Maier-Saupe $<P_2>$ values.

order parameter, $\tau = <\cos(2\pi z/d)>$ is the translational order parameter and $\sigma = <P_2(\cos\theta)\cos(2\pi z/d)>$ is the mixed order parameter describing the correlation on the coupling between the orientational and translational orders. We have obtained the parameter v from the nematic/isotropic transition temperature, assuming the simple mean field result, $kT_c/v = 0.22019$.

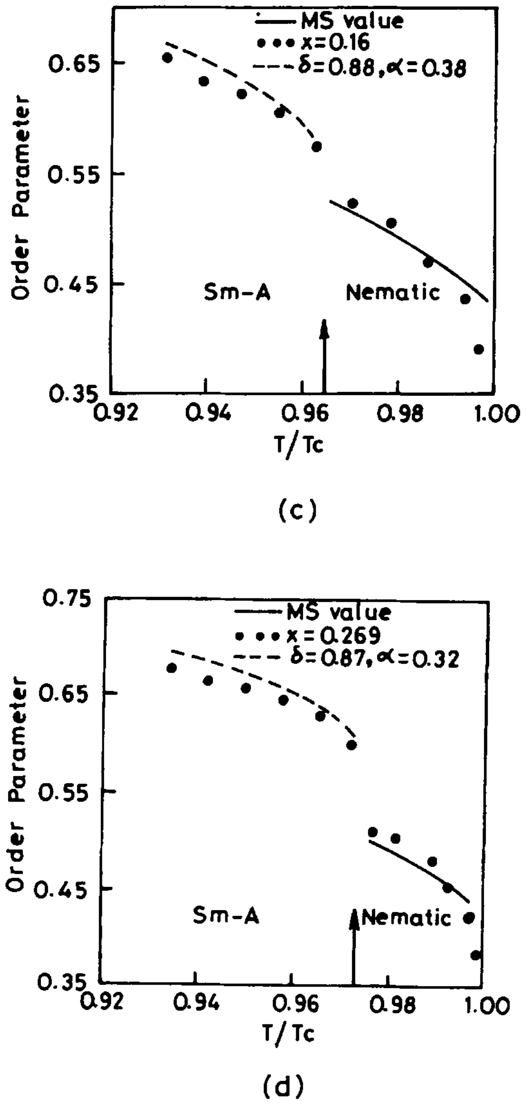
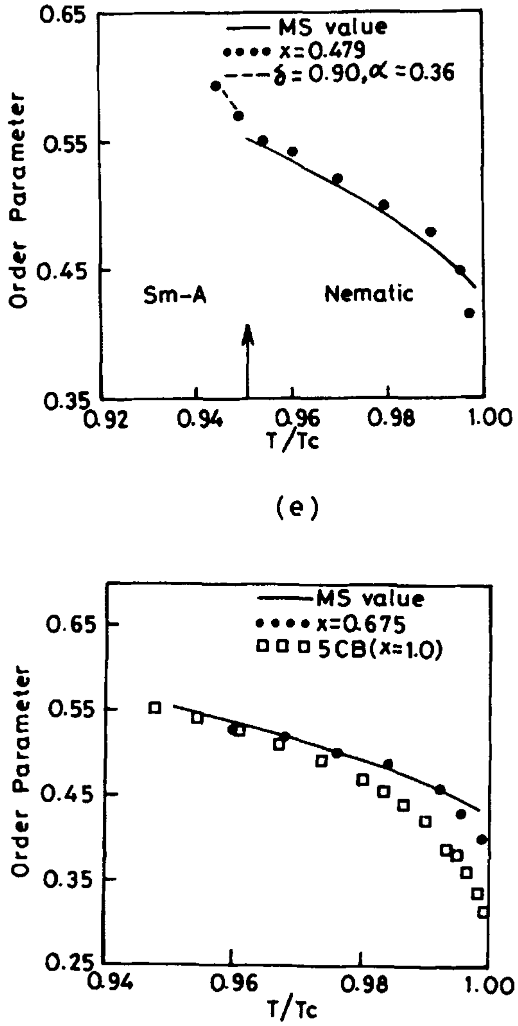


FIGURE 2 (Continued.)

Using the single molecule potential function in the mean field approximation, the single molecule distribution function has been obtained. The potential, V_M, contains the undetermined order parameters η, τ and σ. The three sets of self-consistent equations will give the expected values of η, τ and ρ. In this paper we have replaced the symbol η by the more commonly used $\langle P_2 \rangle$. The theoretical values of order parameters are shown in the respective figures. The values of δ and α which produce the best agreement with the experimental results are also given in each figure. Dunmur et al.[4] have observed an



(e)

(f)

FIGURE 2 (Continued.)

increase in the entropy change at the smectic/nematic transition for another system of binary mixtures having injected smectic A phase. From their measurements on transition enthalpies, refractive indices and electric permitivities of their system they have seen that the entropy reaches maximum in the binary composition where the stability of the smectic A phase is maximum. At the same time they have found a minimum in the birefringence and dielectric anisotropy of such mixtures, which corresponds to the maximum entropy change or maximum stability of the smectic A phase. X-ray studies by Das et al.[17] on this binary system have also confirmed that the orientational order parameter becomes minimum in that composition of the mixture, where the smectic A phase is most stable. Our experimental results on density, refractive indices on our binary system also support the above mentioned findings for the injected smectic A phase.

For the nematic phase we have compared our experimental $<P_2>$ values with Maier-Saupe[9] mean field theory. The temperature dependence of the order parameter of pure 5CB has already been reported.[18] Here we have taken the reported values of $<P_2>$ for 5CB. The agreement of our experimental data with Maier-Saupe theory is quite satisfactory for the nematic phase in the mixtures except near the clearing temperature where the experimental $<P_2>$ values are quite low in comparison with the theoretical values. But for the pure 5CB compound the agreement between theory and experiment is poor. As we go on decreasing the amount of 5CB in the mixtures, the experimental $<P_2>$ values are closer to the Maier-Saupe mean field theory.

Acknowledgments

We are very much thankful to E. Merck for providing us free samples used in this work. We also record our sincere thank to Professor Ranjit Paul, North Bengal University for his kind permission to use some of his instruments.

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