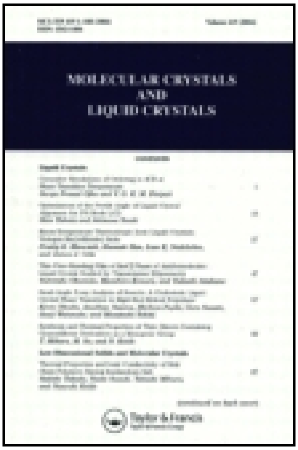

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Phase Diagram, Density and Optical Studies on Binary Mixture of a Cyanobiphenyl (11OCB) and a Benzoate Ester (ME6.O5) Showing Enhanced Smectic Phase

Prithwi Dev Roy [a], Malay Kumar Das [a] & Ranjit Paul [a]
[a] Department of Physics, North Bengal University, Siliguri, 734430, India

Version of record first published: 27 Oct 2006

To cite this article: Prithwi Dev Roy, Malay Kumar Das & Ranjit Paul (2001): Phase Diagram, Density and Optical Studies on Binary Mixture of a Cyanobiphenyl (11OCB) and a Benzoate Ester (ME6.O5) Showing Enhanced Smectic Phase, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 365:1, 607-615

To link to this article: http://dx.doi.org/10.1080/10587250108025340

Mol. Cryst. and Liq. Cryst., 2001, Vol. 365, pp. 607-615
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint,
a member of the Taylor & Francis Group.
Printed in the USA

Phase Diagram, Density and Optical Studies on Binary Mixture of a Cyanobiphenyl (11OCB) and a Benzoate Ester (ME6.O5) Showing Enhanced Smectic Phase

PRITHWI DEV ROY, MALAY KUMAR DAS and RANJIT PAUL

Department of Physics, North Bengal University, Siliguri-734430, India

Binary mixture of undecyloxy cyanobiphenyl (11OCB) and 4-n-pentyl phenyl-4-n′-hexyloxy benzoate (ME6.O5) shows enhanced smectic A phase, where 11OCB has smectic A and ME 6.O5 has nematic phases. We report here the phase diagram, refractive indices, densities and orientational order parameters of different binary mixtures of 11OCB + ME6.O5 throughout the entire composition range. At a reduced temperature, density values increases with mole fraction (x) of 11OCB up to $x = 0.25$ and then decreases continuously having a minimum near $x = 0.8$. The birefringence and $\langle P_2 \rangle$ values follow the same trend showing a maximum near $x = 0.4$ and a minimum near $x = 0.8$.

INTRODUCTION

From the study of phase diagram in bicomponent and multicomponent systems, it has been found that liquid crystalline phases (nematic or smectic) existing in pure compounds enhance their own thermal stability [1,2]. The transition temperatures are increased compared to the corresponding temperatures in the pure state, hence enhancing the respective phases. Some times, it has been observed that although none of the pure compounds is smectic, yet the mixtures of these compounds often show so-called induced smectic phase[3-5]. In many cases smectic phases existing in pure compounds of binary mixtures decrease their smectic stability and new phases of lower order are created. This phases are called ‘phase created by depressing smectic stability’[6].

We have observed an enhanced smectic phase from the bicomponent mixtures of undecyloxy cyanobiphenyl (11OCB) and 4-n-hexyl phenyl-4-n′-pentyloxy benzoate (ME6.O5), where 11OCB and ME6.O5 show smectic A and nematic phases respectively. In the present paper we report the phase diagram, density, refractive indices of different binary mixtures of 11OCB + ME 6.O5 throughout the entire composition range. For better understanding of this system we have also presented the different physical parameters with molar concentration.

EXPERIMENTAL

The pure samples 11OCB and ME 6.O5 were donated by E. Merck, U.K. and were used without further purification. The phase diagram of this system is obtained by studying the transition temperatures and textures of different mixtures under crossed polarisers with a polarizing microscope equipped with a hot stage (Mettler FP 80/82). The refractive indices for λ= 5780 Å are measured within ± 0.001 with the thin prism method (refracting ∠ 2°). The densities of different mixtures at different temperatures are determined within ± 0.1%. The experimental details have been reported by Zeminder et.al[7].

RESULTS AND DISCUSSIONS

The phase diagram of the binary system 11OCB + ME 6.O5 are presented in figure 1. The pure compounds 11OCB and ME 6.O5 show smectic and nematic phases respectively. From the phase diagram, it has been found that the smectic phase of 11OCB strongly influences the phase behaviour of the system. For mixtures having $x > 0.15$ (x = mole fraction of 11OCB) the nematic phase is completely suppressed. For mixtures with $0.03 < x < 0.15$ both smectic A and nematic phases are found to be present. Only nematic phase is found for $x < 0.03$. A strong positive and a negative deviation from the linearity in the isotropic transition temperatures is obtained for mixtures with $x \approx 0.4$ and 0.8 respectively. In our earlier works[2] only positive deviation from the linearity has been observed. Melting temperature shows a minimum around $x \approx 0.4$, where the thermal stability of the smectic A phase is maximum. The mixtures super-cools by about 20°C in the mesomorphic phase before solidification and the solidification curve follow nearly the melting curve. The variation of refractive indices (n_o ,n_e) for $\lambda = 5780$ Å with temperature are shown in figure 2.

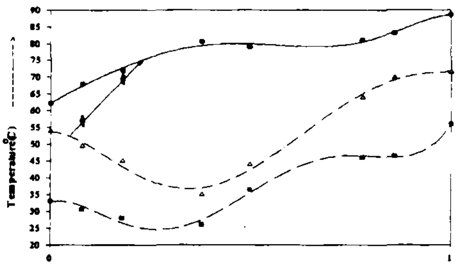

FIGURE 1 Temperature/concentration phase diagram for the binary system of undecyloxy cyanobiphenyl (11OCB) and 4-n-hexyl phenyl-4-n′-pentyloxy benzoate (ME6.O5). x is the mole fraction of 11OCB. • smectic or nematic to isotropic transition temperature; ♦ smectic to nematic transition temperature; Δ Melting temperature; ■ Super cooled liquid crystal to solid transition.

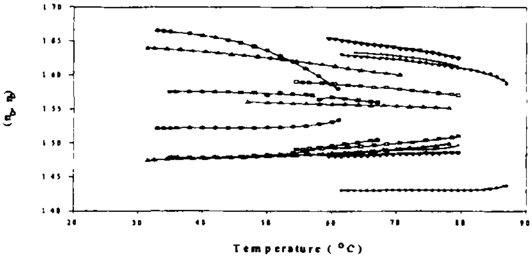

FIGURE 2 Refractive indices (n_o, n_e) as function of temperature for different mixtures and pure compounds. ● ME6.O5; ◆ 11OCB; ■ x=0.08; ▲ x=0.18; ▼ x=0.38; Δ x=0.5; + x=0.78; □ x=0.86.

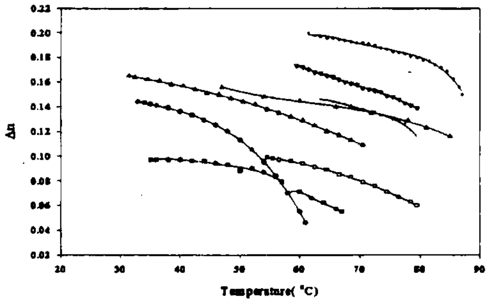

FIGURE 3 Birefringence ($\Delta n = n_e - n_o$) as a function of temperature for different mixtures and pure compounds. ● ME6.O5; + 11OCB; ■ x=0.08; ▲ x=0.18; ▼ x=0.38; △ x=0.5; ◆ x=0.78; □ x=0.86.

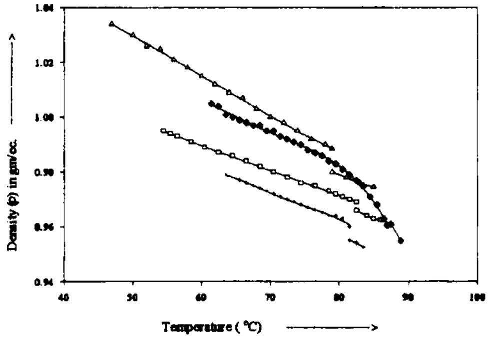

FIGURE 4a Temperature variation of density (ρ) for different mixtures., △ x=0.50; ✚ x=0.78; □ x0.86; ◆ x=1.0.

We have plotted optical birefringence ($\Delta n = n_e - n_o$) as a function of temperature in figure 3. The results of our density measurements are presented in figures 4a and 4b. Birefringence values of ME 6.O5

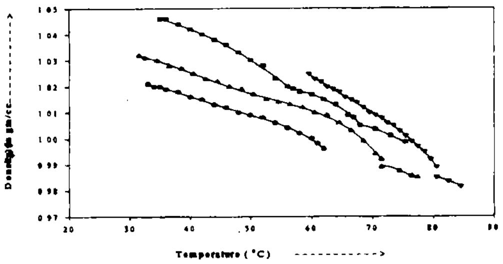

FIGURE 4b Temperature variation of density (ρ) for different mixtures. ● x=0.0(ME6.O5); ■ x=0.08; ▲ x=0.18; ▼ x=0.38.

are lower than those obtained from 11OCB. This is expected because it is well known that cyanobiphenyls have greater birefringence than ester mesogens. On the other hand density values of ME6.O5 are higher than those obtained from 11OCB. A discontinuity in the density as well as Δn values at the smectic A to nematic phase transition is observed for mixtures having x = 0.08, indicating a first order smectic A to nematic phase transition. At a temperature 5° C below the isotropic transition temperature the density values increases slowly with mole fraction of 11OCB up to x = 0.25 and then decreases continuously having a broad minimum near $x \approx 0.8$. On the other hand birefringence values increases up to $x \approx 0.4$ and then continuously decreases creating a minimum near x= 0.8 (Figure 5). It is to be noted that while density values of 11OCB are lower than the values obtained from ME6.O5, the birefringence values are somewhat higher.

In figure 6 we have also plotted thermal expansivity $\beta = d\rho/dT$ in the smectic A phase along with the relative change of density during smectic A (nematic) /isotropic phase transition. In both the cases the

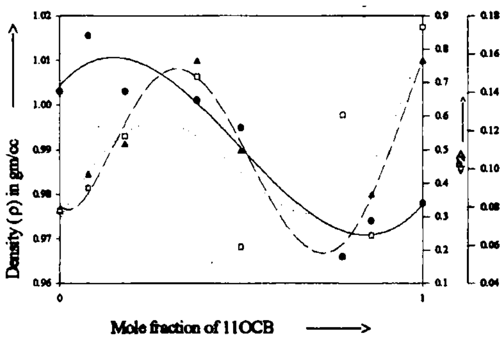

FIGURE 5 Density (ρ), <P$_2$> and Δn against mole fraction of 11OCB at T=T$_{SI}$(T$_{NI}$) - 5 °C. ● ρ; ▲ <P$_2$>; ◻ Δn

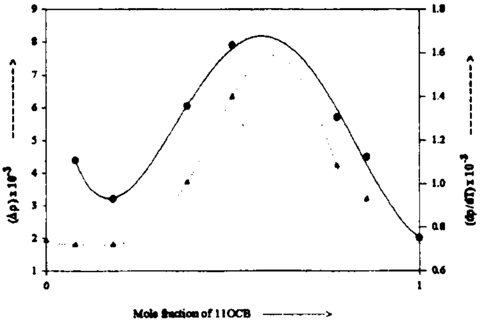

FIGURE 6 Change in density (Δρ) during smectic A or nematic to isotropic phase transition and (dρ/dT) in the smectic A phase with mole fraction of 11OCB. ● Δρ and ▲ dρ/dT

respective values increases gradually with increase of x having a maximum near equimolar concentration. Similar behaviour have also been observed in our earlier publication[2] .

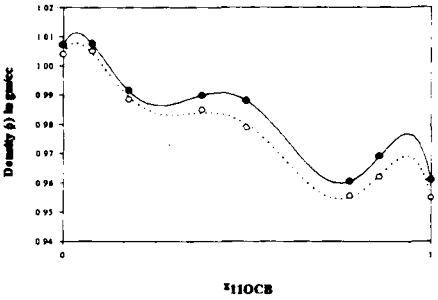

FIGURE 7. Density values (ρ) just below (•) and above (o) the clearing temperature with mole fraction of 11OCB (x).

In figure 7 we have plotted density values in the mesomorphic and isotropic phases just below and above the mesomorphic to isotropic phases transition against mole fraction. From this curve it has been found that for both the cases two minima are observed near $x \approx 0.3$ and $x \approx 0.8$, where enhancement and depression of clearing temperature has been observed.

The refractive index data can be used in conjunction with density data to determine the orientational order parameter. The order parameter and optical properties of the system is connected by the relation

$$<P_2>\Delta\alpha = (\alpha_e - \alpha_o)$$

where α_e and α_o are the effective polarizabilities for extraordinary and ordinary rays which are measured from refractive index values

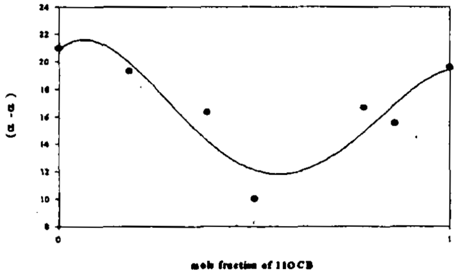

FIGURE 8 Variation of $(\alpha_{||} - \alpha_{\perp})$ against mole fraction of 11OCB.
● Neugebauer's method.

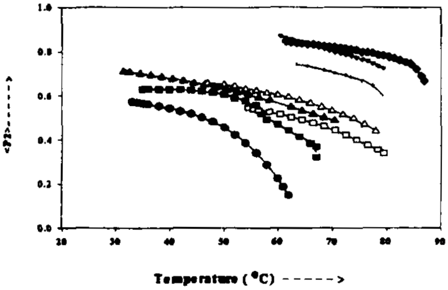

FIGURE 9 Temperature variation of order parameter $\langle P_2 \rangle$ for different mixtures and pure compounds ● ME6.O5 ; ◆ 11OCB; ■ x=0.08; ▲ x=0.18; ▼ x=0.38; △ x=0.5; + x=0.78; □ x=0.86.

using Neugebauer's method[8]. $\Delta\alpha = (\alpha_{||} - \alpha_{\perp})$ is the polarizability anisotropy, can be estimated by applying the well known Haller's extrapolation procedure[9]. In figure 8 we have plotted the polarizability anisotropy values for pure as well as different mixtures. Although polarizability anisotropy values obtained from Haller's procedure are some what scattered, we observe a minimum in $\Delta\alpha$ near equimolar concentration.

Figure 9 shows a plot of the variation of $<P_2>$ values with temperature for different mixtures and pure components. $<P_2>$ values of ME6.O5 are lower than those obtained from 11OCB. Our experimental order parameter values at the smectic A to nematic phase transition appears to be discontinuous for $x = 0.08$ implyiing a first order phase transition. Maximum $<P_2>$ values are obtained for mixtures with $x = 0.38$ where the stability of smectic phase is also maximum. Variation of $<P_2>$ with mole fraction (x) of 11OCB follow the same trend as observed from birefringence and density measurements [Figure 5].

Acknowledgements

We are grateful to M/S E. Merck, U.K. for kindly donating the liquid crystal samples used in this work. One of the authors (MKD) is thankful to the University Grants Commission , New Delhi for financial help.

References

[1] B. Engelen, H. Heppke, R. Hopf and F. Schneider, *Ann. Phys.* **3**,403 (1978).
[2] M. K. Das, B. Jha and R. Paul, *Mol. Cryst. Liq. Cryst.*, **261**, 95 (1995).
[3] M.K. Das and R. Paul, *Phase Transitions*, **46**, 185 (1994).
[4] M.K. Das and R. Paul, *Phase Transitions*, **48**, 255 (1995).
[5] D. A. Dunmur, R. G. Walker, P. Palffy Muhoray, *Mol. Cryst. Liq. Cryst.* **122**, 321 (1995).
[6] R. Dabrowski, B. Wazynska and B. Sasnnowska, Liq. Cryst., **1**,415 (1986).
[7] A. K. Zeminder, S. Paul and R. Paul, *Mol. Cryst. Liq. Cryst.* **61**,191, (1980).
[8] H.E.J. Neugabauer, Can. J. Phys., **32**,1 (1954).
[9] I. Haller, H.A. Huggins, H.R. Llilienthal, T.R. McGuire, *J. Phys. Chem.* **77**, 900 (1973).