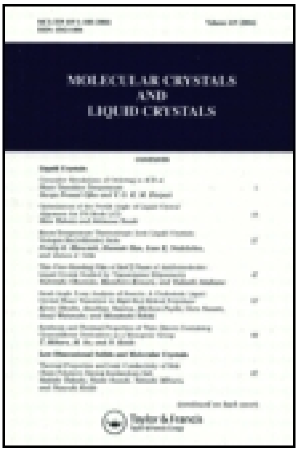
This article was downloaded by: [Moskow State Univ Bibliote]
On: 15 April 2012, At: 12:57
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Induced Smectic Phase in a Binary Mixture of Nematogens

Suchismita Datta Sarkar [a] [b], TH. Kiranmala Devi [b], Basana Choudhury [b] & Malay Kumar Das [c]

[a] Department of Physics, Karimganj College, Karimganj, Assam, India

[b] NIT Silchar, Silchar, India

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

Available online: 20 Mar 2012

To cite this article: Suchismita Datta Sarkar, TH. Kiranmala Devi, Basana Choudhury & Malay Kumar Das (2012): Induced Smectic Phase in a Binary Mixture of Nematogens, Molecular Crystals and Liquid Crystals, 557:1, 134-143

To link to this article: http://dx.doi.org/10.1080/15421406.2012.640565

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Mol. Cryst. Liq. Cryst., Vol. 557: pp. 134–143, 2012
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2012.640565

Downloaded by [Moskow State Univ Bibliote] at 12:57 15 April 2012

Induced Smectic Phase in a Binary Mixture of Nematogens

SUCHISMITA DATTA SARKAR,[1,2] TH. KIRANMALA DEVI,[2]
BASANA CHOUDHURY,[2,*] AND MALAY KUMAR DAS[3]

[1]Department of Physics, Karimganj College, Karimganj, Assam, India
[2]NIT Silchar, Silchar, India
[3]Department of Physics, North Bengal University, Siliguri, West Bengal, India

The phase diagram of binary system of nematogenic compounds 4-n-pentyl phenyl 4-n′-hexyloxy benzoate (ME6O.5) and 4-cyanophenyl 4-heptyl benzoate (CPHB) shows the presence of induced smectic phase. In the present paper, we report the results of DSC, refractive index, and density measurements of different binary mixtures of (ME6O.5 + CPHB) throughout the entire composition range. The density and refractive index values have been analyzed to obtain orientational order parameters. We have fitted the experimental order parameters with the theoretical values from McMillan's theory for mixtures having smectic phase, and Maier–Saupe theory for others having nematic phase only.

Keywords: Induced smectic phase; transition entropy; refractive indices; density; orientational order parameter

1. Introduction

It is well established that in binary mixtures of strongly polar compound with nonpolar compound-induced smectic phases normally appear [1–5]. Earlier studies also reflect the effect of polarity of the end group, core structure, overall length of the molecule, chain length of the polar component, etc., on the phase-induction phenomenon [6–10]. Our aim in this study is to present the optical and thermal characterization of a new binary system (ME6O.5+CPHB) exhibiting induced smectic phase through the entire concentration range.

2. Experimental

The compounds ME6O.5 and CPHB were purchased from AWAT Co. Ltd., Warsaw, Poland, and were used without further purification. The structural formulas and transition temperatures of the pure compounds are shown in Figs. 1 and 2.

Eight mixtures of (ME6O.5+CPHB) with mole-fractions of CPHB equal to 0.18, 0.22, 0.26, 0.32, 0.50, 0.54, 0.59, and 0.76 were prepared.

---

[*] Address correspondence to Basana Choudhury, NIT Silchar, Silchar-788010, India. E-mail: basana_
choudhury@rediffmail.com

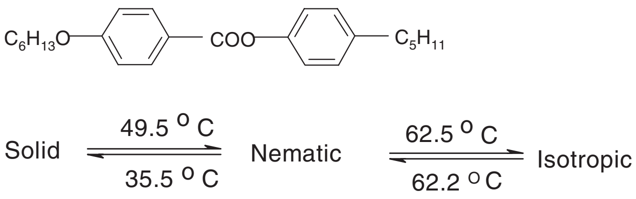


Figure 1. Component 1: 4-n-pentyl phenyl 4-n′-hexyloxy benzoate (ME6O.5).

Differential scanning calorimetric (DSC) studies (at a heating / cooling rate of 1°C/min) was done by using Perkin Elmer Diamond set up at IACS, Kolkata. Transition enthalpies and transition entropies were calculated.

The densities of the pure compounds and all the binary mixtures were measured with the help of a dilatometer of the capillary type which was placed in a water-bath heated electrically and controlled manually. The length of the sample column was measured by a travelling microscope. The densities were calculated by correcting for the expansion of the glass capillary. Experimental uncertainty in density measurements is 0.1%.

For refractive indices measurements sample was introduced in thin prism (refracting angle less than 2^0) formed with glass slides whose inner surfaces were treated with 1% PVA solution and rubbed unidirectionally for homogeneous alignment of sample. The prism was then placed inside an electrically heated brass thermostat with a circular aperture, which is controlled manually to ± 0.5°C. He-Ne laser (λ=633 nm) beam was used to get two refracted spots from the LC-filled prism corresponding to extraordinary and ordinary rays on a screen placed at a distance of about 5 m from the prism. The distance d_2^e and d_2^o of these two spots from the initial direct spot were measured as a function of temperature. The average distance d_1 between the position of the direct spot and reflected spots formed by reflected beams from the two reflecting surfaces when the prism was placed symmetrically with apex facing the direct beam was also measured. The extraordinary and ordinary refractive indices were then calculated using the formulas [11]:

$$n_e = \left(1 + \frac{2d_2^e}{d_1}\right) \tag{2.1}$$

$$n_o = \left(1 + \frac{2d_2^o}{d_1}\right). \tag{2.2}$$

The accuracy in refractive index measurements is up to fourth decimal.

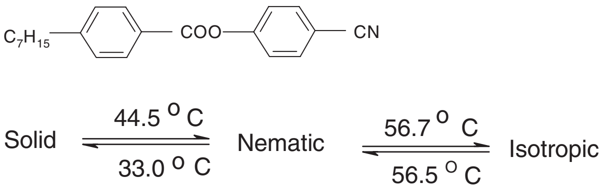


Figure 2. Component 2: 4-cyanophenyl 4′-n-heptyl benzoate (CPHB).

Downloaded by [Moskow State Univ Bibliote] at 12:57 15 April 2012

Downloaded by [Moskow State Univ Bibliote] at 12:57 15 April 2012

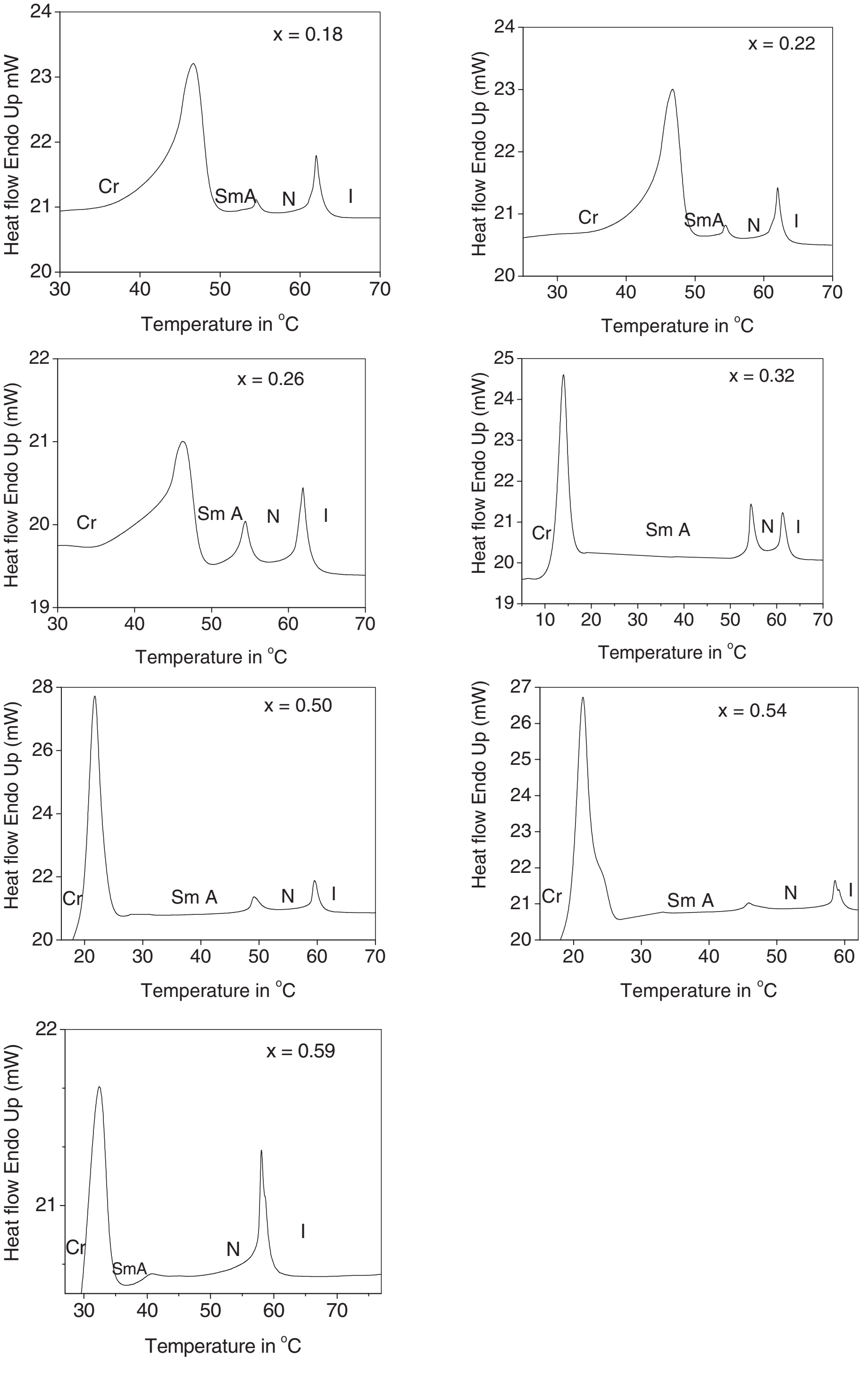


Figure 3. DSC scans of the binary mixtures showing induced smectic phase during heating run.

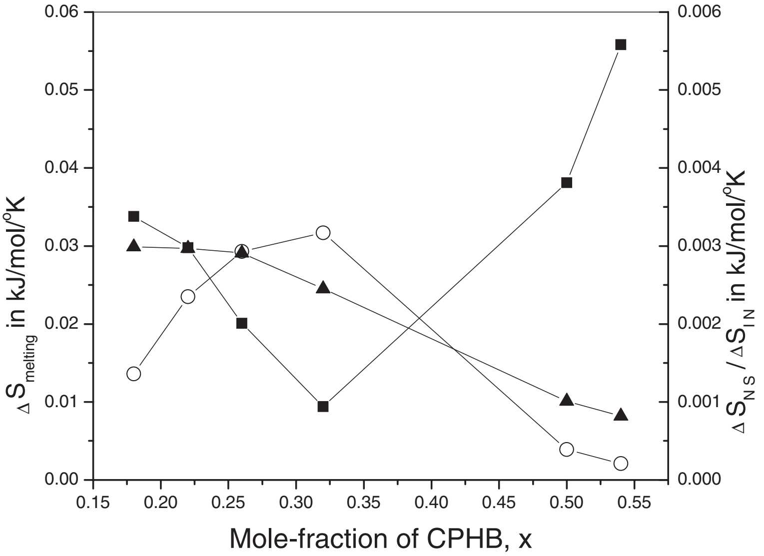


Figure 4. Transition entropies (ΔS) as a function of mole-fraction of CPHB. ■ denotes melting; ○ denotes nematic-smectic (NS) transition; ▲ denotes isotropic-nematic (IN) transition.

3. Results and Discussion

The phase diagram of the binary system (ME6O.5+CPHB) as obtained from the texture and DSC study shows enantiotropic-induced smectic A phase in the range $0.18 \leq x \leq 0.59$, where x is the mole-fraction of CPHB [12].

DSC scans of the binary mixtures showing induced smectic phase is shown in Figure 3. Here, for the two mixtures with $x = 0.26$ and $x = 0.32$, the McMillan ratio $((T_{\downarrow}NS/(T_{\downarrow NI})) >$ 0.87 The DSC study shows that nematic–smectic transition is strong enough for these two mixtures with associated enthalpy changes 0.96 kJ/mol and 1.04 kJ/mol, respectively. Other nematic–smectic transitions are also well realizable.

In Fig. 4, the results of the transition entropy are plotted as a function of mole-fraction of CPHB. The entropy change associated with nematic–smectic phase transition (ΔS_{NS}) is largest around $x \approx 0.32$ where the thermal stability of induced smectic phase is maximum. The peak in nematic–smectic phase transition entropy (ΔS_{NS}) is accompanied by a minimum in entropy associated with melting ($\Delta S_{\mathrm{melting}}$). So it appears that induced smectic phase with maximum thermal stability is relatively ordered. The highest thermal stability smectic phase is associated with small transition entropy corresponding to isotopic-nematic transition (ΔS_{IN}), indicating relatively disordered nematic phase.

The temperature variation of the density values for the pure compounds and all the mixtures is shown in Fig. 5. Density values of pure ME6O.5 are lower compared to CPHB. The density values in induced smectic phase show a maximum for mixture having $x = 0.32$. This indicates the molecules in the system are more tightly packed where thermal stability of the induced smectic phase ishigher.

The variation of the principal refractive indices n_o and n_e with temperature and variation of birefringence with mole fraction of CPHB at wavelength $\lambda = 633$ nm for all the mixtures and the pure compounds are shown here in Fig. 6.

Downloaded by [Moskow State Univ Bibliote] at 12:57 15 April 2012

Downloaded by [Moskow State Univ Bibliote] at 12:57 15 April 2012

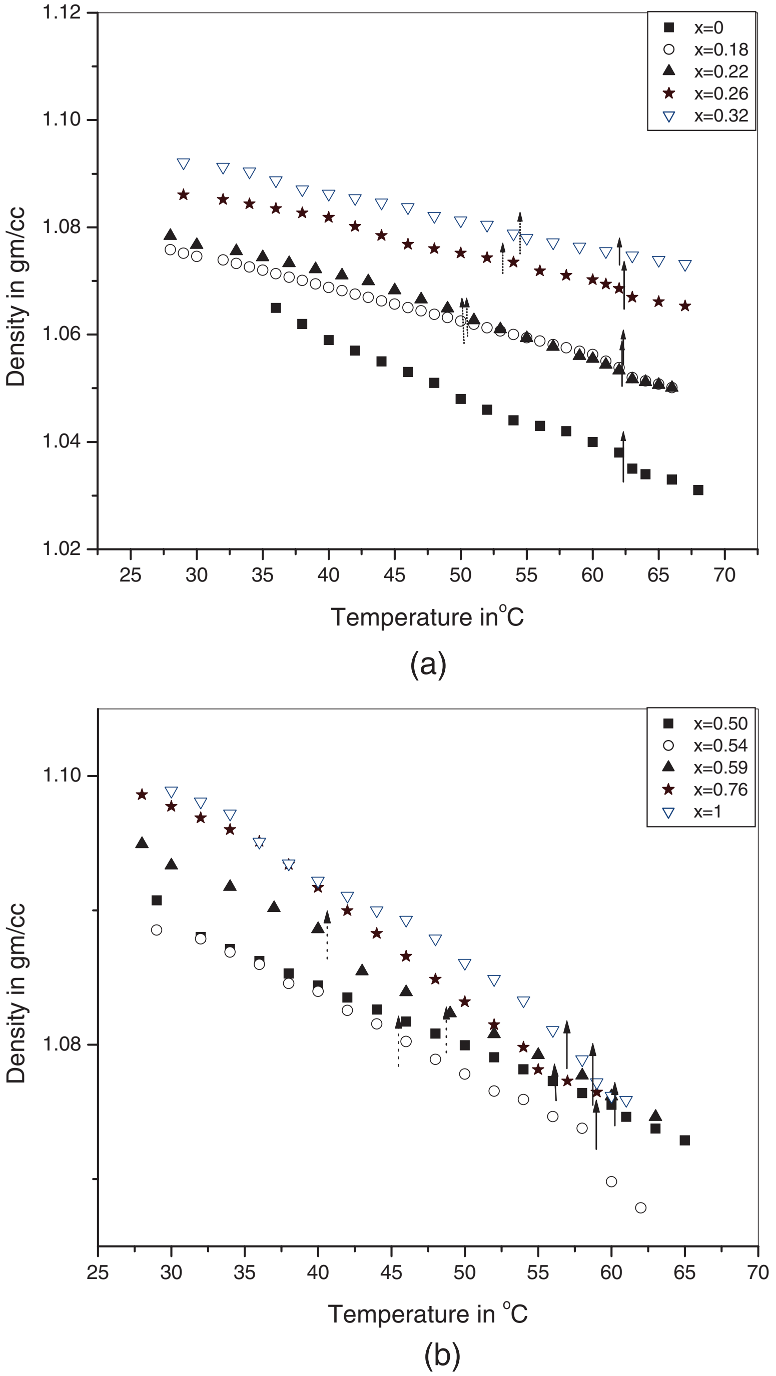


Figure 5. Variation of density as a function of temperature for (a) $x = 0.00, 0.18, 0.22, 0.26, 0.32$, (b) $x = 0.50, 0.54, 0.59, 0.76, 1.00$. ↑ indicates isotropic to nematic transition, and ↑ indicates nematic to smectic transition.

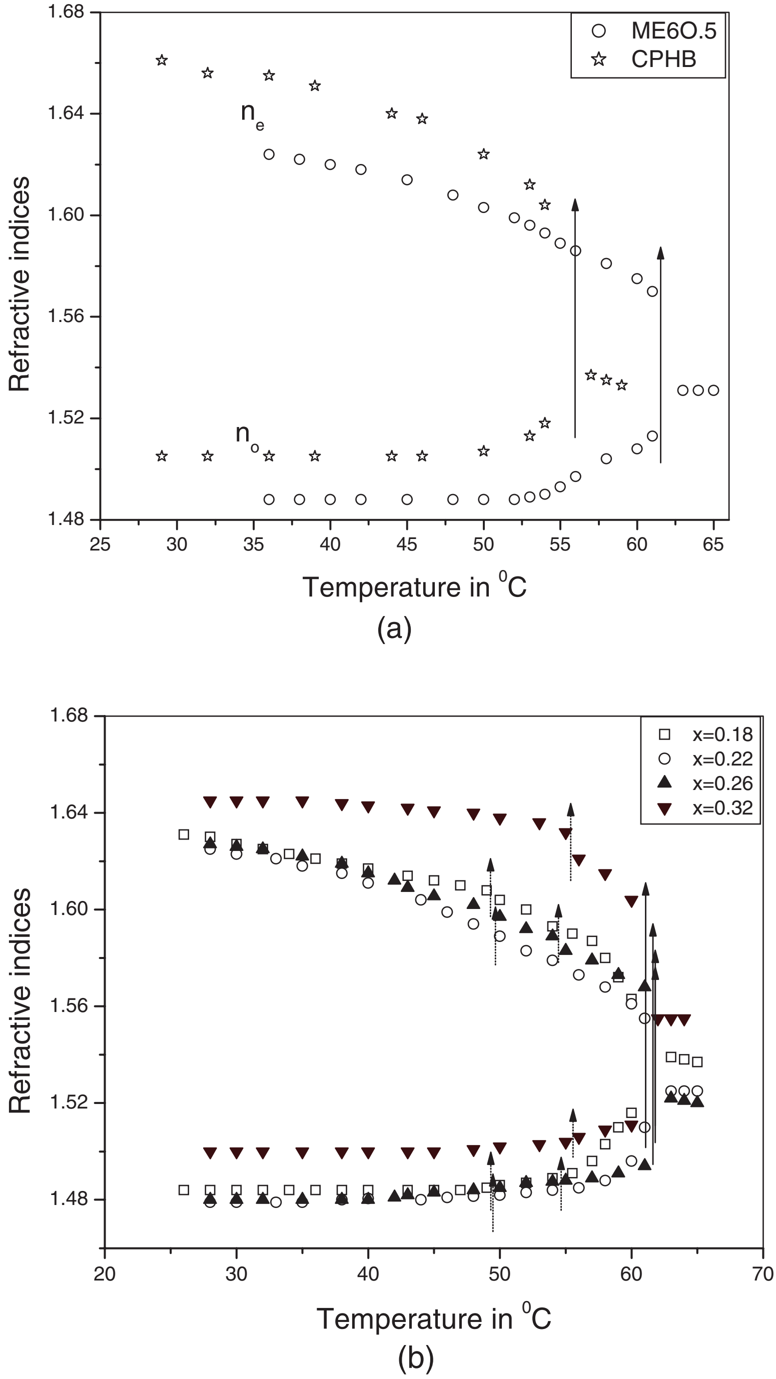
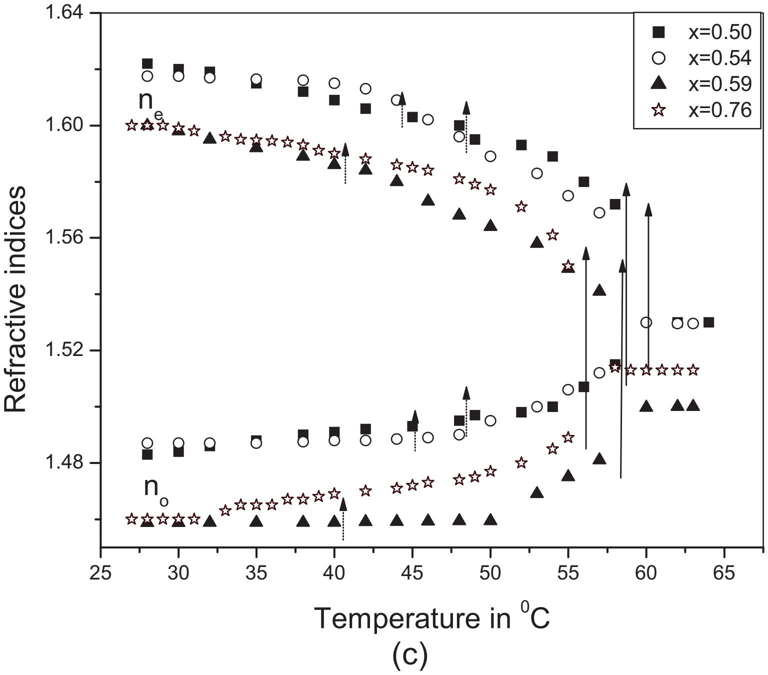
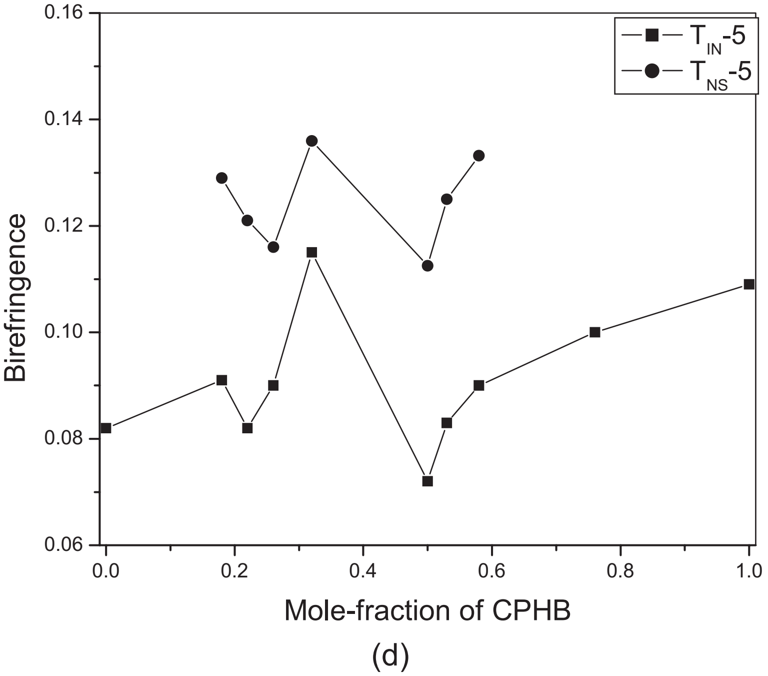


Figure 6. Temperature variation of refractive indices for (a) ME6O.5, CPHB, (b) $x = 0.18$, 0.22, 0.26, 0.32, and (c) $x = 0.50$, 0.54, 0.59, 0.76. ↑ indicates isotropic to nematic transition, and ↑ indicates nematic to smectic transition. (d) Variation of birefringence with mole-fraction of CPHB. *(Continued)*

Downloaded by [Moskow State Univ Bibliote] at 12:57 15 April 2012



(c)



(d)

Figure 6. (Continued)

Downloaded by [Moskow State Univ Bibliote] at 12:57 15 April 2012

Downloaded by [Moskow State Univ Bibliote] at 12:57 15 April 2012

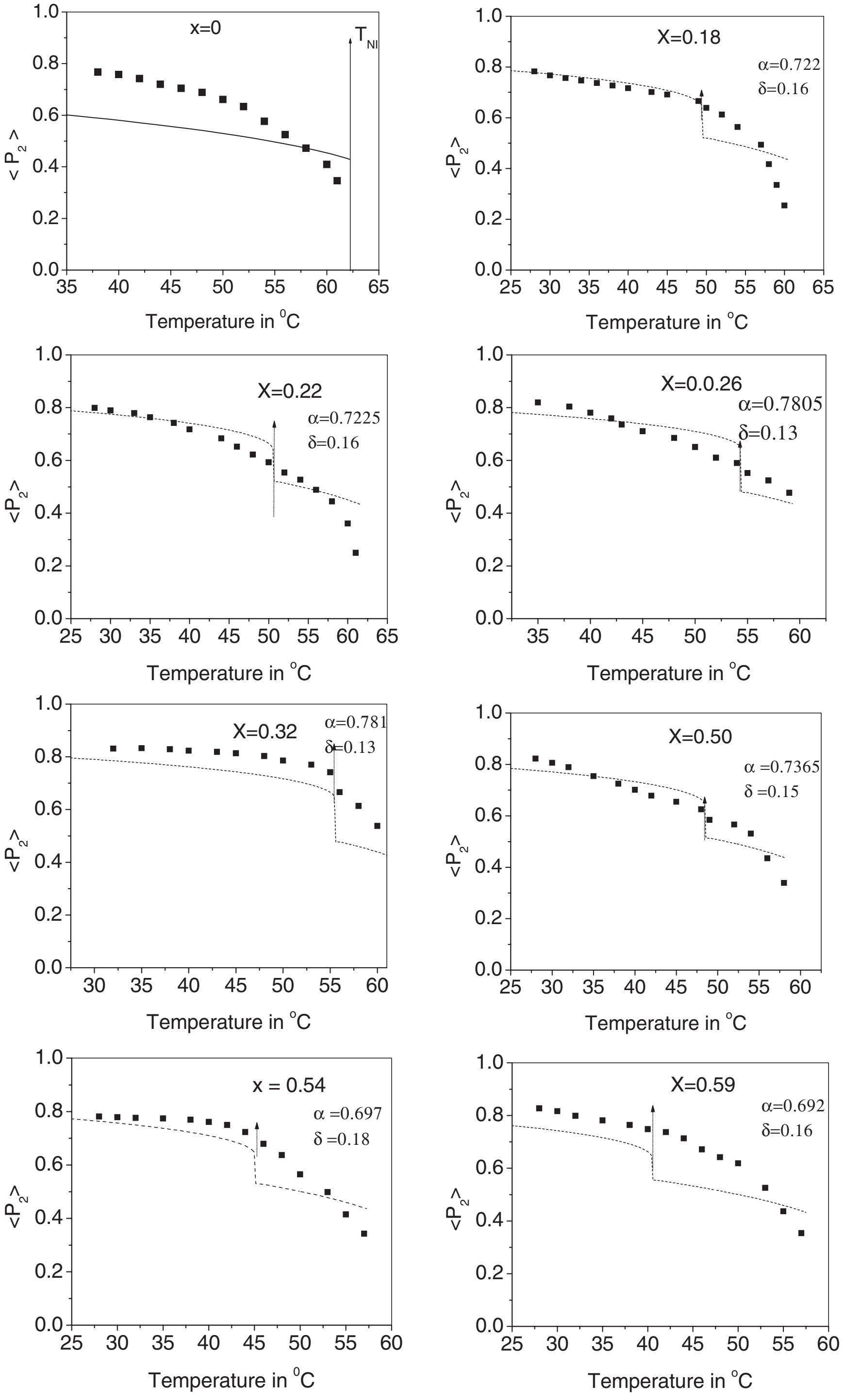


Figure 7. Temperature dependence of $<P_2>$ for (ME6O.5+CPHB) at different compositions: $x =$ mole-fraction of CPHB; solid lines indicate the theoretical $<P_2>$ values (MS values for nematic and McMillan values for smectic); ■ indicates experimental values. ↑ indicates isotropic to nematic transition, and ↑ indicates nematic to smectic transition. *(Continued)*

Downloaded by [Moskow State Univ Bibliote] at 12:57 15 April 2012

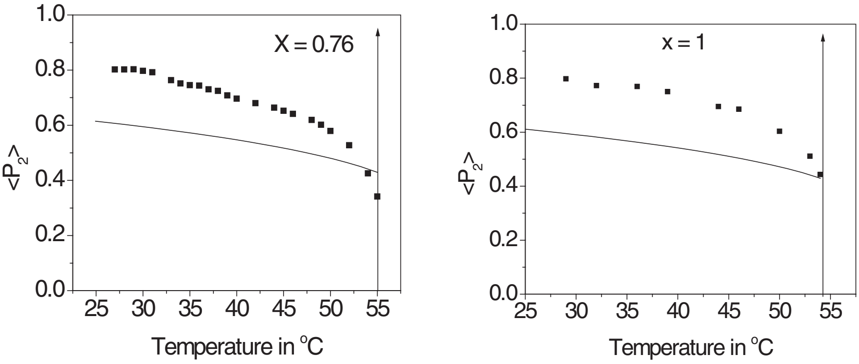


Figure 7. (Continued)

The birefringence in the induced smectic region shows a peak in the mixture having the highest stability of smectic phase. Similar trend of variation of birefringence with mole fraction of CPHB is observed in the nematic phase. This may be due to the formation of quasi-smectic supramolecular complexes within the nematic state which modify the physical properties of such nematics with short-range smectic order. The nature of variation of birefringence in the induced smectic region in this system is reverse of the same in the similar system (ME6O.5+CPPCC) [13] and similar with that of (ME6O.5+CPPB) [14].

The orientational order parameter $<P_2>$ is calculated using experimentally measured values of refractive index and density [15]. We have fitted our experimental order parameter values with the theory of McMillan [16, 17] for mixtures having a smectic A phase using α and δ as two adjustable parameters and those calculated from the theory of Maier–Saupe [18] for others having nematic phases only. The best fitted theoretical curve and the values of α and δ used for this calculation are shown in Fig. 7. Our experimental order parameter values at the smectic A to nematic phase transition appears to be discontinuous for $\mathbf{x} = 0.32$ implying a first order phase transition. Throughout the entire concentration range, in the nematic phase adjacent to nematic-smectic transition the experimental order parameters is higher than the theoretical ones, implying short-range smectic ordering in nematics.

4. Conclusion

The polar- non-polar binary system (ME6O.5 + CPHB) exhibiting enantiotropic-induced smectic phase in the region $0.18 \leq x \leq 0.59$, shows peak in birefringence where the thermal stability of the induced smectic phase is maximum. It appears from DSC study that here induced smectic phase with maximum thermal stability is relatively ordered. This is also reflected in the experimentally measured order parameters.

Acknowledgments

We are grateful to Dr. N. Naskar, IACS, Kolkata, India for DSC study. One of the authors (S.D.S.) is thankful to the U.G.C., New Delhi, India for the award of a teacher fellowship.

References

[1] Engelen, B., & Schneider, F. (1978). *Z. Naturforsch.*, *33a*, 1077.
[2] Oh, C. S. (1977). *Mol. Cryst. Liq. Cryst.*, *42*, 1.
[3] Domon, M., & Billard, J. (1979). *J. Phys.*, *40*, C3–413.
[4] Neuling, H. W., & Stegemeyer, H. (1989). *Liq. Cryst.*, *5*, 495.
[5] Das, M. K., Paul, R., & Dunmur, D. A. (1995). *Mol. Cryst. Liq. Cryst.*, *258*, 239.
[6] Songsheng, L., Jezhen, G., & Liangyu, W. (1983). *Mol. Cryst. Liq. Cryst.*, *100*, 285.
[7] Pelzl, G., Böttger, U., Diele, S., & Demus, D. (1987). *Cryst. Res. Technol.*, *22*, 1321.
[8] Jaishi, B. R., & Mandal, P.K. (2006). *Liq. Cryst.*, *33*, 753.
[9] Raszewski, Z. (1988). *Liq. Cryst.*, *3*, 307.
[10] Sharma, N. K. (1987). *Cryst. Res. Technol.*, *22*, K63.
[11] Yakhmi, J.V., Kelkar, V. K., Shukla, R. P., & Manohar, C. (1979). *Mol. Cryst. Liq. Cryst.*, *53*, 55.
[12] Datta Sarkar, S., & Choudhury, B. (2011). Physics Research International, 786849.
[13] Roy, P.D., Prasad, A., & Das, M. K. (2009). *J. Phys.: Condens. Matter.*, *21*, 075106.
[14] Datta Sarkar, S., Choudhury, B., & Das, M. K. (2011). *Phase Trans.*, 85, 85.
[15] Datta Sarkar, S., & Choudhury, B. (2010). *Acta Physica. Polonica A*, *118*, 665.
[16] McMillan, W. L. (1971). *Phys. Rev. A*, *4*, 1238.
[17] McMillan, W. L. (1972). *Phys. Rev. A*, *6*, 936.
[18] Maier, W., & Saupe, A. (1958). *Z. Naturforsch*, 13a, 564; ibid. (1959). 14a, 882; ibid. (1960). 15a, 287.

Downloaded by [Moskow State Univ Bibliote] at 12:57 15 April 2012