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Sajal Giri [a] , Pradip Mandal [a] & Sukla Paul [a]

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

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Study of Physical Properties of Binary Mixtures of Two Nematogens

SAJAL GIRI, PRADIP MANDAL and SUKLA PAUL

Department of Physics, North Bengal University, Siliguri, India

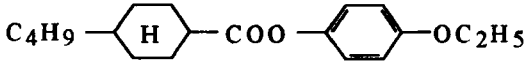
We have reported different physical parameters of binary mixtures of p-ethoxyphenyl trans-4-butylcyclohexane carboxylate and 4′-n-pentyloxy-4-cyanobiphenyl, the two nematogenic compounds. The mixtures are prepared in four different compositions with X_{5OCB}=0.213, 0.434, 0.626 and 0.818. Transition temperatures are determined by studying textures under a polarizing microscope. For all the compounds schlieren textures are observed. X-ray diffraction, optical birefringence study and density measurements have been carried out throughout the mesomorphic range. Only one mixture shows a cybotactic nematic phase. Apparent molecular lengths and order parameters are determined from X-ray studies and n_o, n_e and Δn from optical studies. Variation of all the parameters with temperature and concentration is discussed. Order parameters are compared with theoretical values.

Keywords: Binary mixtures; X-ray Diffraction; Order Parameters; Optical birefringence

INTRODUCTION

In this paper study of different physical parameters of binary mixtures of two nematic liquid crystalline compounds have been reported. The compounds are p-ethoxyphenyl trans - 4- butyl cyclohexane carboxylate (EPBCC) and 4′-n-pentyloxy - 4- cyanobiphenyl (5OCB).

The structural formulae and transition temperatures (°C) of them are given below:

EPBCC 

Cr 36.3 N 74.6 I

5OCB 

Cr2 48 Cr1 53 N 68 I

Both the samples were gifted by Hoffmann La-Roche and Co., Switzerland and used without further purification. Density, optical birefringence, apparent molecular length, intermolecular distance, order parameters and magnetic anisotropy of pure EPBCC had been studied by M. Mitra et al[1-3]. Anomalous behaviour in the variation of density, apparent molecular length and intermolecular distance with temperature were observed by them. Density, optical birefringence and order parameter measurements of pure 5OCB were also done by M. Mitra et al[4]. X-ray diffraction study on this sample was performed by B. Bhattacharjee et al[5]. Crystal structure analysis was undertaken by P. Mandal et al[6].

The mixtures of 5OCB and EPBCC were prepared in four different compositions A to D (x_{5OCB} = 0.213; 0.434; 0.626; 0.818). Transition temperatures were determined with Mettler FP 80/82 thermo-system by studying textures under a polarising microscope. The phase diagram is shown in Figure 1. In all concentrations Cr–N

transition temperatures could not be determined accurately and hence are not shown in the phase diagram. The maximum and minimum Cr–N transition temperatures are ~3°C and ~16°C respectively. It is evident that N–I transition temperatures vary smoothly with concentration (c) of 5OCB and follow the equation $T_{NI} = 74.53 - 0.83c - 5.77c^2$. For all the mixtures schlieren textures were found. Cybotactic nematic phase is observed only at lower temperatures (20°–36°C) in mixture B from x-ray diffraction.

Results of density measurements, optical birefringence and x-ray diffraction studies are reported here. Apparent molecular length

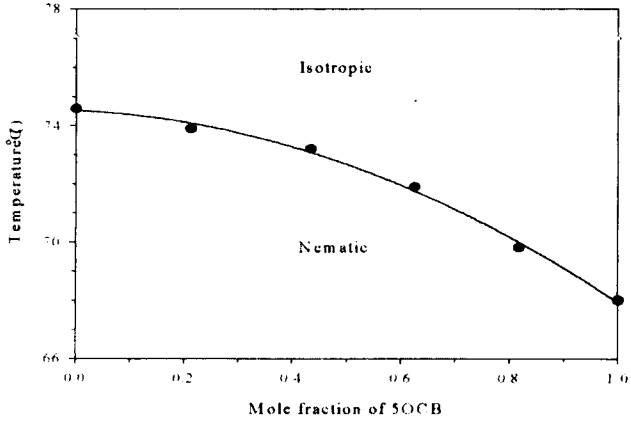


Figure 1 Phase diagram of binary mixture (EPBCC + 5OCB)

(l) and orientational order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ are determined

from magnetically aligned x-ray photographs. $\langle P_2 \rangle$ are also determined from measurement of ordinary and extra-ordinary refractive indices (n_o, n_e). Details of the experimental techniques have been reported earlier[7,8].

Variations of density with temperatures for all the mixtures as well as for the two pure compounds are shown in Figure 2. It is

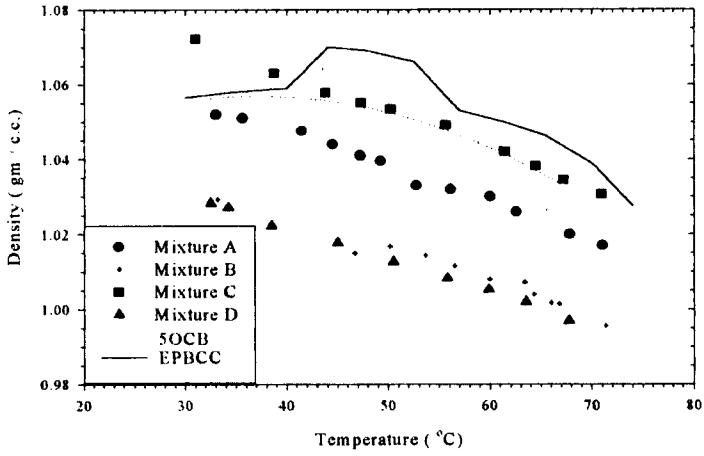


Figure 2 Variation of density with temperature for the binary Mixture (EPBCC + 5OCB)

observed that density of the mixtures decreases smoothly with temperature but with increasing concentration of 5OCB the density variation is quite irregular. For example over an appreciable range of temperature (43.5° to 66°C) density of mixture C almost coincides with the density of 5OCB whereas density of mixture D, in which concentration of 5OCB is maximum, deviates most from the density

of 5OCB. This might be the result of anomalous density behaviours of EPBCC[1] as shown in the Figure 2.

Temperature dependence of apparent molecular length for pure EPBCC and mixtures have been shown in Figure 3. The molecular

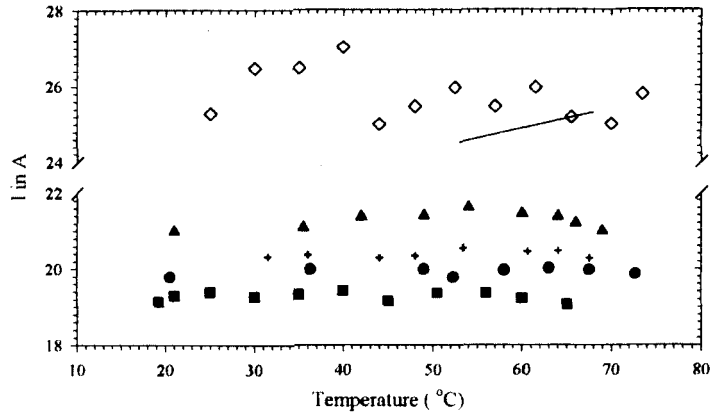


Figure 3 Variation of apparent molecular length with temperature for pure compounds and the mixtures. EPBCC data are from ref.116; 5OCB data are from ref. 107 where only values of l at the ends of nematic range are given.

■ Mixture A ● Mixture B • Mixture C
▲ Mixture D ◇ EPBCC —— 5OCB

lengths of EPBCC (L_A) and 5OCB (L_B) in the most elongated configuration are 19.4Å and 18.5Å respectively. The apparent molecular length for pure EPBCC varies irregularly from 25.0 Å to 27.0 Å and that for pure 5OCB varies from 24.5 Å to 25.3 Å as obtained from x-ray study[2,5]. Thus in both the cases l is about 1.3 to 1.4 times of L indicating the formation of bimolecular associations. It

is noted that for all the mixtures apparent molecular lengths are nearly constant throughout the temperature range and with increasing concentration of 5OCB the l values increase regularly. However, in mixture-A, where concentration of 5OCB is minimum, observed apparent molecular length is 19.3Å which is almost equal to

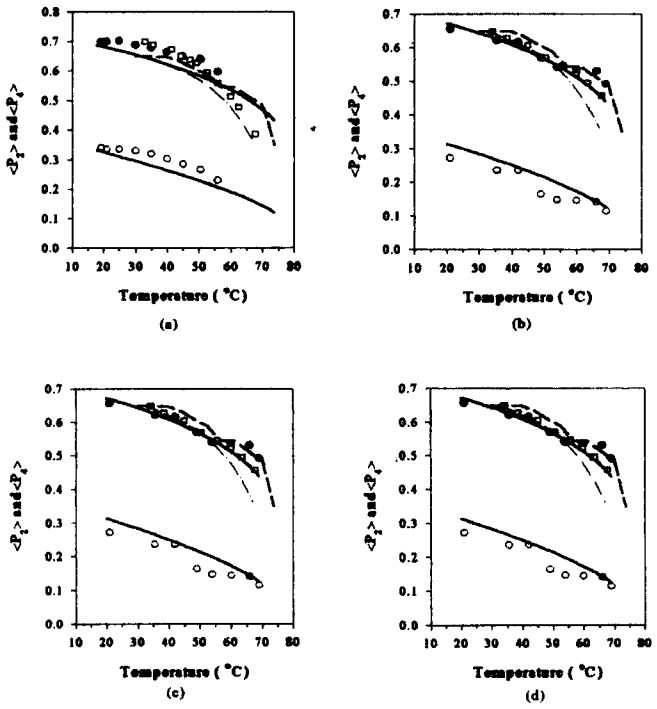


Figure 4 Variation of orientational order parameter with temperature for a) Mixture A, b) Mixture B, c) Mixture C and d) Mixture D

- ● $\langle P_2 \rangle$ of mixture from x-ray
- ○ $\langle P_4 \rangle$ of mixture from x-ray
- □ $\langle P_2 \rangle$ of mixture from R.I.
- — — $\langle P_2 \rangle$ of 5OCB from R.I
- —·— $\langle P_2 \rangle$ of EPBCC from R.I
- —— Calculated value from MS Theory

the average molecular length (19.21 Å) obtained from the following equation[9-12] and considering the mixture contains only monomers :

$$l = x_A L_A + x_B L_B$$

where x_A and x_B are mole fractions of A and B molecules. It implies that due to addition of small amount of 5OCB bimolecular

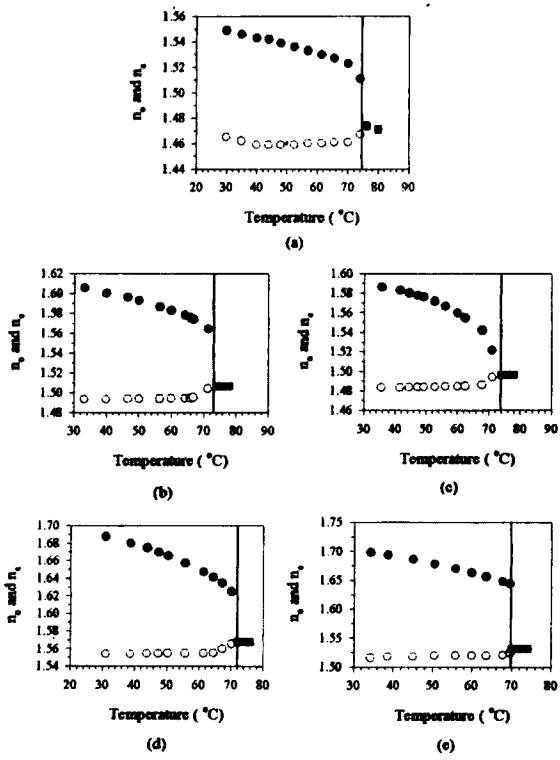


Figure 5 Variation of refractive indices with temperature for a) EPBCC, b) Mixture A, c) Mixture B, d) Mixture C and e) Mixture D

● n_e ○ n_o

associations between the molecules break down almost completely and monomeric concentration is maximum. But in case of mixtures-B, C and D the l values are 19.9 Å, 20.3 Å and 21.2 Å respectively which are greater than the values 19 Å, 18.84 Å and 18.66 Å obtained respectively from the above equation. Therefore, as the concentration of 5OCB is increased, concentration of different types of dimers increases. It is obvious that these dimers are not as strongly associated as observed in pure molecules.

Variation of orientational order parameter $\langle P_2 \rangle$ and $\langle P_4 \rangle$ with temperature are given in Figure 4. Order parameters of the pure compounds obtained from refractive index study[5,13] are also shown in this figure. It is observed that below 55°C, $\langle P_2 \rangle$ values determined from both the methods for mixtures as well as for pure components more or less agree with Maier-Saupe theoretical values. But above 55°C, $\langle P_2 \rangle$ values fall quicker than predicted by Maier-Saupe theory. Such observations have been reported earlier[2,3,14-16]. This

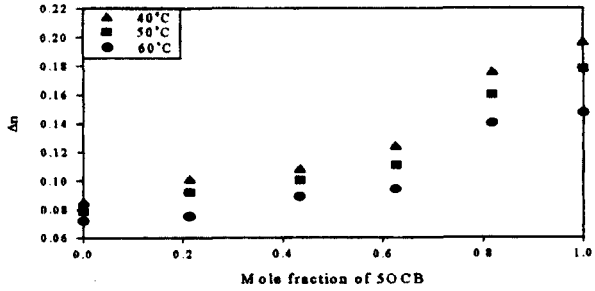


Figure 6 Variation of Δn with concentration for the binary Mixture (EPBCC + 5OCB)

contradiction may be the result of different types of approximations and averaging involved in calculating orientational order parameter from x-ray studies in one hand and birefringence measurements on the other hand. Thermal fluctuation of the chain part near clearing temperature may lower the value of order parameter which was not considered in mean field approximation. Except mixture-A, $\langle P_4 \rangle$ values are lower than Maier-Saupe theoretical values as has been reported in other compounds.

Variations of refractive indices with temperature show typical nematic nature as presented in Figure 5. Variation of Δn with composition at temperatures 40°, 50° and 60°C are shown in Figure 6. It decreases smoothly with decreasing concentration of 5OCB as expected from simple additivity rule.

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