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R. Shashidhar [a] [b] , H. D. Kleinhans [a] & G. M. Schneider [a]

[a] Department of Chemistry, University of Bochum, Bochum, FRG

[b] Humboldt Fellow, on leave of absence from the Raman Research Institute, Bangalore, 560080, India

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EFFECT OF MOLECULAR ORDERING ON THE NEMATIC-ISOTROPIC TRANSITION IN RE-ENTRANT NEMATIC MIXTURES:

A HIGH PRESSURE DTA AND OPTICAL STUDY

R. SHASHIDHAR*, H.D. KLEINHANS and
G.M. SCHNEIDER
Department of Chemistry, University of
Bochum, Bochum, FRG

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ABSTRACT The effect of pressure on the smectic A-nematic (A-N) and the nematic-isotropic (N-I) phase boundaries has been studied as a function of mole fraction in mixtures of 4'-n-hexyloxy-4-cyanobiphenyl (6OCB) and 4'-n-octyloxy-4-cyanobiphenyl (8OCB) by DTA and optical microscopy. The maximum pressure of occurrence of the smectic A phase decreases with increasing 6OCB mole fraction (x) until at $x \approx 0.30$, there is no smectic A phase at all. The plot of dT/dp at 1 bar for the N-I transition versus mole fraction exhibits an anomalous decrease in the mole fraction range of $0.10 < x < 0.28$ implying that the changes in molecular ordering which accompany the formation of the re-entrant nematic phase could manifest at much higher temperatures and affect thereby the pressure behaviour of even the N-I transition.

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[*] Humboldt Fellow, on leave of absence from the Raman Research Institute, Bangalore-560080, India

INTRODUCTION After the discovery of the re-entrant phenomenon by Cladis in mixtures at atmospheric pressure[1] and in pure compounds at high pressures[2] there has been a tremendous surge of activity in the synthesis of materials and a number of pure compounds as well as binary mixtures have been found which exhibit the re-entrant behaviour at atmospheric pressure.[3-5] There have also been several experimental reports on this phenomenon. Quite a few of these studies are on binary mixtures of 4'-n-hexyloxy-4-cyanobiphenyl (6OCB) and 4'-n-octyloxy-4-cyanobiphenyl (8OCB).[6-10] We have undertaken a detailed investigation of the effect of pressure on the smectic A-nematic (A-N) and nematic-isotropic (N-I) phase boundaries as a function of concentration in 6OCB-8OCB mixtures.

EXPERIMENTAL Both 6OCB and 8OCB were purchased from BDH England and were used without further purification. The A-N and N-I transition temperatures of 8OCB were 67.0°C and 80°C, while the N-I transition temperature of 6OCB was 76.5°C, these values being in very good agreement with those reported in literature. In order to minimize the errors in the concentration determination, rather large quantities of the mixture were made ($\sim$ 150 mg) for each 6OCB concentration. In every case, the N-I transition was extremely sharp and could be determined to a reproducible accuracy of better than ±0.1 K. The A-N transition temperatures were relatively broader in nature.

Two kinds of high pressure cells were used, a differential thermal analysis (DTA) cell for the N-I transition and a diamond anvil cell essentially for the A-N transition, since it was not possible to detect the A-N transition by DTA. The data on the A-N transition were brought to an absolute scale by normalizing the N-I transition values obtained from the two different cells. (See references 11 and 12 for details of these cells as well as for the calibration procedure).

RESULTS The temperature-mole fraction diagram for the 6OCB-8OCB mixture evaluated at 1 bar is shown in Figure 1, the concentration (x) being

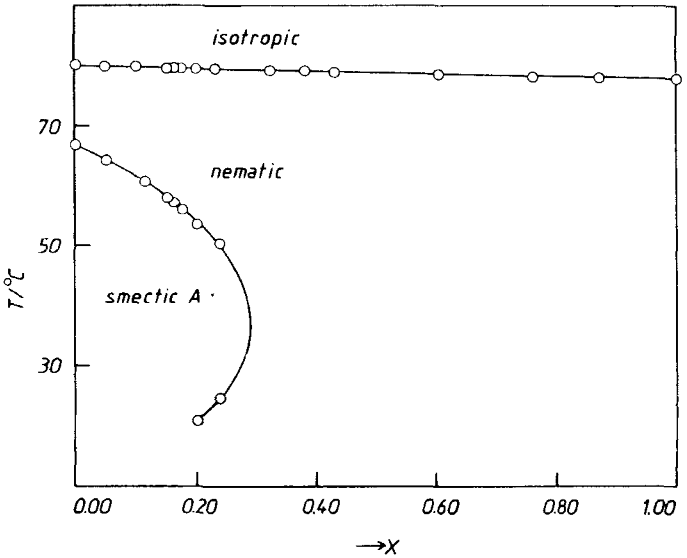

Figure 1 Temperature (T) - mole fraction (x) diagram for the 6OCB - 8OCB mixture at 1 bar. x is the mole fraction of 6OCB in the mixture.

given in mole fraction of 6OCB. This agrees very well with the earlier data of Guillon et al.[6] The smectic A-re-entrant nematic transition could be determined even for x slightly less than 0.20. For still lower values of x, the smectic A phase crystallized before the formation of the re-entrant nematic phase.

A-N TRANSITION The A-N phase boundaries for pure 8OCB (x = 0) and for 7 different concentrations are shown in Figure 2. The maximum pressure (p_M) at which the smectic A phase (and the re-entrant nematic phase) can occur is 1.96 kbar for 8OCB and it decreases rapidly with increasing x. The variation of p_M with x is shown in Figure 3. An extrapolation of this curve shows that p_M should be zero for $x \approx 0.30$. This is in fact exactly what is observed experimentally also (see Fig.1), i.e. there is no

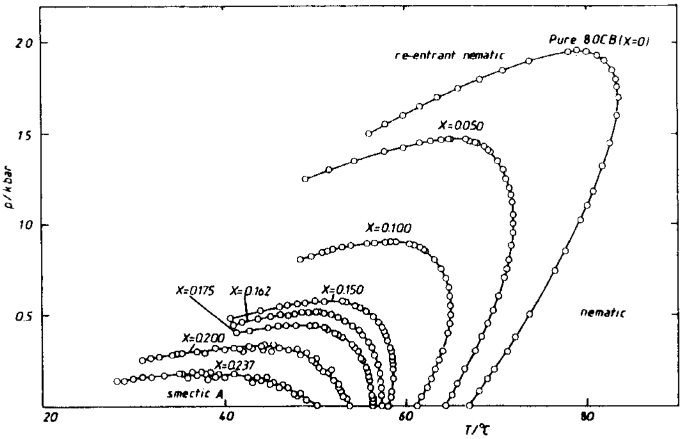

Figure 2 p-T boundaries of the smectic A-nematic transition for pure 8OCB (x = 0) and for different mole fractions of 6OCB.

smectic A phase beyond $x = 0.30$. These results are in good agreement with the recent experiments of Cladis.[13]

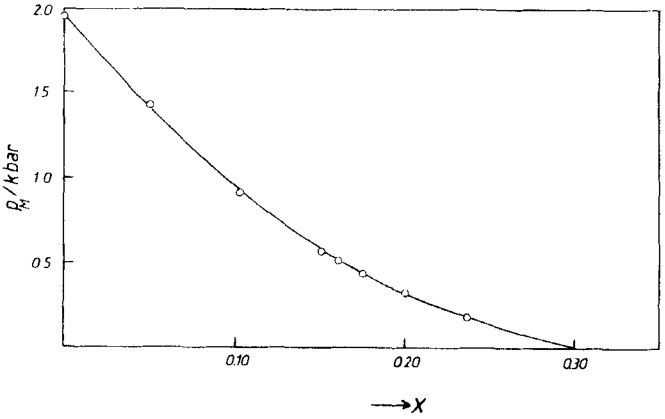

Figure 3 Variation of p_M, the maximum pressure of occurrence of the smectic A phase, with the mole fraction of 6OCB.

N-I TRANSITION Generally the N-I phase boundary looks rather uninteresting compared to the A-N phase boundary at high pressures. It was nevertheless thought worthwhile to carry out a detailed investigation of the p-T curves for the N-I transition to see if any special features are seen. In all, mixtures of 12 different mole fractions were studied in addition to the pure compounds. The dT/dp at 1 bar was evaluated from each of the p-T curve by a least square fit to the set of data points. The accuracy in the determination of dT/dp is reckoned to be ±0.3 $K \cdot kbar^{-1}$. Figure 4 shows the plot of $(dT/dp)_{1\ bar}$ vs x. Considering that the N-I transition at 1 bar evolves continuously (see Fig.1), one would intuitively expect the dT/dp vs x curve also

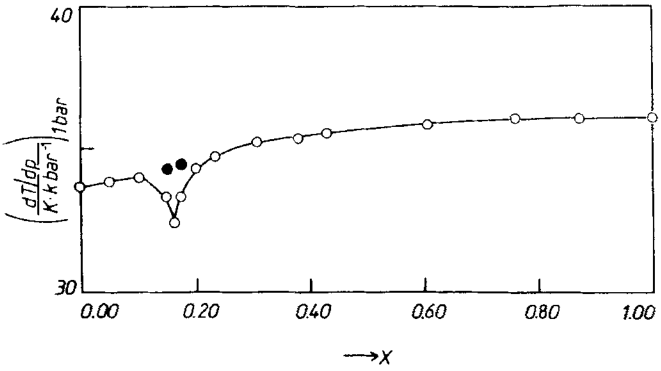

Figure 4 Variation of (dT/dp) at 1 bar for the nematic-isotropic transition versus the mole fraction of 6OCB. The open and closed circles denote the data points obtained under different experimental conditions (see text).

to show a smooth variation between the pure 6OCB and 8OCB values. However, Fig.4 shows that this is not the case. Although the dT/dp vs x curve does show the expected smooth variation at higher x values, there is a marked anomaly at lower x values, the lowest dT/dp value occurring at $x \approx 0.17$. The maximum drop in dT/dp (taken from a 'base line' joining the $x = 0.0$ and $x = 1.0$ data points) is 2.1 $K\cdot kbar^{-1}$ which is several times larger than the accuracy in the determination of dT/dp. Considering that these deviations are large only in the range $0.10 < x < 0.30$, it is natural to ascribe this to the presence of the smectic A and re-entrant nematic phases at lower temperatures (see Fig.1).

It must be mentioned that all the data points marked as open circles in Figure 4 were obtained in the following manner: At each pressure, the substance was cooled till it crystallized before it was re-heated again. Experiments were also conducted for two mole fractions ($x = 0.15$ and 0.17) in a different manner, viz, the sample was cooled just a few degrees (∿ 4 to 5 K) below the T_{NI} at each pressure and was then re-heated to determine the T_{NI} at another pressure. In other words, the p-T curves were obtained without appreciable cooling of the sample. The dT/dp values obtained when the experiment was conducted in this manner are shown as closed circles in Fig.4. They lie much higher than the corresponding data points obtained by heating the substance which has been cooled to the solid phase. The closed circles in fact now fall exactly on the curve joining the $x = 0.0$ and $x = 1.0$ data points. No such difference was however observed in the dT/dp values for $x > 0.30$ when the experiment was conducted with and without supercooling.

We therefore believe that the pressure behaviour of the N-I transition gets drastically affected by structural changes occurring at lower temperatures. Although it is still not possible to ascertain whether this effect is due to the influence of the smectic ordering or due to the presence of the re-entrant nematic phase at farther temperatures or due to a combination of both (it could even be due to some kinetic effects), we tentatively conclude that the normal or high temperature nematic phase, in the concentration range of existence of the re-entrant nematic phase, has a molecular ordering which is somewhat different from the ordering of the nematic phase occurring at higher concentrations. A detailed thermodynamic analysis of these results along with some more experimental results will be published separately.

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