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Effect of Molecular Ordering on the Pressure Behaviour of the Nematic–Isotropic Transition in Binary Reentrant Nematic Mixtures†

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Binary mixtures of *N*-*p*-cyanobenzylidene-*p*′-octyloxyaniline (CBOOA) and 4′-*n*-octyloxy-4-cyanobiphenyl (8 OCB) exhibit the reentrant nematic phase at atmospheric pressure over a certain range of composition. We have studied the effect of pressure on the nematic–isotropic transition of these mixtures. It is found that a plot of dT/dP versus the molar concentration of CBOOA shows two minima which occur almost exactly at the same concentrations at which the reentrant nematic phase makes its appearance at atmospheric pressure. These results indicate that the structural changes which accompany the formation of the reentrant nematic phase are strong enough to affect the pressure behaviour of even the nematic–isotropic transition.

INTRODUCTION

After the observation of the reentrant nematic phase in 4′-*n*-octyloxy-4-cyanobiphenyl (8 OCB) at high pressure,[1] there have been several pressure studies on different reentrant nematogens. Most of these experiments have been concerning the behaviour of the smectic A-nematic (A–N) phase boundary.[2-7] We undertook pressure studies of

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the nematic-isotropic (N–I) transition in binary mixtures of 8 OCB and 4′-*n*-hexyloxy-4-cyanobiphenyl (6 OCB) in order to see if any special features are observed for the N–I transition at high pressures. These studies[4] showed that dT/dP versus concentration curve for the N–I transition shows an anomalous behaviour although the N–I transition temperature (at atmospheric pressure) evolves continuously. Since this anomaly is observed in the concentration range of occurrence of the reentrant nematic phase, it was postulated that the anomaly could be due to the presence of smectic A and reentrant nematic phases at lower temperatures although it could also conceivably be due to some kinetic effects. However, subsequent experiments[8] carried out very carefully under different thermal conditions of the sample ruled out kinetic effects and hence the anomaly was ascribed to the influence of molecular ordering. In this paper we present the results of our studies on another binary system, viz., mixtures of *N*-*p*-cyanobenzylidene-*p*′-octyloxyaniline (CBOOA) and 8 OCB.

EXPERIMENTAL

The sample of 8 OCB used in the experiments was purchased from BDH England and used without further purification, while CBOOA was synthesized by us. The transition temperatures, as determined by a polarizing microscope equipped with a Mettler FP52 hot stage, are given in Table I. In order to minimize the errors in concentration determination, rather large quantities (~ 150 mg) of the mixture were made for each CBOOA concentration. In every case the N–I transition temperature was very sharp and could be measured to a reproducible accuracy of ±0.1 K.

TABLE I

Transition temperatures of 8 OCB and CBOOA

	Transition	Temperature (°C)
8 OCB	crystal–smectic A	54.8
	smectic A–nematic	66.9
	nematic–isotropic	80.0
CBOOA	crystal–smectic A	73.2
	smectic A–nematic	81.7
	nematic–isotropic	107.1

The pressure dependence of the N–I transition temperature was studied by differential thermal analysis. The sample was sealed in an indium capsule. An identical but empty capsule of indium served as the reference. The temperatures of the reference and the sample were determined by using a chromel–alumel thermocouple, the thermocouple junctions being located in small holes made at the bottom of the capsules. (See reference 9 for further details of the experimental set up.) Pressures were determined to an accuracy of ±5 bar and temperature to ±0.1 K.

RESULTS AND DISCUSSION

The binary phase diagram evaluated at atmospheric pressure for the 8 OCB/CBOOA mixtures is shown in Figure 1. It is seen that the smectic A phases of both the compounds are completely miscible. Although for both the pure compounds the smectic A phase crystallizes before the formation of the reentrant nematic phase (both compounds exhibit the reentrant nematic phase only at high pressures[1,2]), the mixtures exhibit the reentrant nematic phase over a range of mole fraction (x) of CBOOA, viz., $0.26 < x < 0.78$. A previous investigation of the phase diagram of the same mixtures by Engelen *et al.*[10] had also shown the appearance of the reentrant nematic phase at exactly the same concentrations. This is somewhat surprising since the smectic A–reentrant nematic transition is monotropic and is expected to be sensitive to the experimental conditions.

The pressure studies have been carried out for mixtures of 11 different concentrations in addition to the pure compounds. The experiments were always conducted in the same manner, viz., the pressure was kept constant and the temperature increased from the solid phase at about 1 K/min to record the N–I transition. The value of dT/dP was evaluated for each concentration by a least squares fit to the set of data points. The accuracy in the determination of dT/dP is ±0.2 K/kbar. The dT/dP vs. x curve for the N–I transition of the 8 OCB/CBOOA mixtures is shown in Figure 2. It is seen that the curve exhibits two minima although T_{NI} at atmospheric pressure evolves continuously (see Figure 1). Interestingly these minima occur almost exactly at those concentrations at which the reentrant nematic phase makes its appearance at atmospheric pressure. It therefore appears that the structural changes which accompany the formation of the reentrant nematic phase are strong enough to influence the pressure behaviour of the N–I transition.

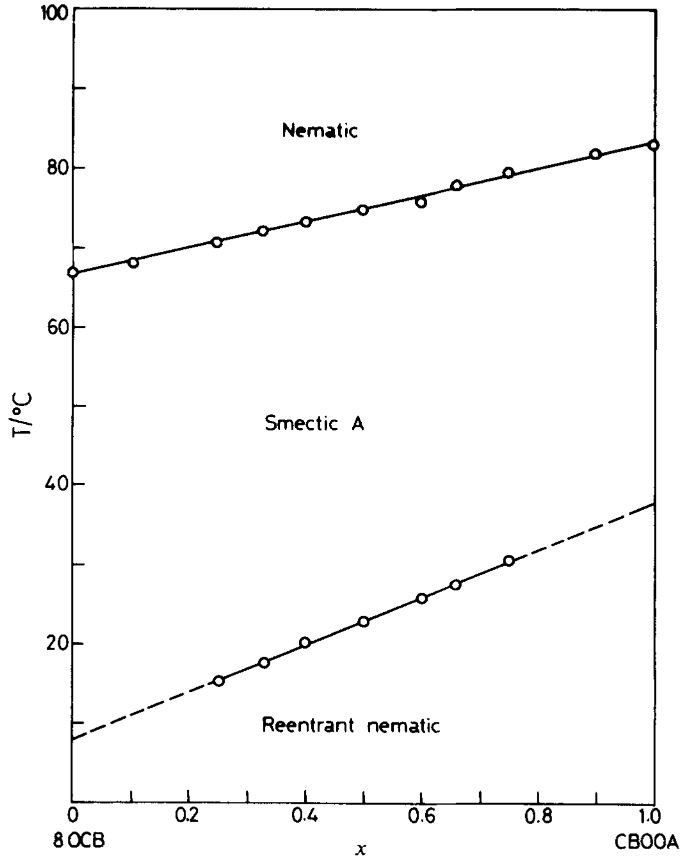

FIGURE 1 Temperature-concentration diagram of 8 OCB/CBOOA mixtures evaluated at 1 bar. x is the mole fraction of CBOOA in the mixture.

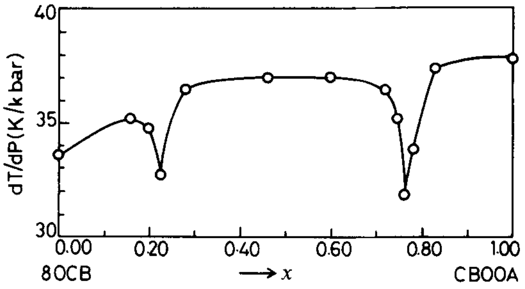

FIGURE 2 dT/dP versus x for the nematic-isotropic transition in 8 OCB/CBOOA mixtures. (x is the mole fraction of CBOOA).

It may be recalled that Achard *et al.*[11] have recently shown that the smectic ordering influences the enthalpy of the N–I transition. The question therefore arises if the effect that we have observed for the dT/dP vs. x curve owes its origin to an anomaly in the behaviour of either the heat or the volume change associated with the N–I transition. Detailed DSC as well as volumetric measurements are envisaged to check this possibility.

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