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Coupling Between Nematic and Smectic Ordering in Reentrant Nematic Systems

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We present here experimental evidence of the coupling between smectic and nematic ordering in systems exhibiting the reentrant nematic phase. Pressure-temperature diagrams of a large number of systems have been studied. In every case the major axis of the elliptically shaped smectic A-nematic phase boundary is found to be nearly parallel to the nematic-isotropic phase boundary although the slopes vary widely from system to system. Similar correlations are also shown to exist in the temperature-concentration diagram of binary systems. A few representative phase diagrams are presented which illustrate this point.

Keywords: smectic-nematic coupling, reentrant nematics, phase diagrams

1. INTRODUCTION

The problem of coupling between smectic and nematic ordering has been discussed theoretically by de Gennes[1] and also by Halperin and Lubensky.[2] Recent pressure experiments[3,4] as well as volumetric studies[5] on binary mixtures of 4′-n-octyloxy-4 cyanobiphenyl (8OCB) and 4′-n-hexyloxy-4-cyano biphenyl (6OCB) have clearly shown that the thermodynamic behaviour of the nematic-isotropic (N-I) transition is extremely sensitive to smectic ordering. In our earlier paper[6] we reported pressure-temperature (P-T) diagrams of several single component systems which exhibit reentrant nematic behavior. Although these data were of somewhat low precision (± 15 bars), it was apparent from the P-T diagrams that the major axis of the elliptically shaped smectic A-nematic (A-N) boundary has nearly the same slope as that of the N-I line. In order to confirm this point we have re-

determined with improved accuracy (± 2 bars), the P-T diagrams of a large number of compounds. In addition we have also obtained the temperature-concentration (T-X) diagrams of several binary systems which exhibit the reentrant nematic (N_{re}) phase over a range of concentrations. In this paper we shall present a few representative phase diagrams.

2. RESULTS AND DISCUSSION

The high pressure data were obtained using the experimental set up described in an earlier paper.[7] The binary phase diagrams were obtained by optical microscopic observations of the mixtures. Figures 1–4 give the P-T diagrams of four single component systems. (For the transition temperatures of these compounds see ref. 6.) The following features which are common to all the four compounds are clear from the phase diagrams: (i) the A phase is bounded in the P-T plane, (ii) the A-N boundary is, as expected, elliptically shaped

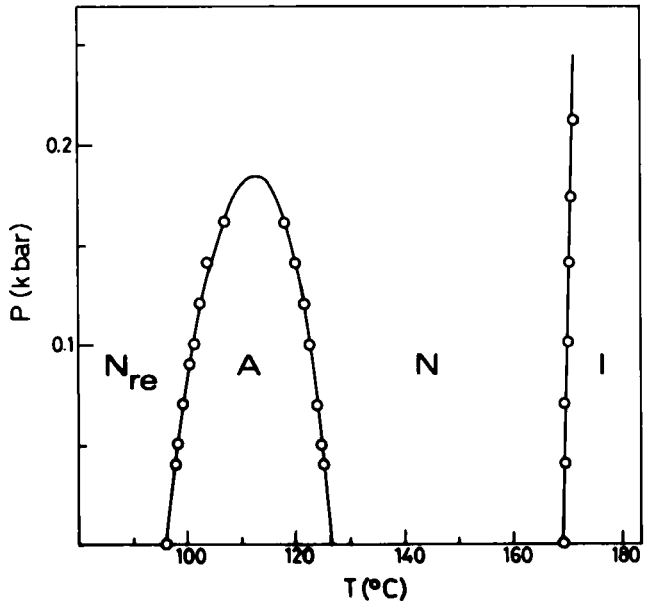

FIGURE 1 Pressure-temperature (P-T) diagram of 4-cyanophenyl-3′-methyl-4′-(4″-n-undecyloxy-α-methyl cinnamoyloxy)benzoate. The solid curves are obtained by the computer fits of the A-N and N-I data to the equations of an ellipse and a straight line respectively (see text).

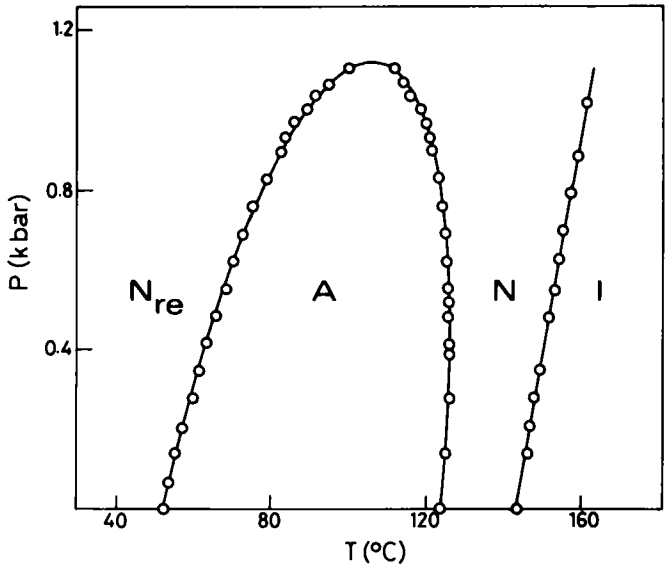

FIGURE 2 P-T diagram of 4-cyanophenyl-3′-methoxy-4′-(4″-n-undecyloxy-α-methyl cinnamoyloxy)benzoate. (see also legend of Figure 1).

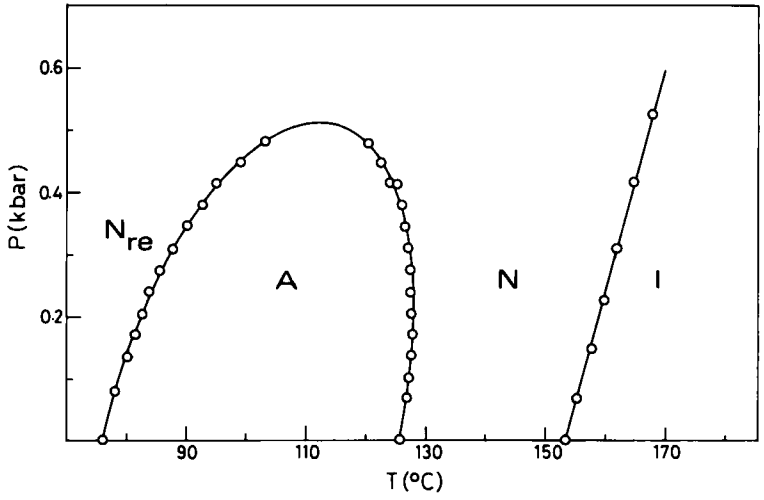

FIGURE 3 P-T diagram of 4-cyanophenyl-3′-methyl-4′-(4″-n-undecylbenzoyloxy) benzoate. (see also legend of Figure 1).

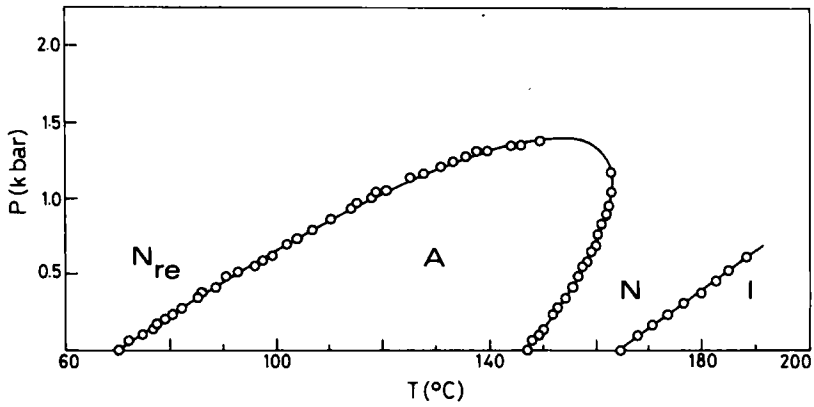

FIGURE 4 P-T diagram of 4-cyanophenyl-3'-methyl-4'-(4"n-dodecyloxy-α-methyl cinnamoyloxy)benzoate. (see also legend of Figure 1).

and (iii) the tilts of the major axis of the elliptic A-N boundary and of the N-I line are nearly the same. We shall now quantitatively examine the slopes of the major axis and the N-I boundary in the P-T plane.

It has been shown previously[8-10] for several reentrant nematogens that the P-T data for the A-N transition fit the equation to an ellipse very well. Following the same approach we have fitted our data for the four compounds studied here to the equation to an ellipse. The solid lines in Figures 1–4 are obtained by such a fit which can be seen to be very good. From these computations we have obtained the coordinates of the centre of the ellipse (P_o, T_o) and the tilt of the major axis with respect to the temperature axis ($\theta_{\text{major axis}}$). These are given in Table I. We have also computed the tilt of the N-I phase boundary (θ_{NI}) by fitting the data for the N-I transition to a straight line. These values are also given in Table I. It is clear that although

TABLE I

Parameters obtained from the fits of the pressure data for A-N and N-I transitions to an ellipse and a straight line respectively (see text)

	A-N boundary			N-I boundary
Compound	P_o(kbar)	T_o(°C)	$\theta_{\text{major axis}}$ (in deg.)	$\theta_{N\,I}$ (in deg.)
11 CPMαMCB	−0.813	103.48	88.5	88.4
11 CPMeOαMCB	−0.327	82.56	80.5	80.4
11 CPMBB	0.021	100.83	73.3	74.0
12 CPMαMCB	−1.915	47.28	38.4	37.2

the θ values for the different compounds are widely different, in every case the inclination of the major axis of the elliptic phase boundary in the P-T plane agrees closely with that of the N-I phase line.

We present in Figures 5–8 the T-X diagrams of four binary systems. It should be remarked here that the shape of A-N phase boundary in the T-X plane has not been investigated for many systems. In the case of 8OCB-6OCB mixtures it was concluded[14-16] that the A-N boundary is parabolic in the T-X plane. We have fitted our T-X data (X being the concentration expressed in weight per cent) for AN and NI transitions to the equation to an ellipse and a straight line respectively. Figures 9(a)–(d) show that these fits are extremely good, the solid lines in these figures being the computer fits. The computer evaluated values of θ as well as coordinates (T_o, X_o) of the centre of

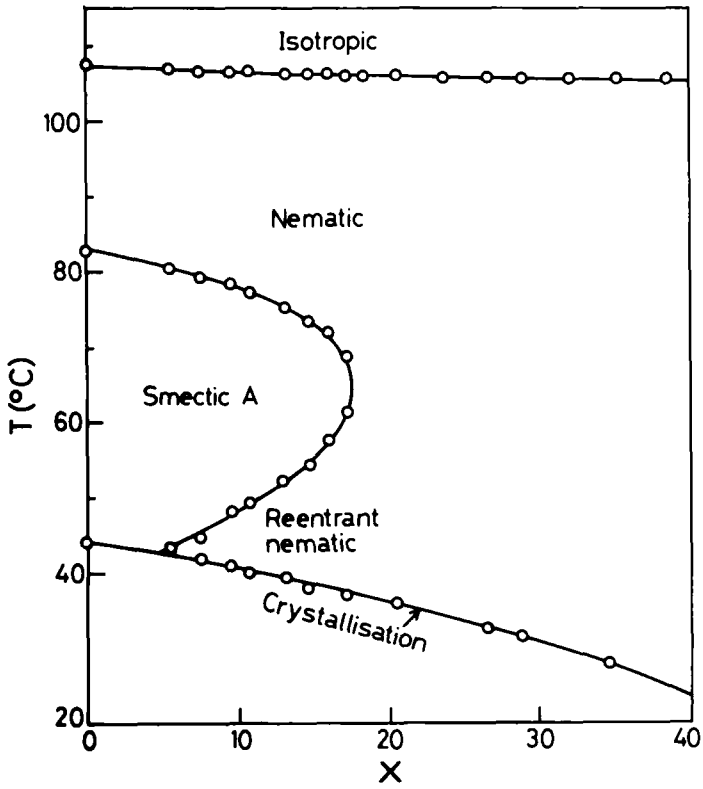

FIGURE 5 Temperature-concentration (T-X) diagram of binary mixtures of 4-cyanobenzylidene-4'-octyloxyaniline (CBOOA) and 4-cyano-ethylphenyl-4'-octyloxycinnamate (CEPOOC).[11] X is the weight percent of CEPOOC in the mixture.

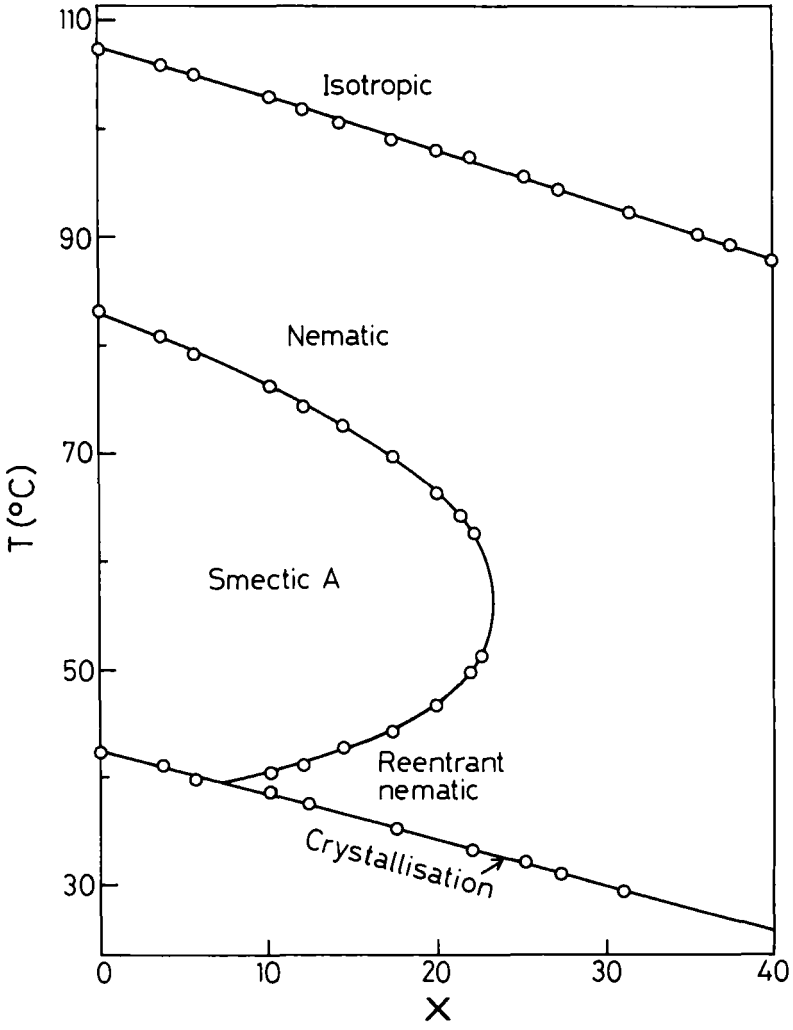

FIGURE 6 T-X diagram of binary mixtures of CBOOA and 4-cyanoethylphenyl-4'-octyloxybenzoate (CEPOOB).[12] X is the weight percent of CEPOOB in the mixture.

the ellipse are given in Table II. It is seen that, as in the case of the P-T diagrams, the major axis of the elliptic A-N boundary is nearly parallel to the N-I line in the T-X plane in every case.

Thus we have shown that the coupling between the smectic and nematic ordering is manifested in the phase diagrams of reentrant nematogens both in the pressure-temperature and the temperature-concentration planes. It is relevant to recall that recently Keyes[17] has

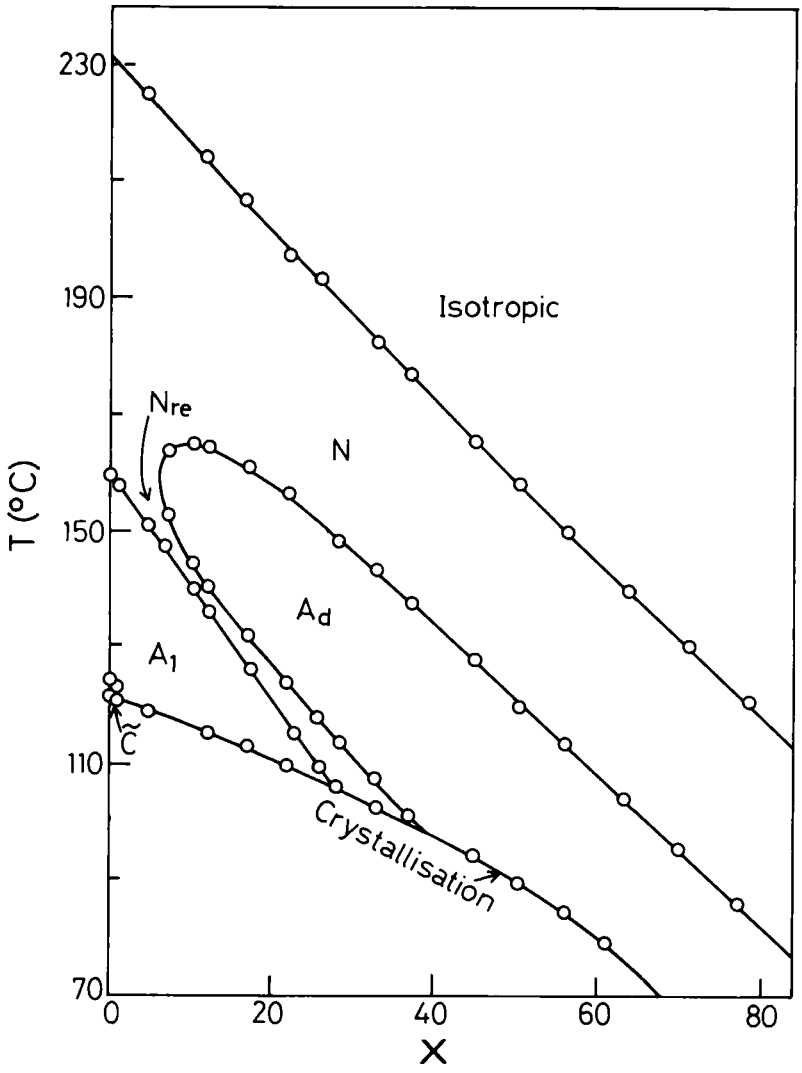

FIGURE 7 T-X diagram of binary mixtures 8OCB and 4-n-octyloxybiphenyl-4'-cyanobenzoate (8OBCB).[13] X is the weight per cent of 8OCB in the mixture.

developed a mean field theory for reentrant nematics by taking into account the coupling of smectic and nematic orders. By incorporating the lowest order coupling terms in the Landau free energy expansion, he has shown that observed features of the smectic A-nematic phase boundary come out as a consequence of this coupling. Exact comparisons between theory and experiments are yet to be worked out.

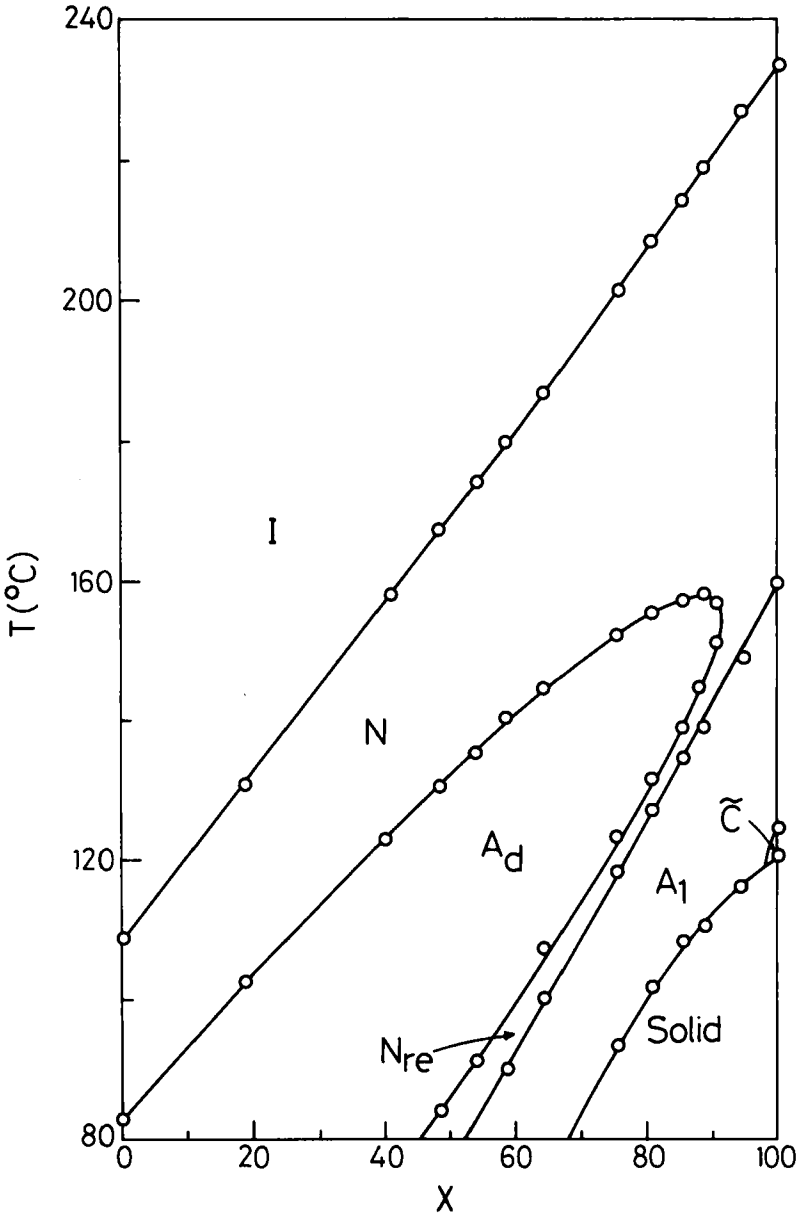

FIGURE 8 T-X diagram of binary mixtures of CBOOA and 8OBCB. X is the weight per cent of 8OBCB in the mixture.

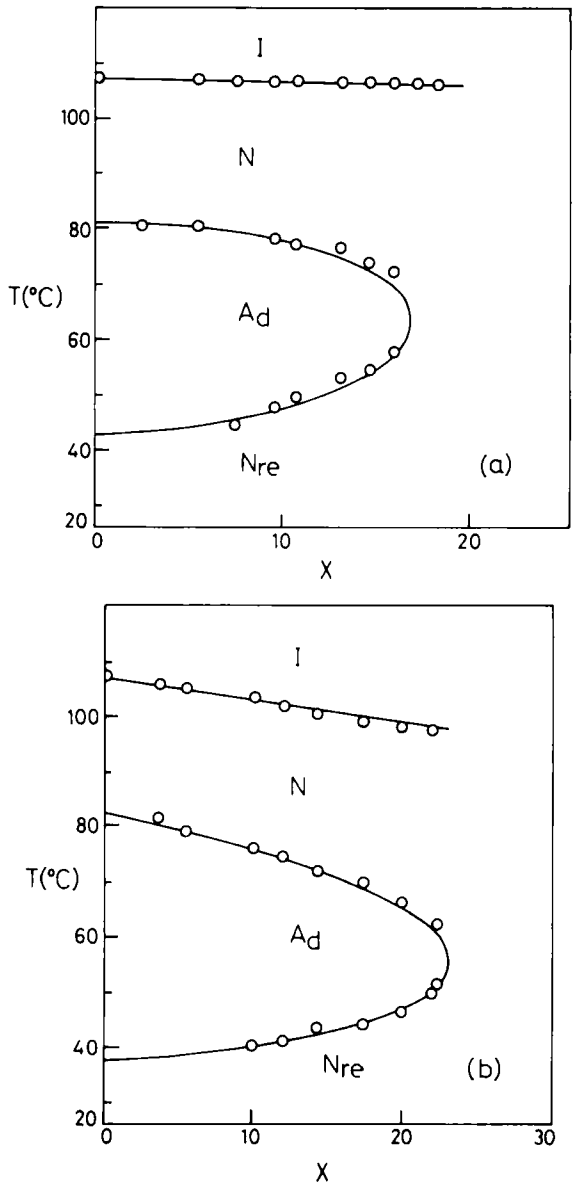

FIGURE 9 T-X diagrams for 4 binary systems showing the computer fits of the T-X data for the A-N and N-I transitions to the equation to an ellipse and a straight line respectively. The circles are the data points and the solid curves are obtained by computer fits (see text). The binary systems are (a) CBOOA/CEPOOC, (b) CBOOA/CEPOOB, (c) 8OCB/8OBCB and (d) CBOOA/8OBCB. In every case X denotes the weight per cent of the second component.

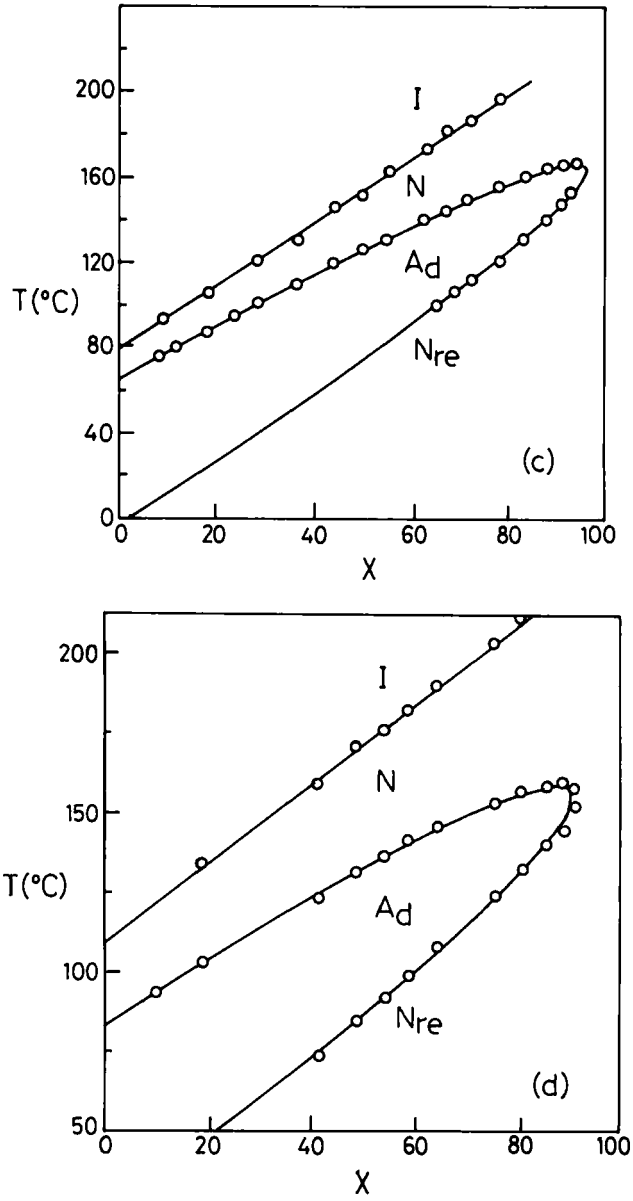

FIGURE 9 (continued)

TABLE II

Parameters obtained from the fits of the T-X data for the A-N and N-I transitions to an ellipse and a straight line respectively (see text)

	A-N boundary			N-I boundary
Binary system	T_o(°C)	X_o(weight %)	$\theta_{major\ axis}$ (in deg.)	$\theta_{N\text{-}I}$ (in deg.)
CBOOA/CEPOOC	61.83	−0.77	90.0	91.95
CBOOA/CEPOOB	69.72	−52.02	96.0	98.0
8OCB/8OBCB	−117.89	−108.79	57.6	57.0
8OBCB/CBOOA	36.39	−15.92	55.6	53.5

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