

High pressure studies of liquid crystalline transitions: Recent results

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Abstract. For sometime now we have been conducting high pressure studies on various types of liquid crystalline phase transitions. Two topics of current interest in liquid crystalline systems are (i) the phenomenon of reentrance, and (ii) multicritical points. In this paper we present some of the recent results of our pressure studies dealing with these two aspects.

Keywords. Liquid crystalline phase transitions; multicritical points; reentrant nematics; P-T diagrams; high pressure studies

1. Introduction

Of late a problem that has attracted considerable attention is the phenomenon of reentrance in liquid crystals. This phenomenon was first discovered in binary mixtures at atmospheric pressure (Cladis 1975) and later in a single component system at high pressure (Cladis *et al* 1977). Subsequently it was also observed in pure compounds at atmospheric pressure (Hardouin *et al* 1979; Madhusudana *et al* 1979). We present in § 2 some important results of our pressure experiments on several substances which exhibit reentrant polymorphism.

There has also been a great deal of current interest in multicritical points in liquid crystalline systems. The nematic-smectic A-smectic C (NAC) multicritical point was first observed in binary mixtures (Johnson *et al* 1977, Sigaud *et al* 1977). We undertook pressure studies on a number of compounds with a view to observing the multicritical point in a single component liquid crystal. The results of these studies are presented in § 3.

2. Pressure studies on reentrant nematogens

Cladis *et al* (1977) made the interesting discovery that 4'-n-octyloxy-4-cyanobiphenyl (8OCB) exhibits in the pressure range of 1.6–1.8 kbar the following sequence of transitions on cooling (see figure 1):

isotropic liquid → nematic → smectic A → nematic → solid.

Thus we have here an unusual sequence of a phase of higher symmetry or lower order appearing at a lower temperature. The second or lower temperature nematic phase has been designated as the reentrant nematic phase in analogy with similar phenomena observed in condensed matter physics (Anderson *et al* 1963; Riblet and Winzer 1971). Two important features of the P-T diagram of 8OCB shown in figure 1 are (i) there is a maximum pressure (P_m) of occurrence of the smectic A phase, and (ii) the smectic A-nematic (A-N) phase boundary curves towards the pressure axis resembling the arc of an ellipse. We have carried out high pressure studies on a number of compounds exhibiting reentrance in order to understand these two features.

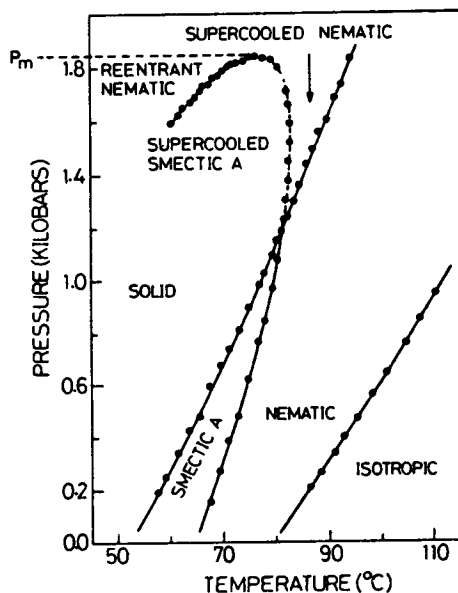


Figure 1. P-T diagram of 8 OCB showing the reentrant nematic phase. P_m is the maximum pressure up to which the smectic A phase exists.

2.1 P-T diagrams

The pressure dependence of the phase transition temperatures was studied by optical transmission technique using an optical high pressure cell (Kalkura *et al* 1983) equipped with sapphire windows. The P-T diagrams of eight pure compounds which exhibit the reentrant nematic phase at 1 bar have been studied. These compounds have been synthesized in our chemistry laboratory (Sadashiva 1979; Urs and Sadashiva 1982) and are listed in table 1. They all possess a highly polar cyano-end group attached to one end of the molecule. Their molecular structures are given in table 2.

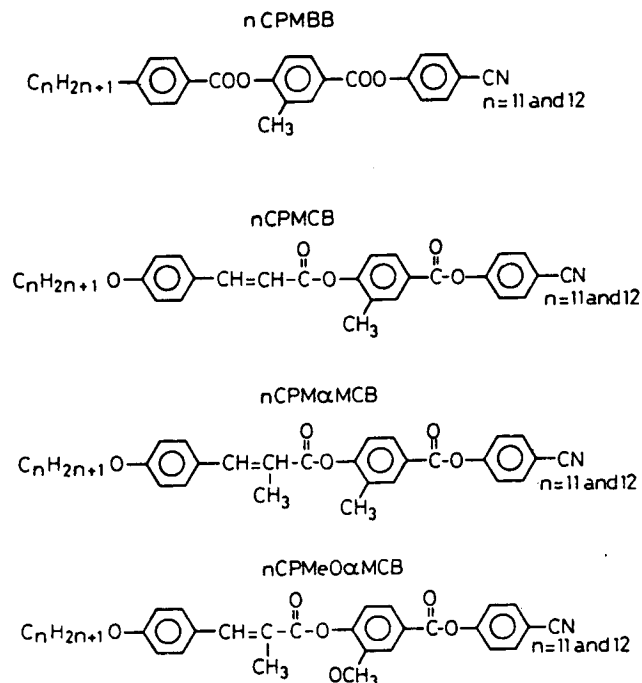
The P-T diagrams for all the compounds are essentially similar. Two representative phase diagrams are shown in figures 2 and 3. They all exhibit a maximum pressure (P_m) up to which the smectic phase exists (see table 3). In figure 4, P_m (which is also referred to as the maximum pressure of smectic stability) for the different compounds are plotted, on a semi-log scale, against the range of the nematic phase $R (= T_{NI} - T_{AN})$ at 1 bar. T_{NI} and T_{AN} are the nematic-isotropic and smectic A-nematic transition temperatures. It is seen that the data fall on a straight line (line A) so that they can be represented by

$$P_m = P_o \exp(-mR).$$

Table 1. List of reentrant nematogens studied

1. 4-Cyanophenyl-3'-methyl-4'-(4"-n-undecylbenzoyloxy)benzoate (11 CPMBB)
2. 4-Cyanophenyl-3'-methyl-4'-(4"-n-dodecylbenzoyloxy)benzoate (12 CPMBB)
3. 4-Cyanophenyl-3'-methyl-4'-(4"-n-undecyloxycinnamoyloxy)benzoate (11 CPMCB)
4. 4-Cyanophenyl-3'-methyl-4'-(4"-n-dodecyloxycinnamoyloxy)benzoate (12 CPMCB)
5. 4-Cyanophenyl-3'-methyl-4'-(4"-n-undecyloxy- α -methyl-cinnamoyloxy)benzoate (11 CPM α MCB)
6. 4-Cyanophenyl-3'-methyl-4'-(4"-n-dodecyloxy- α -methyl-cinnamoyloxy)benzoate (12 CPM α MCB)
7. 4-Cyanophenyl-3'-methoxy-4'-(4"-n-undecyloxy- α -methyl-cinnamoyloxy)benzoate (11 CPMEO α MCB)
8. 4-Cyanophenyl-3'-methoxy-4'-(4"-n-dodecyloxy- α -methyl-cinnamoyloxy)benzoate (12 CPMEO α MCB).

Table 2. Molecular structures of the reentrant nematogens.



The constants P_0 and m determined from a least square fit are 3769 bar and $0.071/^\circ\text{C}$. Thus we find that with increasing nematic range P_m decreases.

Since the P-T diagrams are known for several other reentrant nematogens, pure compounds as well as mixtures (Cladis *et al* 1978; Cladis 1980 and 1981; Shashidhar *et al* 1981), it is worthwhile to see if such a relation is valid in these cases also. The plot of $\ln P_m$ versus R for these substances is also shown in figure 4. These data again fall on a straight line (line B) but with a different slope. The constants for line B are $P_0 = 14050$ bar and $m = 0.140/^\circ\text{C}$. It is interesting to note that all the substances whose P_m data fall on line A have three phenyl rings while all those compounds whose P_m values fall on line B possess two phenyl rings. We therefore conclude that for a reentrant

Table 3. P_m of the reentrant nematogens

Compound	P_m (kbar)
11 CPMBB	0.55
12 CPMBB	2.50
11 CPMCB	0.29
12 CPMCB	1.05
11 CPM α MCB	0.19
12 CPM α MCB	1.35
11 CPMeO α MCB	1.14
12 CPMeO α MCB	3.45

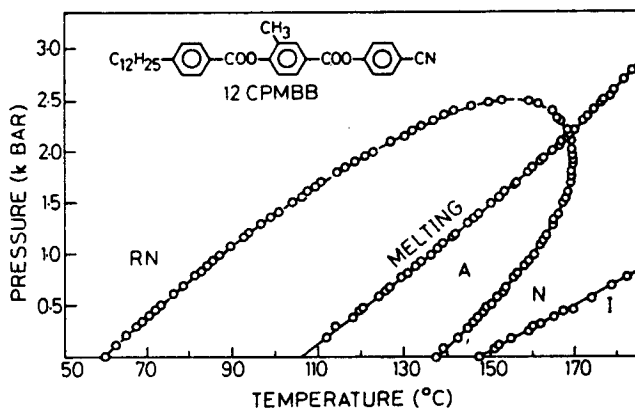


Figure 2. P-T diagram of 12 CPMBB, N-nematic, RN-reentrant nematic, A-smectic A.

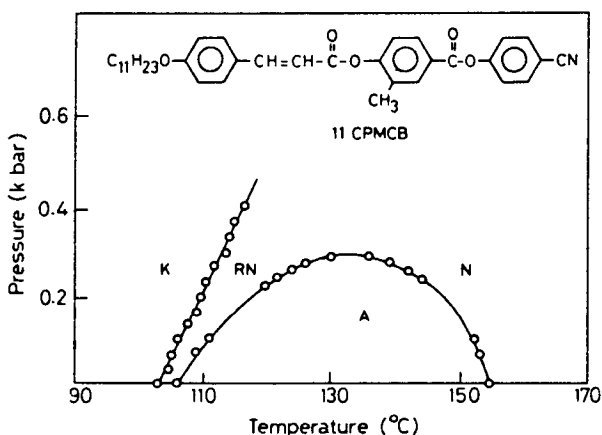


Figure 3. P-T diagram of 11 CPMCB, K-crystal. See also legend of figure 2.

nematogen P_m is uniquely related to the nematic range and hence the stability of the nematic ordering *vis-a-vis* the molecular structure (Kalkura *et al* 1983). Also the values of P_o for the lines A and B indicate that the smectic stability is greater for compounds with two phenyl rings compared to that of three phenyl ring compounds. Hence the formation of the reentrant nematic phase is more favoured for the latter compounds.

There have been some theoretical attempts to analyse the shape of the smectic A-nematic phase boundary and to understand the thermodynamics of the smectic A-reentrant nematic transition. Pershan and Prost (1979) have shown that the smectic A-reentrant nematic phase transition follows from the Landau theory if one assumes the existence of an optimum density for smectic ordering. A thermodynamic model has been developed by Clark (1979) and independently by Klug and Whalley (1979). They have shown that the general equation of the A-N phase boundary in the P-T plane when expressed as the difference in the Gibb's free energy between the nematic and smectic A phases is an equation to a conic. Using the data of Cladis on 8 oCB Clark has shown that the best fit of the experimental data is obtained with an

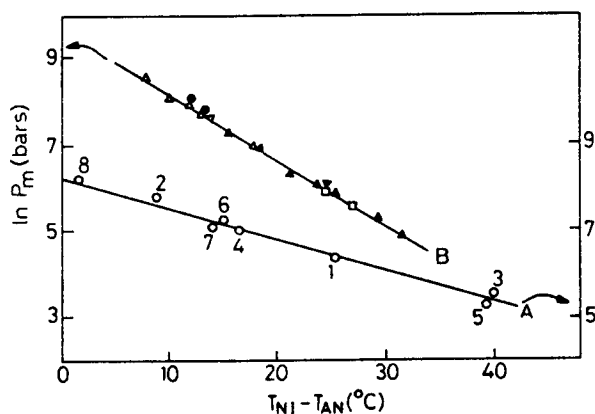


Figure 4. Plot of maximum pressure of smectic stability (P_m) versus range of the nematic phase ($T_{NI} - T_{AN}$) at 1 bar. The data points 1, 2, 3 etc. on line A are for three phenyl ring compounds (see table 3). The data points on line B are for two phenyl ring compounds which are not listed here (see text).

ellipse. We have ascertained that the fit of an ellipse to the data for all the compounds studied by us is very satisfactory. Figures 5 and 6 give two representative examples. The circles in these diagrams denote the data points while the solid curve represent the least square fit for the data points to the equation of an ellipse (Kalkura 1982).

2.2 Pressure behaviour of the nematic-isotropic ($N-I$) transition in reentrant nematic mixtures

So far we have discussed the effect of pressure on the A-N phase boundary of reentrant nematogens. In order to see if any special features are observed for the N-I transition at high pressures, we have carried out, by differential thermal analysis (DTA), a detailed investigation of the P-T curves of the N-I transition in binary mixtures of 8 OCB and

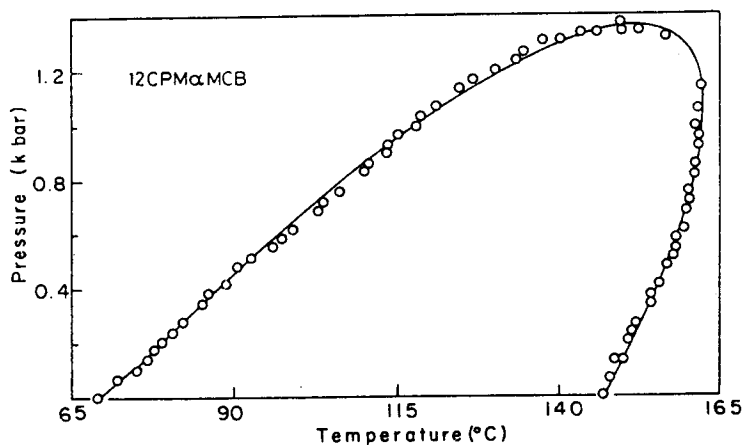


Figure 5. Computer fit of the data points for 12 CPM α MCB to the equation of an ellipse. The circles are experimental data points and the solid curve is the computer drawn curve.

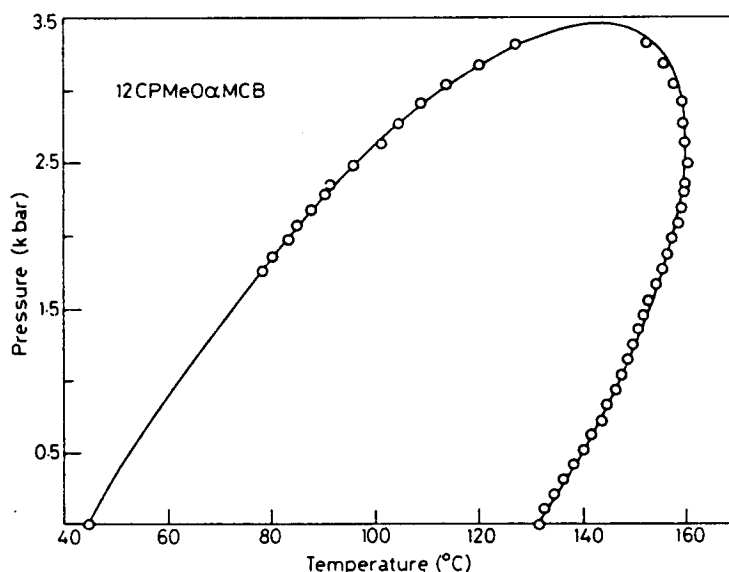


Figure 6. Computer fit of the data points for 12CPMeO α MCB to the equation of an ellipse.

4'-*n*-hexyloxy-4-cyanobiphenyl (6 OCB). In the DTA experiments the sample was sealed in an indium capsule so that it was completely isolated from the pressure transmitting medium. Pressures were measured to ± 5 bar and temperatures to $\pm 0.25^\circ\text{C}$.

The temperature-molar concentration ($T-X$) diagram evaluated at 1 bar for these mixtures is shown in figure 7. The reentrant nematic phase exists for $0.18 < X < 0.30$. In all, we have studied the N-I phase boundary for mixtures of 12 different concentrations as well as for the pure compounds. The $(dT/dP)_{1\text{ bar}}$ was evaluated from each of the P-T curves by a least square fit to the set of data points. The accuracy in the determination of dT/dP is $\pm 0.2\text{ K kbar}^{-1}$. Figure 8 shows the plot of dT/dP vs X (Shashidhar *et al* 1981). Considering that the N-I transition temperature at 1 bar evolves continuously (see figure 7) one would intuitively expect the dT/dP vs X curve also to show a smooth variation. But, as seen in figure 8 this is not the case and instead the curve exhibits an anomaly, the lowest value of dT/dP occurring at $X \approx 0.18$. The maximum drop in dT/dP (taken with respect to a smooth line joining the data points for the two pure compounds) is 2.1 K/kbar which is 10 times larger than the accuracy in the determination of dT/dP . Considering that these deviations occur only in the concentration range of occurrence of the reentrant nematic phase, it is natural to ascribe this anomaly to the presence of the smectic A and reentrant nematic phases at lower temperatures. This anomaly could also conceivably be due to kinetic effects. Subsequent experiments (Kleinhans *et al* 1982a) carried out very carefully under different thermal conditions of the sample, have ruled out kinetic effects. Hence this anomaly is essentially due to the influence of molecular ordering—due to smectic-like ordering or due to the presence of the reentrant nematic phase at lower temperatures or due to a combination of both.

We have subsequently studied the N-I transition in mixtures of 8 OCB and N-(4-*n*-cyanobenzylidene)-4'-octyloxy-aniline (CBOOA) whose temperature-concentration dia-

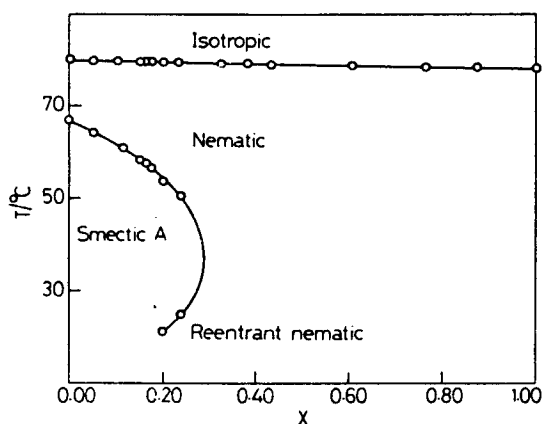


Figure 7. Temperature-concentration diagram of 6 OCB/8 OCB mixtures at 1 bar.

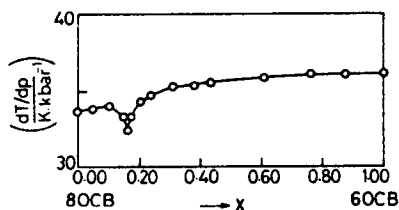


Figure 8. dT/dP vs X for the N-I transition of 6 OCB/8 OCB mixtures.

gram obtained at 1 bar is shown in figure 9. In this case both the pure compounds exhibit the smectic A and nematic phases while the reentrant nematic phase is exhibited over a range of concentration, *viz.* $0.26 < X < 0.78$, X being the mole fraction of CBOOA in the mixture. The dT/dP versus X curve for the N-I transition of the 8 OCB/CBOOA mixtures is given in figure 10 (Kleinhans *et al* 1982b). It is seen that there are two minima in the curve. Interestingly, these minima occur almost exactly at those concentrations at which the reentrant nematic phase makes its appearance at atmospheric pressure (see figure 9). It, therefore, appears that the changes in molecular ordering which accompany the formation of the reentrant nematic phase are manifested at much higher temperatures and affect thereby the pressure behaviour of the N-I transition.

3. A new multicritical point in a single component liquid crystal

The nematic-smectic A-smectic C multicritical point (hereafter referred to as the NAC point) is the point of intersection of the smectic C-smectic A, smectic A-nematic and smectic C-nematic phase boundaries. Such a point was first observed in the temperature-concentration (T - X) diagram of binary liquid crystal systems by Johnson *et al* (1977) and independently by Sigaud *et al* (1977). Subsequently more binary

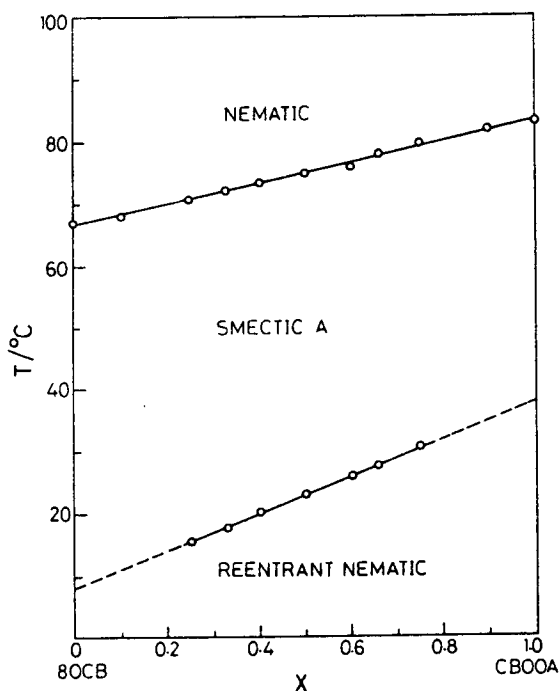


Figure 9. Temperature-concentration diagram of 8 OCB/CBOOA mixtures at 1 bar. X is the mole fraction of CBOOA.

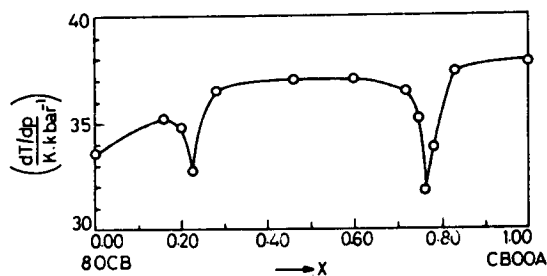


Figure 10. dT/dP for the N-I transition in 8 OCB/CBOOA mixtures vs the CBOOA concentration (X).

systems have been found which show the NAC point in the T-X diagram (Brisbin *et al* 1983). One of these diagrams is reproduced in figure 11. There have also been high resolution AC calorimetric (De Hoff *et al* 1981, 1982) and x-ray studies (Safinya *et al* 1981, 1983) which have initiated explicit comparisons with theoretical predictions (Chen and Lubensky 1976; Chu and McMillan 1977). We undertook pressure studies on a number of compounds with a view to observe a multicritical point in a single component liquid crystal. Our earlier results on N-(4-*n*-pentyloxybenzylidene)-4-*n*-hexylaniline showed that although the range of the A phase decreased with increase of pressure, the A phase continued to exist with a narrow range (about 0.4°C) up to

8 kbar (Shashidar *et al* 1980). The NAC point hence proved to be elusive. We have subsequently taken up pressure studies on another compound, *viz.*, 4(4-*n*-decyloxybenzoyloxy)benzylidene-4'-cyanoaniline (DOBBCA) and these studies have led to the observation of a new kind of multicritical point.

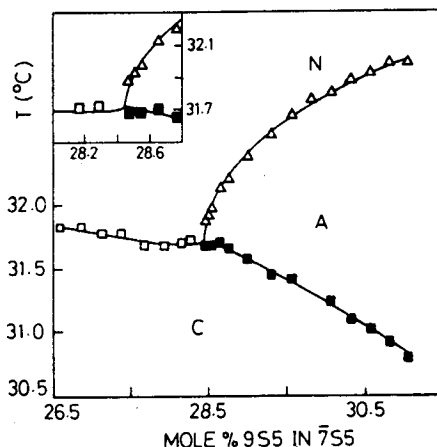


Figure 11. Temperature-concentration diagram of binary mixtures of 9S5 and 7S5. The point at which the C-A, A-N and C-N lines intersect is the NAC multicritical point. (From Brisbin *et al* 1983).

3.1 Results on DOBBCA

DOBBCA exhibits the nematic, smectic A, smectic C and reentrant nematic phases in that order on cooling from the isotropic phase. The high pressure experiments were conducted using the optical cell described in section A. There was however a significant improvement in the experiments conducted to locate the multicritical point, *viz* pressure was measured electronically and was continuously monitored during the experiment. The accuracy in the determination of pressure was ± 0.3 bar (compared to our earlier accuracy of ± 15 bar). We have followed only the reentrant nematic-smectic C (RN-C) and smectic C-smectic A (C-A) transitions as functions of pressure. Figure 12 gives the P-T diagram of DOBBCA showing these transitions (Shashidhar *et al* 1982a).

It is seen that the range of the smectic C phase decreases with increasing pressure until it is ultimately bounded resulting in the reentrant nematic-smectic C-smectic A (RN-C-A) point at 0.55 ± 0.01 kbar and $86.8 \pm 0.1^\circ\text{C}$. We also conducted high pressure DTA experiments to determine the nature of the transitions close to the RN-C-A point. All the transitions, *viz.*, RN-C, C-A and RN-A, were undetectable even at the maximum sensitivity of the set up and hence are presumed to be of second order. We have thus observed a new type of multicritical point.

We shall now consider the topology of the P-T diagram close to the RN-C-A multicritical point. Figure 13 shows an enlarged section of the P-T diagram in the

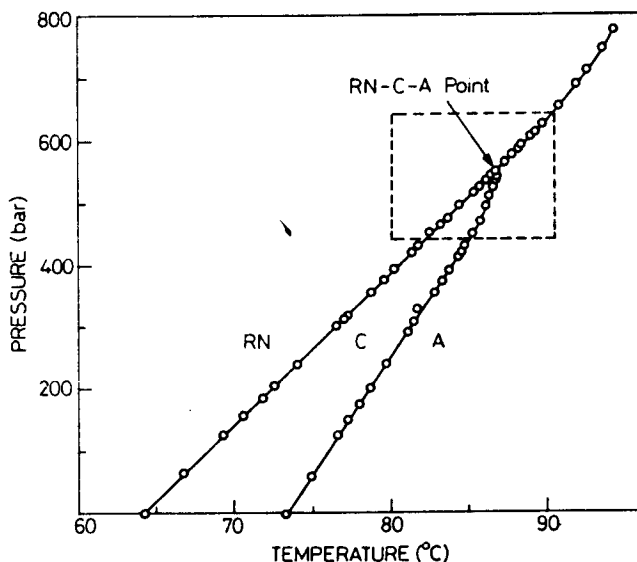


Figure 12. P-T diagram of DOBBA. The section of this diagram within the dashed lines is shown in figure 13 on an enlarged scale.

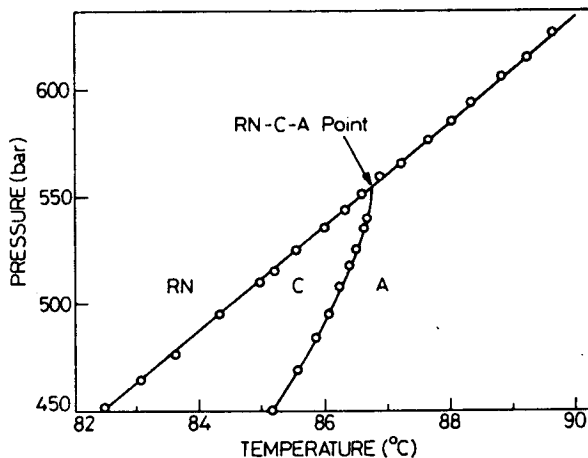


Figure 13. Enlarged section of the P-T diagram of DOBBA in the vicinity of the RN-C-A point.

vicinity of this point (Shashidhar *et al* 1982b). The following points are seen from the diagram: (i) The RN-C and RN-A boundaries are collinear at the RN-C-A point. The RN-A line continues to be straight till about 620 bars beyond which it starts showing a pronounced curvature towards the pressure axis (see figure 12); (ii) The C-A boundary is initially straight but exhibits a curvature as it approaches the RN-C-A point.

After the completion of these experiments we learnt that Sigaud *et al* (1982) have observed a similar RN-C-A point (they have referred to it as the *inverted NAC point*) in

the temperature-concentration (T-X) diagram of a binary liquid crystal system consisting of DOBBCA and 4-cyano-benzylidene-4'-(4"-decyloxybenzoyloxy) aniline. Figure 14 shows the T-X diagram obtained by them. Interestingly the topology of this diagram is very similar to that of our P-T diagram of DOBBCA.

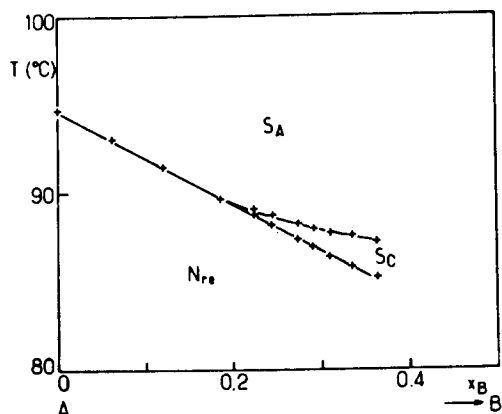


Figure 14. Binary phase diagram (at 1 bar) of mixtures of DOBBCA (B) in 4-cyanobenzylidene-4'-(4"-decyloxybenzoyloxy)aniline (A). (From Sigaud *et al* 1982).

It must be mentioned that very recently Brisbin *et al* have concluded, on the basis of their high resolution T-X diagrams, that the topology of the phase diagram in the vicinity of the NAC point is universal. They showed that N_A and N_C lines show universal singularities. In the RN-C-A multicritical point no such strong singularities are observed. Instead the nematic-smectic line is continuous. More systems exhibiting the RN-C-A point need to be studied both at high pressures and at atmospheric pressure to decide whether the RN-C-A diagram is also universal.

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