

## CHAPTER VII

### EXPERIMENTAL STUDIES ON TERMINALLY NON-POLAR MATERIALS

#### 7.1 INTRODUCTION

As discussed in the previous chapter reentrant nematic behaviour is exhibited generally by materials whose constituent molecules possess a strongly polar cyano or nitro end group.<sup>1</sup> However, recently Pelzl et al.<sup>2</sup> reported the observation of a reentrant nematic phase in binary systems whose constituent compounds do not possess a strongly polar terminal group. Several phase diagrams of terminally non-polar materials have been presented<sup>3-4</sup> which show a reentrant nematic phase. X-ray studies<sup>3,4</sup> on two binary systems appeared to show that the A phase below which reentrant nematic phase appears is of the monolayer type. On the other hand, in strongly polar systems  $N_{re}$  invariably occurs only below a partially bilayer ( $A_d$ ) phase. We therefore undertook accurate high pressure as well as X-ray studies on this binary system with a view to compare the behaviour of terminally non-polar reentrant materials with those of strongly polar systems. The results of these studies are presented in Section 7.2.

So far the partially bilayer ( $A_d$ ) phase has been observed only in compounds with a terminally polar cyano or nitro end group. However because of the reentrant behaviour of the terminally non-

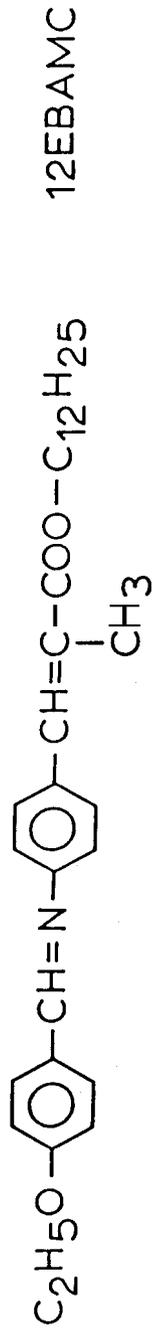
polar mixtures, it seemed reasonable to expect that this system may also exhibit the  $A_d$  phase. With this in view X-ray and high pressure studies have also been conducted on pure 12EBAMC (one of the components of the terminally non-polar reentrant nematic mixture referred to earlier). These studies have led to the first observation of the  $A_d$  phase in a terminally non-polar compound and are discussed in Section 7.3.

## 7.2 STUDIES ON A BINARY REENTRANT NEMATOGENIC MIXTURE OF TERMINALLY NON-POLAR MATERIALS

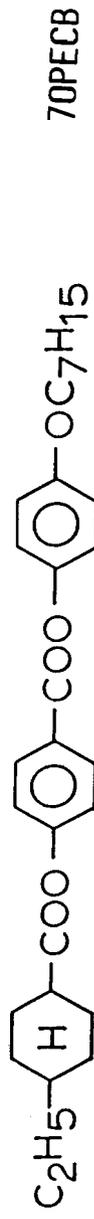
### A. Materials

The compounds constituting the binary mixture are n-dodecyl-4-(4-ethoxybenzylideneamino)- $\alpha$ -methyl cinnamate or 12EBAMC and 4-n-heptyloxyphenyl-4-(4-ethyl cyclohexanoyloxy) benzoate or 7OPECB. Their chemical formula as well as transition temperature are given in Fig. 7.1. It is seen that both compounds are terminally non-polar. 12EBAMC shows only a smectic A phase while 7OPECB exhibits nematic phase as well as smectic C phases.

The binary phase diagram of the 12EBAMC and 7OPECB system as reported by Pelzl et al.<sup>5</sup> is given in Fig. 7.2. It is seen that over a narrow region of 7OPECB concentration (between 40 - 45%) the reentrant nematic ( $N_{re}$ ) phase is exhibited although this is somewhat metastable owing to the A- $N_{re}$  transition occurring about 20°C below the melting temperature. We have selected for our study



K 69 A 81 I



K 61.5 C (41.5) N 183 I

Figure 7.1

Chemical structure of *n*-dodecyl-4-(4-ethoxybenzylideneamino)- $\alpha$ -methylcinnamate (12EBAMC) and 4-*n*-heptyloxyphenyl-4-(4-ethylcyclohexanoyloxy)benzoate (7OPECB).

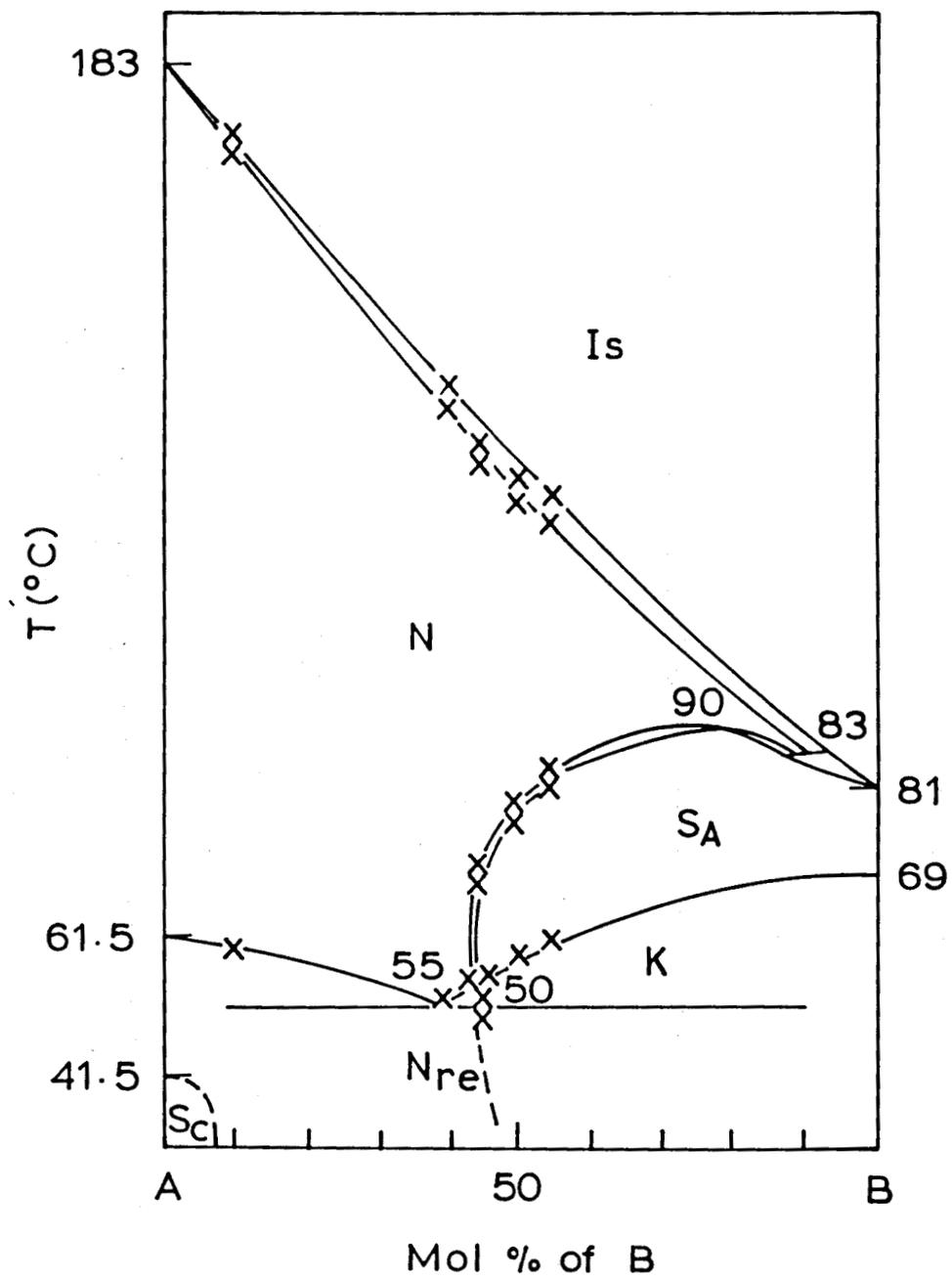


Figure 7.2

Temperature-concentration diagram of 12EBAMC and 7OPECB.  
(From Ref. 8).

a 44 mol % mixture. The transition temperatures of the mixture are isotropic-nematic: 132.5°C, nematic-smectic A: 68°C and smectic A-reentrant nematic: 42°C.

## B Results and Discussion

### X-ray Studies

The thermal variation of the layer spacing in the A phase of the reentrant nematic mixture (X = 44 mol%) is given in Fig. 7.3. The layer spacing (d) exhibits a small but continuous decrease with decrease in temperature throughout the A phase. The  $d/l$  value, calculated using the average molecular length for the mixture, comes out to be 1.03 at 65°C and reduces to 1.02 at 42°C. Thus it appears that the A phase of the mixture is probably of the  $A_d$  kind although owing to the uncertainty in the determination of  $d$ , the possibility of its being a monolayer A phase cannot be completely ruled out. It should also be remarked here that a pronounced cybotactic A-like ordering was observed in the  $N_{re}$  phase also, although this is not as strong as that seen in the  $A_d$  phase of DB9.0.NO<sub>2</sub> discussed in the previous chapter.

### High Pressure Studies

The pressure-temperature diagram for the mixture is given in Fig. 7.4. The diagram shows the following features:

- i) the A-N boundary has an elliptical shape. This has been confirmed by a computer-fit of the data to an ellipse;

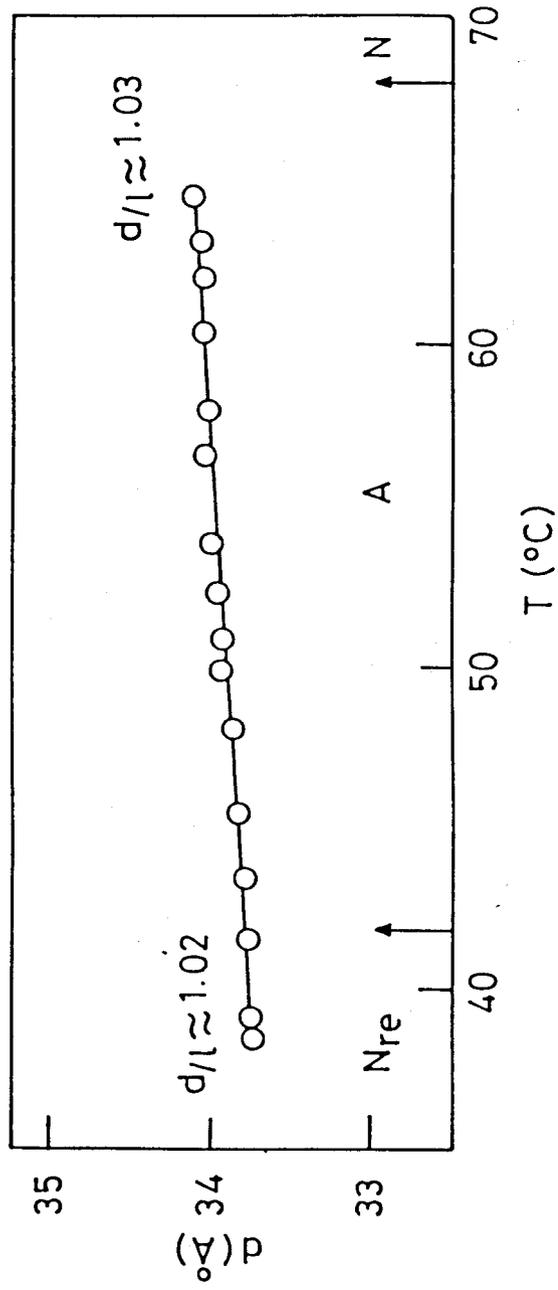


Figure 7.3

Thermal variation of the layer spacing for  $X = 44$  mol % of 12EBAMC.

Here arrow indicates the transition temperature.

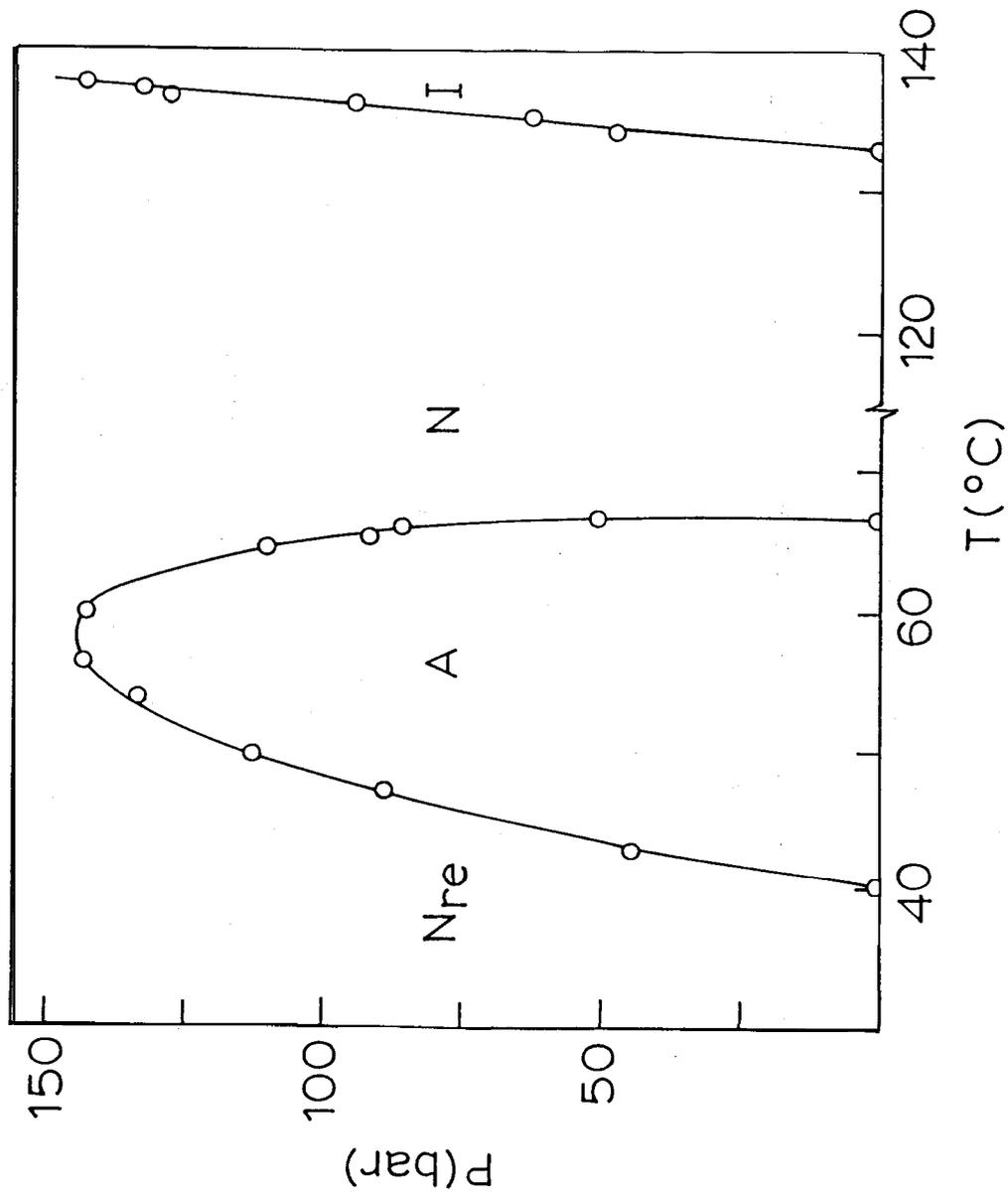


Figure 7.4

P-T diagram of X=44 mol % of 12EBAMC in 70PECB. The solid curves are obtained by computer-fits of the A-N data to an allipse and the N-I data to a straight line.

ii) the maximum pressure of smectic A stability ( $P_m$ ) is 0.14 kbar. Considering that monolayer A-nematic phase boundary is generally found to be linear,<sup>5,6</sup> the fact that the A phase of this mixture gets bounded under pressure supports our X-ray results that the A phase is probably a partially bilayer ( $A_d$ ) phase. Another notable feature of the P-T diagram is that the axis of the elliptical A - N curve has the same tilt ( $\sim 85^\circ$ ) as the nematic-isotropic (N-I) phase boundary indicating a strong coupling between smectic and nematic orders. Evidence of such a coupling has already been demonstrated in reentrant systems composed of terminally polar material. Thus the results of the high pressure studies on this reentrant nematogenic mixture consisting of terminally non-polar compounds are very similar to those observed for strongly polar reentrant systems.<sup>8</sup>

Recently, Dowell<sup>9</sup> has shown on the basis of a molecular lattice theory that dipolar interactions are not necessary for the appearance of the reentrant nematic phase. By considering the difference in the steric (hard-repulsive) packing of the rigid cores and the semiflexible chains it is possible to obtain stable smectic A and reentrant nematic phases in non-polar systems as well. The packing difference between the cores and the chains is predicted to force the molecules to form smectic A layers in certain ranges of temperature and pressure. Also it is expected that as

the temperature decreases tails become more rigid (i.e., rod-like) and the resulting packing becomes unfavourable for the smectic A phase. Consequently the smectic A phase disappears resulting in a reentrant nematic phase. Based on this model Dowell has also predicted that non-polar compounds can also exhibit partially bilayer type of smectic A phase. The results of our studies on 12EBAMC, presented below do in fact confirm the existence of the  $A_d$  phase in a terminally non-polar compound.

### 7.3 STUDIES ON N-DODECYL-4(ETHOXYBENZYLIDENEAMINO)- $\alpha$ -METHYL CINNAMATE (12EBAMC)

The structural formula of 12EBAMC, a terminally non-polar material has already been given in Fig. 7.1. It exhibits a smectic A phase, but no nematic phase. We have conducted X-ray and high pressure studies on this material. The results of these investigations will be presented here. Fig. 7.5 shows the variation of the layer spacing ( $d$ ) with temperature in the A phase of 12EBAMC. The value of  $d$  decreases slightly with decrease of temperature, from  $40.5 \text{ \AA}$  at  $75^\circ\text{C}$  to  $39.9$  at  $50^\circ\text{C}$ . This corresponds to a decrease in  $d/l$  from 1.13 to 1.11, where  $l$  is the length of the fully stretched molecule measured using a Dreiding model. Thus the A phase in this material can be classified as the partially bilayer ( $A_d$ ) phase. It is interesting that the  $d/R$  ratio of 12EBAMC is comparable with that seen for many compounds with a cyano end group.<sup>10,11</sup> In the case of terminally polar compounds the ratio

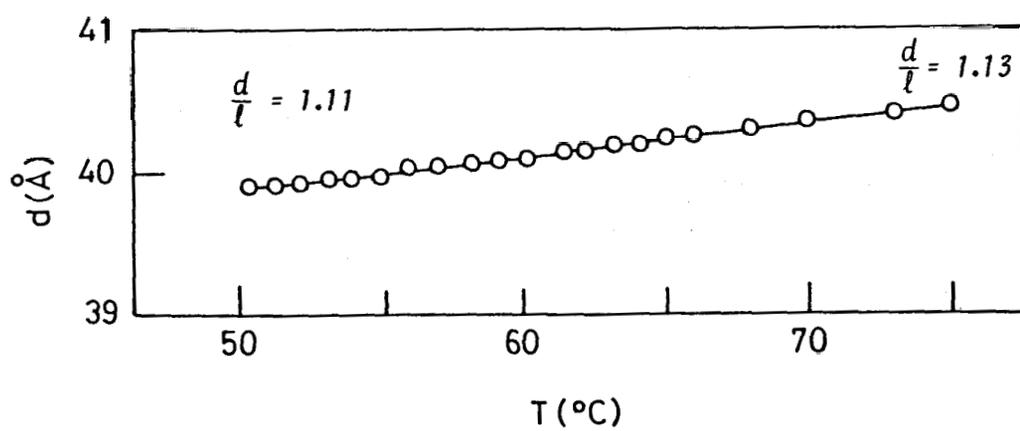


Figure 7.5

*Thermal variation of the layer spacing of 12EBAMC in the smectic A phase.*

$\frac{d}{\ell} > 1$  is known to arise from molecular association, which has been interpreted due to a monomer-dimer equilibrium.<sup>12,13</sup> The results of our X-ray investigations show that similar association effects, should play an important role in the case of 12EBAMC also. As far as we are aware, this is the first observation of the  $A_d$  phase in a terminally non-polar compound.

#### High Pressure Studies

Since a large number of terminally polar materials exhibiting the  $A_d$  phase show reentrant behaviour at high pressure<sup>14</sup> we undertook the study of the pressure-temperature (P-T) diagram of 12EBAMC and is shown in Fig. 7.6. At low pressures the P-T diagram shows only the smectic A - isotropic transition. A nematic phase gets induced at high pressures leading to a smectic A - nematic - isotropic triple point at 0.45 kbar, 87.2°C. We have identified the induced phase as the nematic phase by optical microscopic observations at high pressures. Similar instances of a pressure-induced nematic phase appearing in smectogenic materials have been reported earlier.<sup>15,16</sup> It is clear from the diagram that the range of the pressure-induced nematic phase increases with increasing pressure and the A-N phase boundary is a straight line right up to the maximum pressure studied and hence there was no evidence of any reentrant nematic behaviour at low temperatures.

Thus, our studies have shown that a terminally non-polar

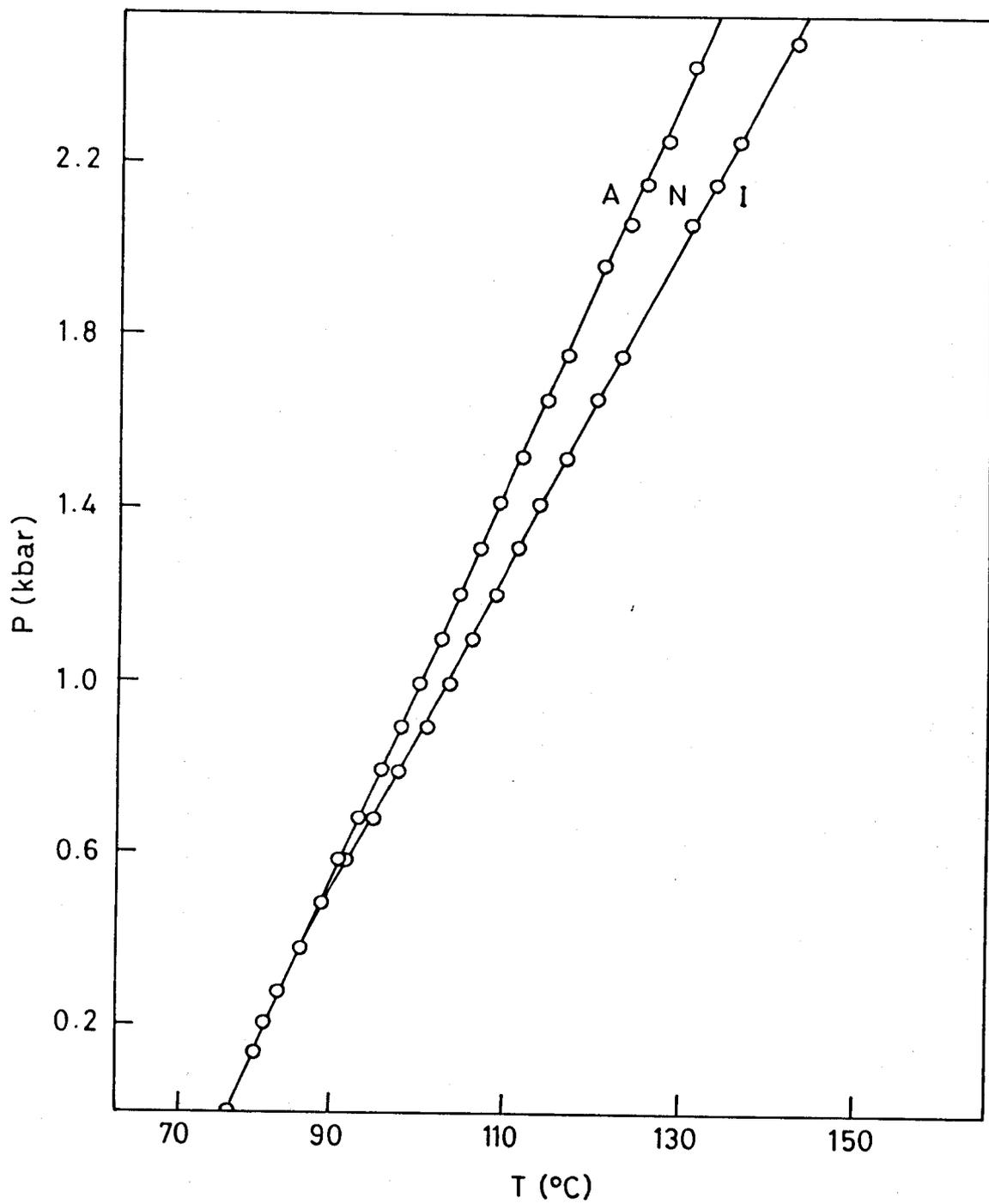


Figure 7.6

*P - T diagram of 12EBAMC.*

compounds can exhibit a partially bilayer phase  $A_d$  with a  $d/R$  ratio comparable with those observed in strongly polar systems. The stability of this  $A_d$  phase is found to be unaltered at high pressures. Further studies on other terminally non-polar substances will be of interest.

## REFERENCES

- 1 For a review of strongly polar materials exhibiting reentrant nematic behaviour, see Nguyen Huu Tinh, *J. Chim. Phys.*, 80, 83 (1983)
- 2 G.Pelzl, S.Diele, I.Latif, W.Weissflog and D.Demus, *Cryst. Res. & Technol.*, 17, 78 (1982)
- 3 G.Pelzl, I. Latif, S. Diele, M.Novak, D.Demus and H.Sackmann, *Mol. Cryst. Liq. Cryst.*, 139, 333 (1986)
- 4 S. Diele, G. Pelzl, I. Latif and D.Demus, *Mol. Cryst. Liq. Cryst.*, 92, 27 (1983)
- 5 P.E.Cladis, in "Liquid Crystals", Proc. Int. Conf., Bangalore, Ed. S.Chandrasekhar (Heyden, London, 1980), p. 105.
- 6 S.Krishna Prasad, R.Shashidhar, A.N.Kalkura, K.A.Suresh, G.Heppke and R.Hopf, *Mol. Cryst. Liq. Cryst.*, 99, 185 (1983)
- 7 R.Shashidhar, S.Somasekhar and B.R.Ratna, *Mol. Cryst. Liq. Cryst.*, 133, 19 (1986)
- 8 A.N.Kalkura, R.Shashidhar and M.S.Urs, *J. de Phys.*, 44, 51 (1983)
- 9 F.Dowell, *Phys. Rev. A*, 31, 2464 (1985); *ibid*, 31, 3214 (1985)
- 10 A.M.Levelut, F.Hardouin and G.Sigaud, in "Liquid Crystals", Proc. Int. Conf., Bangalore, Edited by S.Chandrasekhar (Heyden, London, 1980), p. 148.

- 11 K.A.Suresh, R.Shashidhar, G.Heppke and R.Hopf, *Mol. Cryst. Liq. Cryst.*, 99, 249 (1983)
- 12 S.Diele, U. Baumeister and D.Demus, *Z. Chem.*, 21, 27 (1981)
- 13 L.Longa and W.H. de Jeu, *Phys. Rev.*, A26, 1632 (1982)
- 14 See e.g., S.Krishna Prasad, S.Pfeiffer, G.Heppke and R.Shashidhar, *Z. Naturforsch.*, 40a, 632 (1985) and references cited therein.
- 15 P.E.Cladis, D.Guillon, W.B.Daniels and A.C.Griffin, *Mol. Cryst. Liq. Cryst. Lett.*, 56, 89 (1979)
- 16 J.Herrmann, H. D. Klienhaus and G.M.Schneider, *J. Chim. Phys.*, 80, 111 (1983).