

CHAPTER IV

ANALYSIS OF THE SMECTIC A - NEMATIC PHASE BOUNDARY OF REENTRANT NEMATOGENS

4.1 Introduction

As mentioned in the previous chapter, Gladis ¹ made the observation that in a pure compound of 4-n-octyloxy-4'-cyanobiphenyl (8 OCB), the smectic A - nematic (or A-H for short) phase boundary curls around in the P-T plane so that at sufficiently high pressures, i.e., in the range of 1.6 to 1.8 kbar, smectic A to nematic phase transition is obtained upon both cooling and heating a smectic A phase. The main features of the P-T diagram of 8 OCB are that there is a maximum pressure P_m up to which the smectic A phase exists and that the smectic A - nematic phase boundary has an elliptic shape. This behaviour represents an exciting departure from the normally observed A - N phase boundary and presents an excellent opportunity to correlate the experimental results with the phenomenological theories based on the molecular structures.

Pershan and Prost² have shown that smectic A to

reentrant **nematic phase transition** follows from the Landau theory, if one assumes the existence of an **optimum density** for smectic ordering. Recent high resolution X-ray experiments of Kortan et al.³ strongly support* this concept of 'optimum density'. Extending the McMillan's treatment of the smectic A phase, Luckhurst and Timini⁴ have developed the molecular theory for the reentrant nematic and smectic A **mesophases**.

Clark⁵ and independently Klug and Whalley⁶ analysed the shape as well as the thermodynamics of the smectic A - nematic **phase** boundary in the P-T plane. We shall briefly discuss the thermodynamic model of Clark which accounts for the elliptical **shape** of the phase boundary and thus facilitates the determination of the ratios of the various thermodynamical parameters determining the phase boundary. We shall see how the data for eight compounds studied by us can be analysed on the basis of the thermodynamical model developed by Clark.

4.2 Thermodynamics of smectic A - nematic phase transition

Let us begin with a qualitative analysis of the P-T diagram of 8 CB shown in figure 4.1. Along the phase boundary, the molar Gibbs free energy difference between

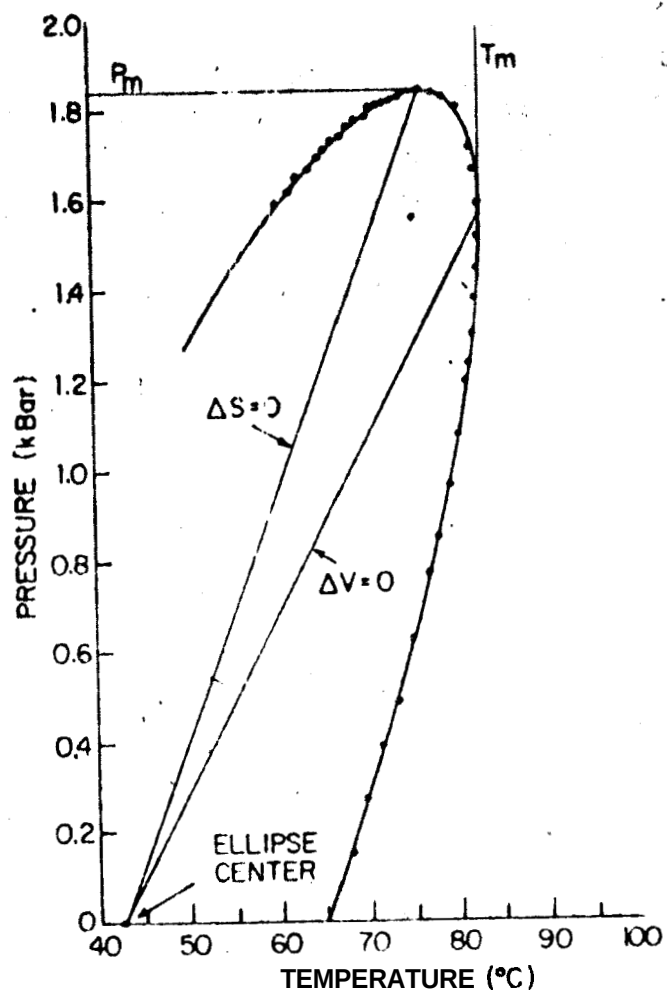


Figure 4.1: Smectic A - nematic (AN) phase boundary of 8 OCB. Solid curve represents the best fit of an ellipse to the data of Gladis et al¹ (after Clark⁵).

the nematic and smectic A phases, viz., $\Delta G = G_N - G_A$ is zero and the Clausius-Clapeyron equation may be applied. Therefore, we have

$$\left(\frac{\delta P}{\delta T}\right)_{\Delta G=0} = \left(\frac{S_N - S_A}{V_N - V_A}\right)_{\Delta G=0} = \left(\frac{\Delta S}{\Delta V}\right)_{\Delta G=0} \quad (1)$$

where ΔS and ΔV represent the difference in the molar entropy and volume between the nematic and smectic A phases respectively. Usually, the smectic A to nematic phase transition at atmospheric pressure is one of first order, and hence the change in the entropy during the phase transition, i.e., $\Delta S > 0$ is a reasonable assumption. Since from figure 4.1, $(\delta P/\delta T)_{\Delta G=0}$ is positive at $P = 1$ bar, we must have $\Delta V > 0$ at atmospheric pressure. As the pressure is increased, $(\delta P/\delta T)_{\Delta G=0}^{-1}$ approaches zero and then changes sign, thereby implying that $\Delta V = 0$ at 1.6 kbar and at 83°C and becomes negative at higher pressures. Defining the compressibility of a phase as $\beta = (\partial V/\partial P)_T$, one can conclude from the above that $\Delta\beta = \beta_N - \beta_A$ is negative. Since, both β_N and β_A are negative, we have $|\beta_N| > |\beta_A|$. If we continue around the phase boundary $(\delta P/\delta T)_{\Delta G=0}$ approaches zero and changes sign. This implies that ΔS goes through zero ($\Delta S = 0$ at $P = P_m = 1.84$ Kbar, $T = 77^\circ\text{C}$) and becomes

negative. Therefore, both ΔS and ΔV are negative in the reentrant portion of the phase boundary. Since the specific heat $C_p = T(\partial S/\partial T)_p$, the fact that ΔS decreases with decreasing temperature implies that the difference in the specific heat between the nematic and smectic A phases at the phase boundary, i.e., $\Delta C_p = C_{pN} - C_{pA}$ is positive, hence we have $\Delta C_{pN} > \Delta C_{pA}$.

The shape of the phase boundary may be quantitatively related to the thermodynamic parameters of the two phases by obtaining an expression for the pressure and temperature dependence of the difference in the Gibbs free energy between the nematic and smectic A phases, i.e., expressing ΔG in terms of P and T . In the vicinity of some reference point (P_0, T_0) , ΔG may be expressed in Taylor's series as

$$\begin{aligned} \Delta G = \Delta G_0 + \Delta V_0(P - P_0) - \Delta S_0(T - T_0) + \frac{\Delta \beta}{2}(P - P_0)^2 \\ + \Delta \alpha(P - P_0)(T - T_0) - \frac{\Delta C_p}{2T_0}(T - T_0)^2 + \dots \end{aligned} \quad (2)$$

where the following notations are used

$$\begin{aligned} \Delta G &= G_N - G_A \\ \Delta S &= S_N - S_A = -(\partial \Delta G / \partial T)_P \\ \Delta V &= V_N - V_A = (\partial \Delta G / \partial P)_T \end{aligned} \quad (3)$$

$$\Delta G_o = \Delta G(P_o, T_o)$$

$$\Delta S_o = \Delta S(P_o, T_o)$$

$$\Delta V_o = \Delta V(P_o, T_o)$$

$$\Delta \beta = (\partial \Delta V / \partial P)_T = (\partial V_N / \partial P)_T - (\partial V_A / \partial P)_T$$

$$\Delta \alpha = (\partial \Delta V / \partial T)_P = -(\partial \Delta S / \partial P)_T$$

$$\Delta C_p = T(\partial \Delta S / \partial T)_P$$

In expression (2), the higher order terms have been neglected which implies that $\Delta \beta$, Δa and ΔC_p are assumed to be sufficiently independent of P and T over the range of pressures and temperatures under consideration here. It shall be seen later that this assumption is reasonable. The nematic-smectic A (A-N) phase boundary in the P-T plane is obtained from the equation (2) by setting ΔG to zero and solving for P(T). Expanding and rearranging equation (2), we have,

$$aP^2 + bT^2 + cPT + dP + eT + f = 0 \quad (4)$$

where

$$\begin{aligned} a &= \Delta \beta / 2 \Delta G_o \\ b &= -\Delta C_p / 2 T_o \Delta G_o \\ c &= \Delta \alpha / \Delta G_o \\ d &= -(\Delta \beta / \Delta G_o) P_o - (\Delta \alpha / \Delta G_o) T_o = -2aP_o - cT_o \end{aligned} \quad (5)$$

$$\begin{aligned}
 e &= (\Delta C_p / \Delta G_o) - (\Delta \alpha / \Delta G_o) P_o = -2bT_o - cP_o \\
 f &= 1 + (\Delta \beta / 2 \Delta G_o) P_o^2 + (\Delta \alpha / \Delta G_o) P_o T_o - (\Delta C_p / 2 \Delta G_o) T_o \\
 &= 1 + aP_o^2 + cP_o T_o + bT_o^2 .
 \end{aligned}$$

Equation (4) is the general equation for a conic section. Thus P-T phase boundaries are at least locally expressible as conic sections and in systems, apparently like the ones under considerations, where $\Delta C_p, \Delta \alpha$ and $\Delta \beta$ do not depend strongly on P and T, the phase boundaries will have the shape of conic sections over a large area in the P-T plane. Elliptical phase boundaries will be obtained from equation (4) if

$$\left| \frac{T_o \Delta \alpha^2}{\Delta \beta \Delta C_p} \right| < 1$$

The shape of the nematic - smectic A phase boundary for 8 OCB as shown in figure 4.1 appears to be elliptical. The fit of the data of Cladis to an ellipse was therefore attempted by Clark.⁴ It would, first appear that such a fit involves the varying of eight independent parameters, namely, $\Delta \beta, P_o, \Delta \alpha, T_o, \Delta C_p, \Delta V_o, \Delta S_o$ and ΔG_o . However, since the choice of the reference point is arbitrary, (Clark selected the reference point as the centre of the

fitted ellipse. At this point ΔG_0 is maximum and hence the first derivative of ΔG namely ΔV_0 and ΔS_0 are zero. This effectively eliminates four parameters P_0 , T_0 , ΔV_0 and ΔS_0 . The fitted ellipse will then be characterised by three quantities, the lengths of its major and minor axis, and θ_0 , the angle of orientation of the major axis relative to the temperature axis. one is therefore left with three equations and four unknown quantities, viz., $\Delta\alpha$, $\Delta\beta$, ΔC_p and ΔG_0 , and thus allowing the determination of ratios among any two of these four quantities.

The fit of an ellipse to the data of Gladis et al is shown in figure 4.1 and it is excellent, which therefore, verifies the assumption that $\Delta\alpha$, $\Delta\beta$ and ΔC_p are reasonably constant over the area covered by the phase boundary in the P-T plane. This fit yields the following ratios:

$$\begin{aligned}\Delta\alpha/\Delta\beta &= -0.7930 \text{ cal/cc} \times ^\circ\text{C} \\ \Delta\beta/\Delta C_p &= -0.019 \text{ cc}^2 \times ^\circ\text{C/cal}^2 \\ \Delta\alpha/\Delta C_p &= 15.0 \times 10^{-3} \text{ cc/cal.}\end{aligned}$$

with $P_0 = 4.0$ bars and $T_0 = 42.85^\circ\text{C}$ $\theta_0 = 49.4^\circ$, and

$$\left| \frac{\Delta\alpha^2 T_0}{\Delta\beta \Delta C_p} \right| = 0.51 .$$

While calculating the ratios, following unite have been used.

P (cal/cc), G (cal/mole), V (cc/mole),
 S (cal/mole°C), a (cc/mole°C), β (cc²/mole cal)
 and C_p (cal/mole°C).

4.3 Fit of our data for the various reentrant nematogens

We shall now try to fit the data for the eight reentrant nematogens studied by us and also our data on 8 OCB to the equation to an ellipse. For the sake of simplicity of computation, we have reduced the number of constants in equation (4) by dividing throughout by f, so that equation (4) now reduces to the form

$$a'P^2 + b'T^2 + c'PT + d'P + e'T + 1 = 0 \quad (6)$$

where $a' = a/f$, $b' = b/f$, $c' = c/f$ and so on. The computation have been carried out by using a PDP-11 computer. The constants a' , b' , c' , d' and e' evaluated by least square fit of the data to equation (6) are given in Table 4.1. Using the constants given in Table 4.1 the various thermodynamic parameters $\Delta\alpha/\Delta\beta$, $\Delta\alpha/\Delta C_p$, $\Delta\beta/\Delta C_p$, P_0 and T_0 have been evaluated. These data are given in Table 4.2. This table also gives $|T_0\Delta\alpha^2/\Delta\beta\Delta C_p|$ which

should be less than one for the smectic A - nematic phase boundary is to be an ellipse. It is seen that this is indeed so for all the compounds studied.

The fit of the data to an ellipse for various reentrant compounds studied by us are given in figures 4.2 to 4.10, which have been drawn using Hewlett-Packard programmable calculator with a plotter attachment. The circles denote the data points while the solid curve represents the best fit for the data points to the equation to an ellipse, i.e., the curve obtained by using the constants a' , b' , c' , ... listed in table 4.1.

It is therefore seen that for all reentrant nematogens whether they show reentrant nematic phase at one bar or only at elevated pressures, the smectic A - nematic phase boundary in the P-T plane is characterised by the elliptic shape.

As the centre of the fitted ellipses fall in the smectic A phase, ΔG_0 is positive. Hence from the qualitative analysis of the smectic A - nematic phase boundary, we have $\Delta C_p > 0$ and $\Delta \beta < 0$. Therefore, the entropy and the volume differences between the nematic and the smectic A phases for any value of pressure and

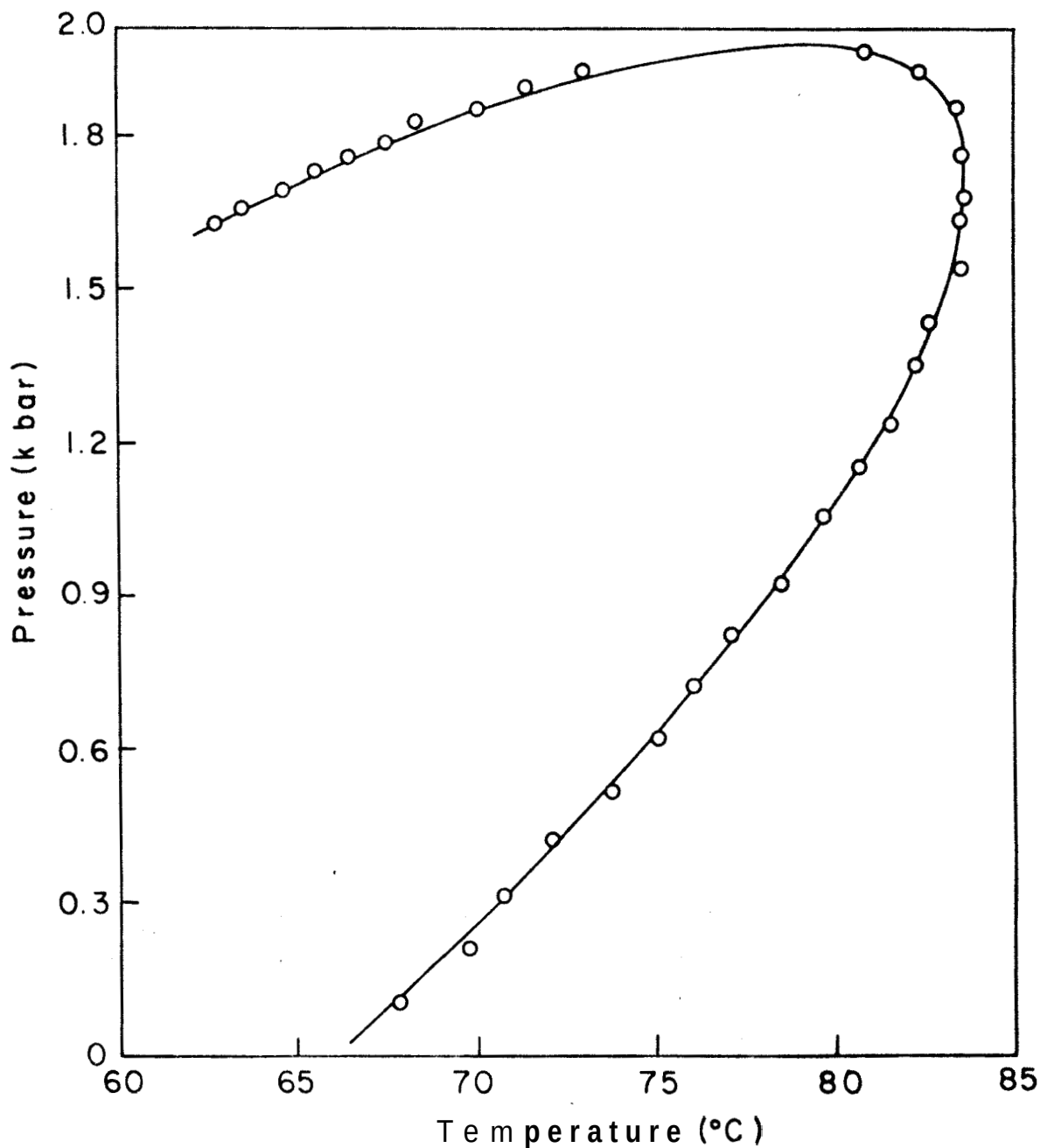


Figure 4.2: AN phase boundary of 8 OCB in the P-T plane. In This as well as the following diagrams the solid ~~is~~ curve represents the best fit of the data points to an ellipse, O represents experimental data points.

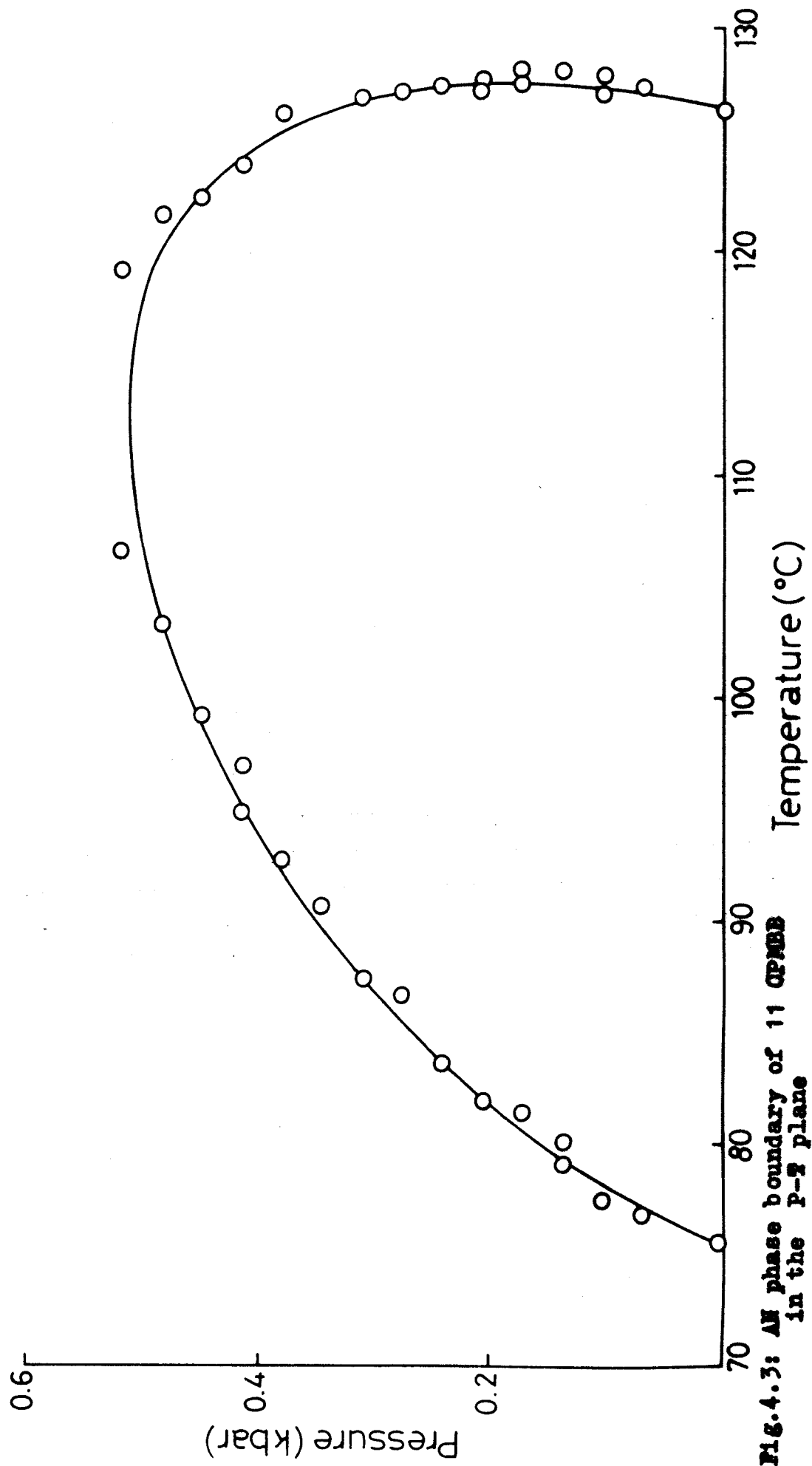


Fig. 4.3: All phase boundary of 11 OPMBB in the P-T plane

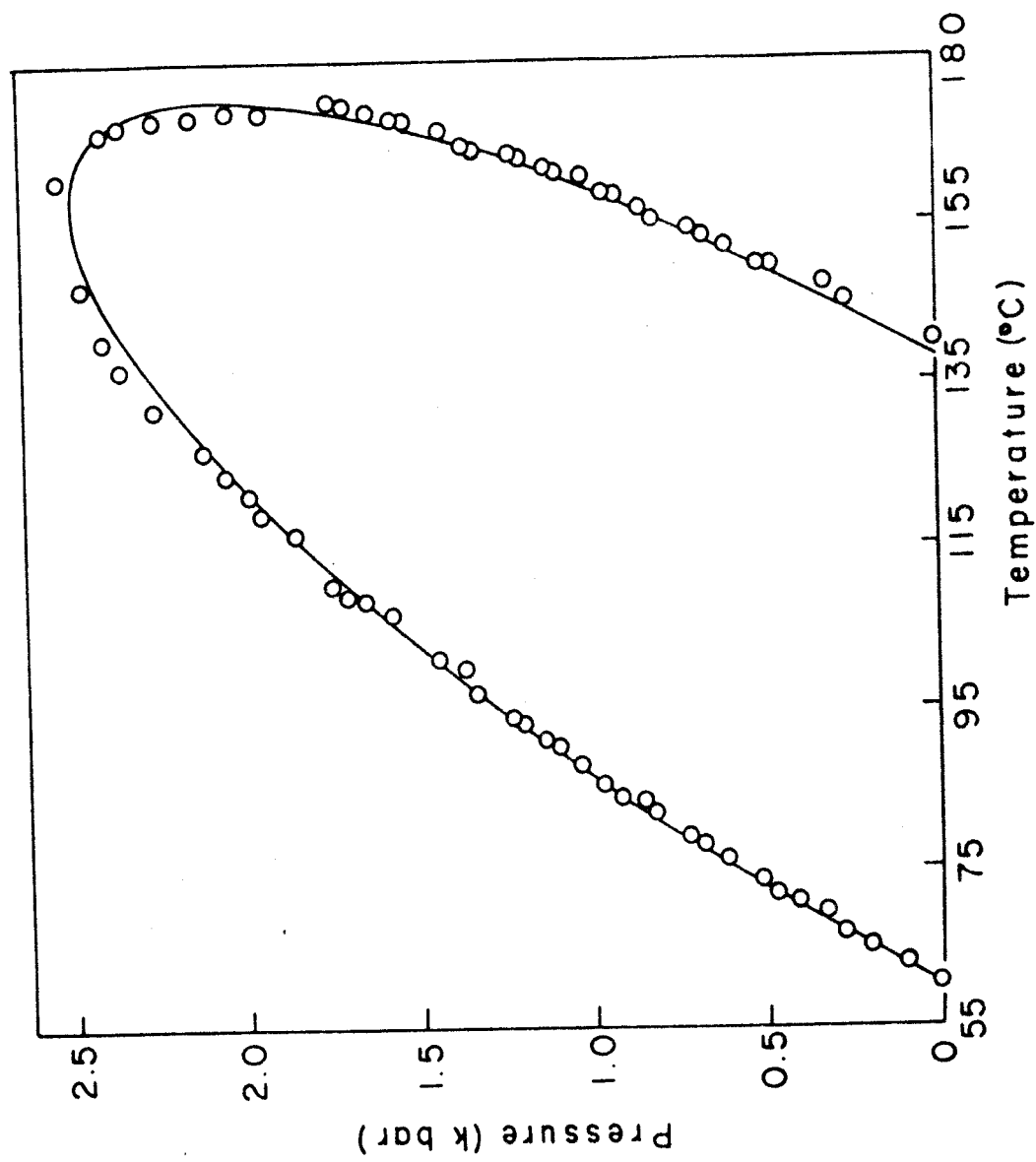


Figure 4.4: AN phase boundary of 12 OPMBB in the P-T plane

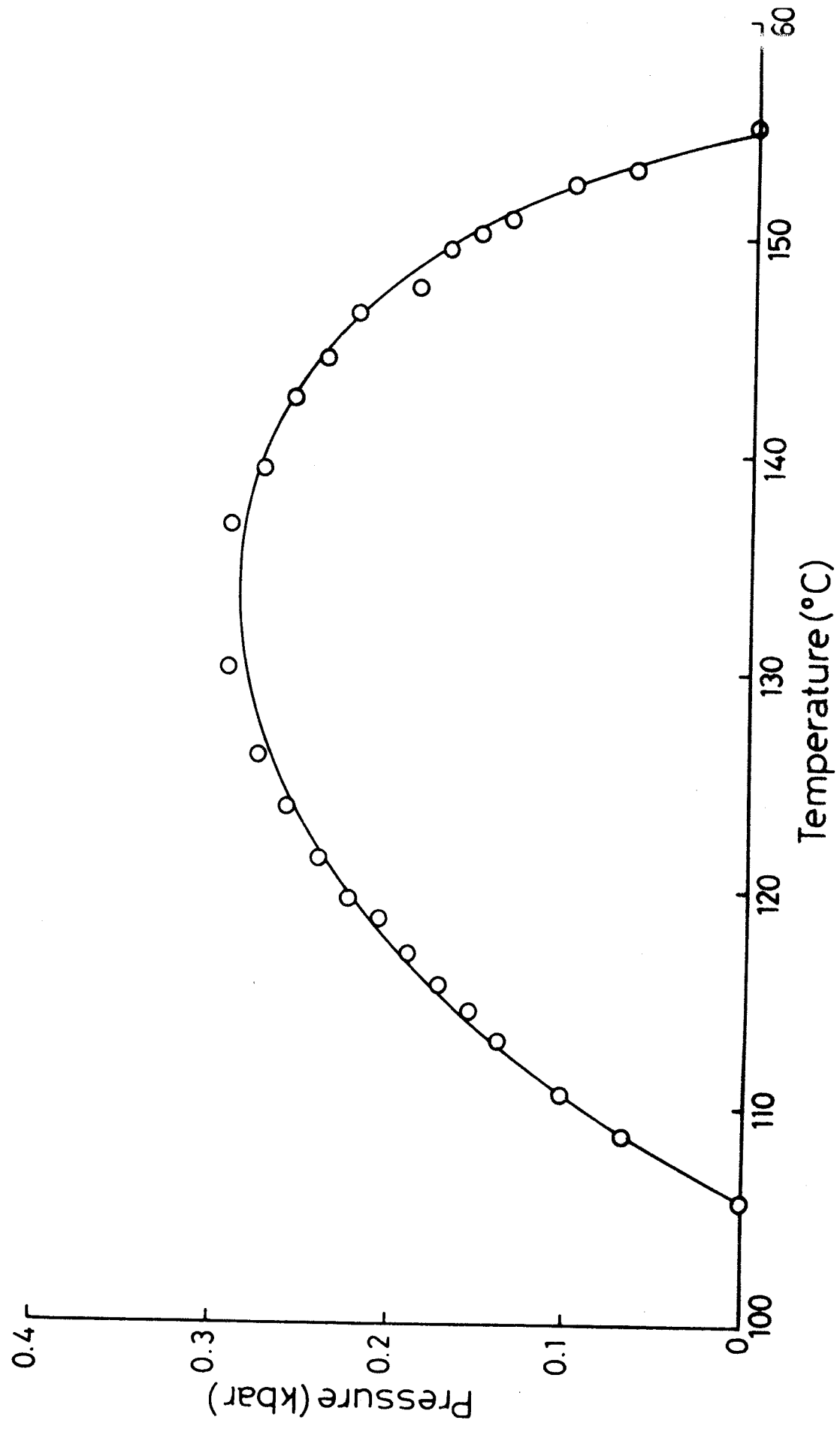


Figure 4.5: AM phase boundary of 11 OPNOB in the P-T plane

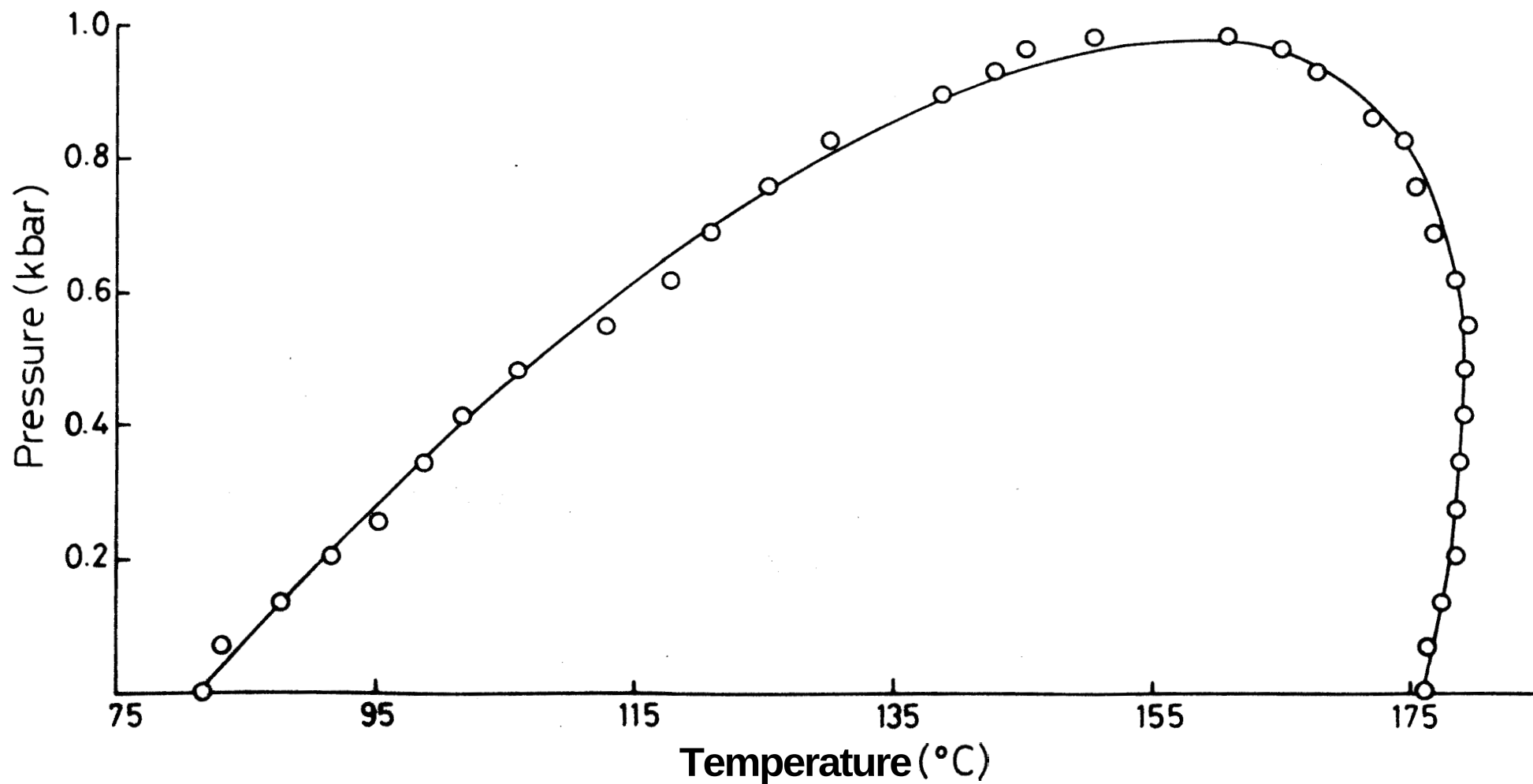


Figure 4.6: AN phase boundary of 12 OPMOB in the P-T plane

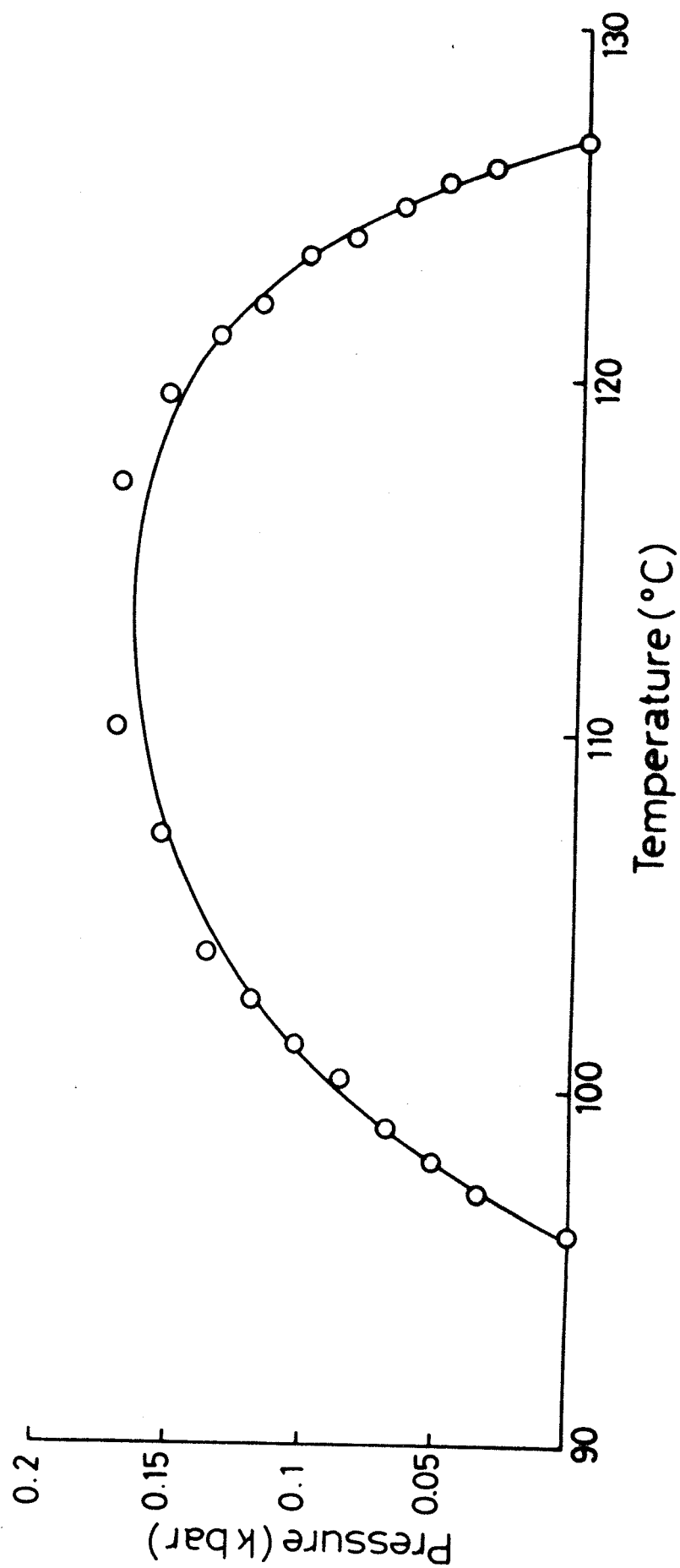


Figure 4.7: AN phase boundary of 11 QPMNOB in the P - T plane

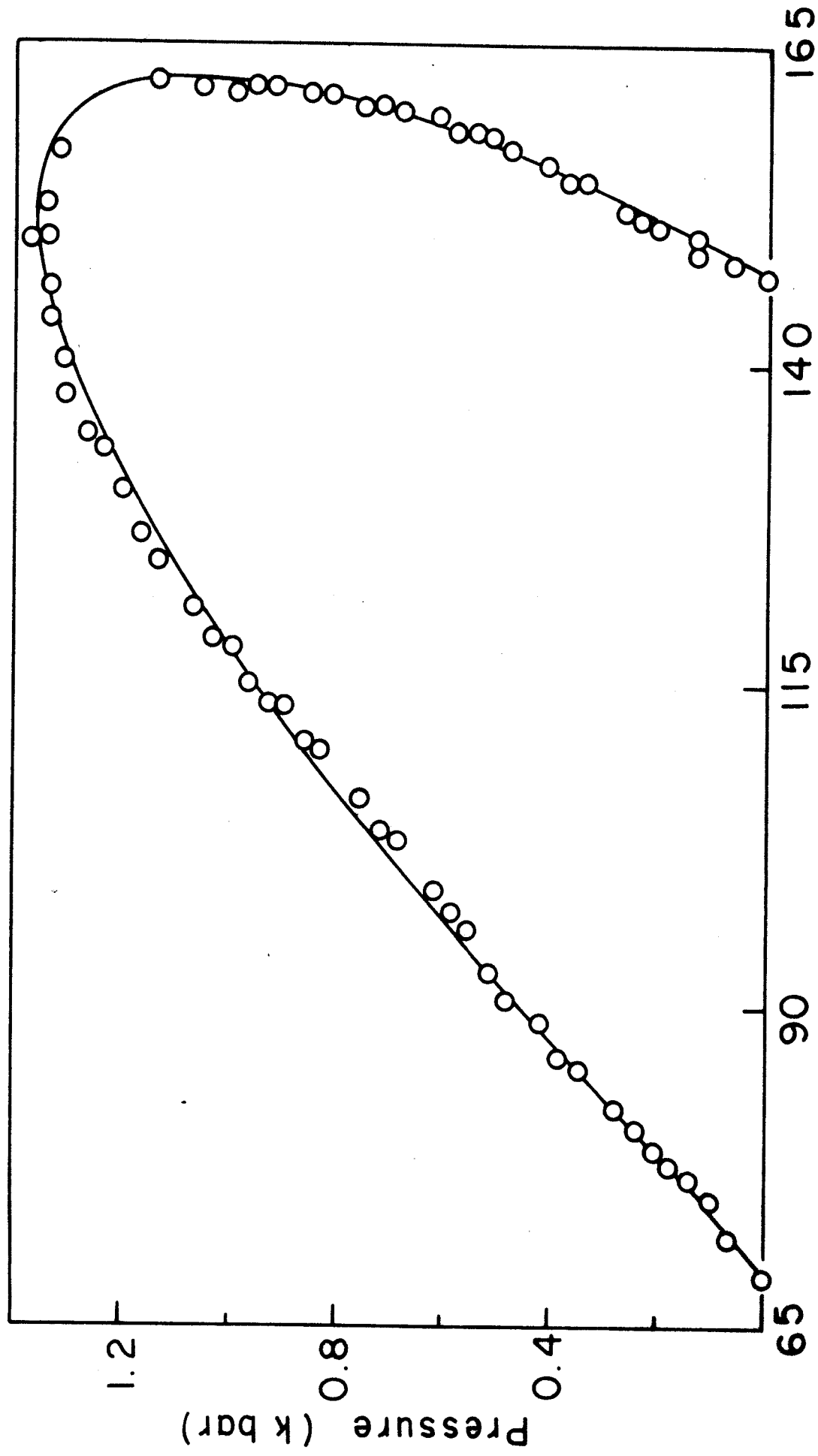


Figure 4.8: AM phase boundary of 12 OPMaMOB in the P-T plane

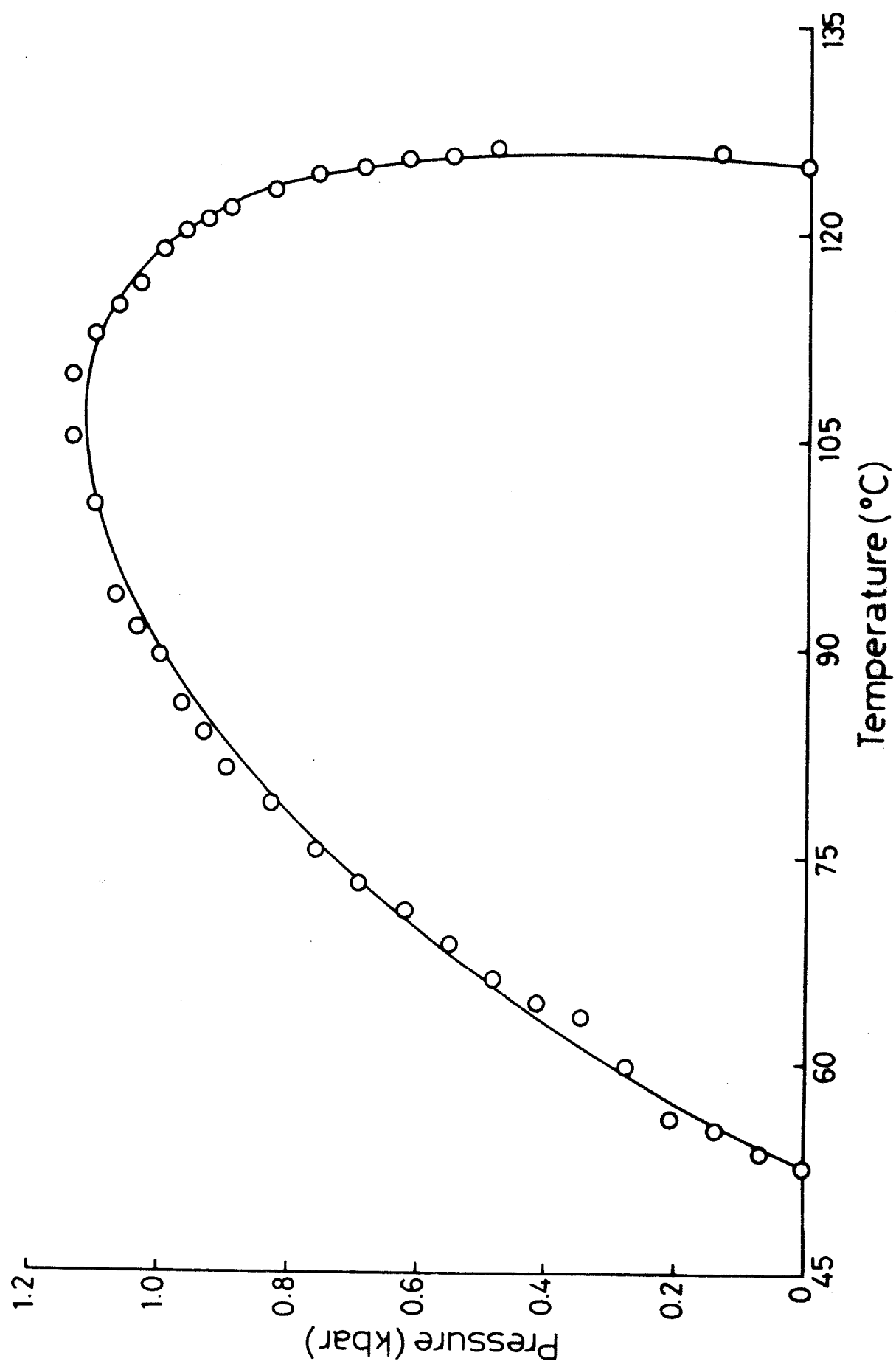


Figure 4.9: AM phase boundary of 11 CPMeOxMB in the P-T plane

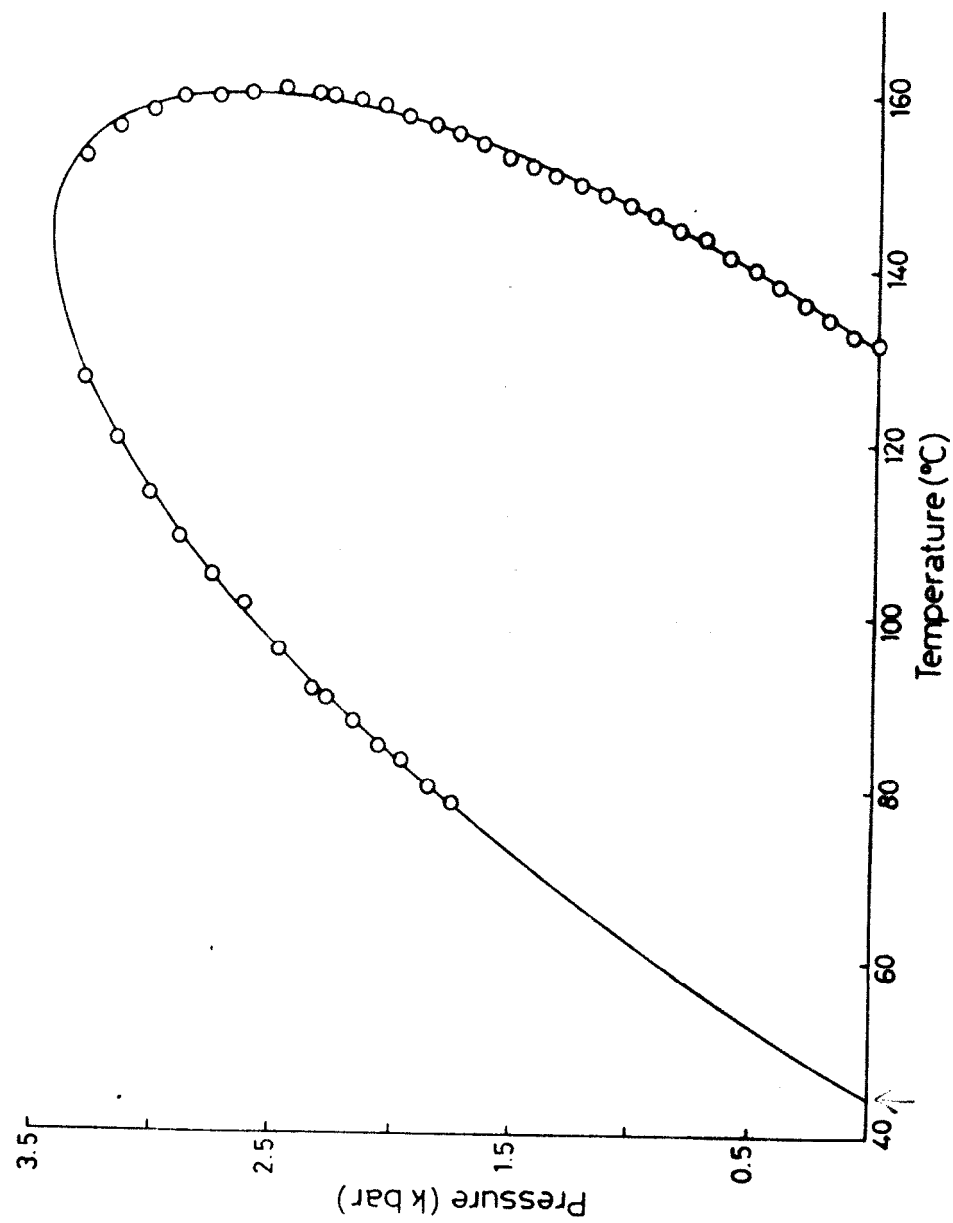


Figure 4.10: AM phase boundary of 12 OPMeOxMB in the P-T plane

temperature obtained from equation (2) are as follows:

$$\begin{aligned}\Delta S(P,T) &= -\Delta\alpha(P - P_0) + \Delta C_p[(T-T_0)/T_0] \\ \Delta V(P,T) &= \Delta\beta(P - P_0) + \Delta\alpha(T - T_0)\end{aligned}\quad (6)$$

Without further data, equations (5) and (6) represent the total quantitative information which may be obtained from the phase diagram. The addition of a single measurement of either ΔS or ΔV at any point on the phase boundary would allow the determination of absolute value of $\Delta\alpha$, $\Delta\beta$, ΔC_p and ΔG_0 with the help of equations (5) and (6). Hence augmenting such P-T measurements with the accurate determination of ΔS and ΔV , would be extremely useful since it is possible to determine the differences of thermodynamical parameters as well as to check the validity of this model. But unfortunately no further information on these compounds can be obtained due to the lack of knowledge of the absolute value of any one parameter, viz., ΔC_p , $\Delta\alpha$ and $\Delta\beta$ for these compounds.

Table 4.1

Constants **evaluated from** the fit of the experimental data of the A-N phase boundary to ^{an} ellipse $a^1 P^2 + b^1 T^2 + c^1 PT + d^1 P + e^1 T + 1 = 0$

Sl. No.	Compound	Constants of the fitted ellipse				
		$a^1 \times 10^{-4}$	$b^1 \times 10^{-4}$	$c^1 \times 10^{-4}$	$d^1 \times 10^{-2}$	$e^1 \times 10^{-2}$
1	8 OCB (Cladis' data)	5.598	7.863	-11.153	5.169	-6.715
2	8 OCB (our data)	3.153	5.423	- 7.286	3.522	-5.111
3	11 CPMBB	6.06	1.057	- 2.075	2.002	-2.123
4	12 CPMBB	1.702	1.195	- 2.314	2.245	-2.373
5	11 CPMCB	3.684	0.609	- 0.566	1.009	-1.588
6	12 CPMCB	2.211	0.700	- 1.755	2.646	-1.798
7	11 CPM α MCB	19.710	0.823	- 0.970	0.635	-1.533
8	12 CPM α MCB	2.176	0.969	- 2.563	3.066	-2.105
9	11 CPM α MeOMCB	2.459	1.551	- 2.108	2.123	-2.720
10	12 CPM α MeOMCB	1.247	1.564	- 1.989	1.6011	-2.810

Table 4.2

Thermodynamic parameters evaluated from the constants of the fitted ellipse

Sl. No.	Compound	P_o (kbar)	T_o (°C)	cal/cc°C	$\frac{\Delta\alpha}{\Delta C_p} \times 10^{-3}$ cc/cal	$\Delta\beta/\Delta C_p$ cc ² /cal ²	$\left T_o \frac{\Delta\alpha^2}{\Delta\beta \Delta C_p} \right $
	8 OCB (Gladis' data)	-0.28	37.80	-1.030	19.39	-0.019	0.7548
2	8 OCB(our data)	-0.24	42.88	-1.155	15.61	-0.014	0.7758
3	11 CPMBB	-0.03	101.10	-0.171	9.71	-0.057	0.1680
4	12 CPMBB	+0.19	103.71	-0.680	9.510	-0.011	0.6586
5	11 CPMCB	-0.004	120.67	-0.077	3.85	-0.050	0.0357
6	12 CPMCB	-0.74	106.05	-0.398	11.82	-0.030	0.4986
7	11 CPM α MCB	0.024	112.09	-0.025	5.29	-0.214	0.0147
8	12 CPM α MCB	-1.23	69.74	-0.589	18.96	-0.032	0.7787
9	11 CPM e O α MCB	-0.33	82.56	-0.429	8.23	-0.019	0.2913
10	12 CPM e O α MCB	0.64	99.58	-0.798	6.38	-0.008	0.5070

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