

CHAPTER VII

HIGH PRESSURE STUDIES ON COMPOUNDS EXHIBITING THE CHIRAL SMECTIC C PHASE

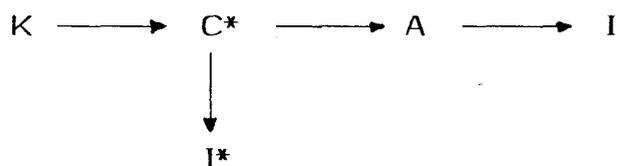
7.1 Introduction

The smectic C phase may be described as the tilted analogue of smectic A: the molecular centres are arranged at random in a liquid like fashion within each layer, as in smectic A, but the preferred molecular axis is tilted with respect to the layer normal. Smectic C is optically biaxial. In 1969, Saupe¹ pointed out that the smectic C phase bears some similarities with the nematic phase as regard to its elastic properties and therefore a twisted form of this phase should exist - resembling nematic and its twisted analogue (cholesteric).

Subsequent experimental studies by Arora et al² and Helfrich and Oh³ established the occurrence of the twisted smectic C (also known as smectic C*) in binary mixtures as well as in pure compounds. In recent years there is a considerable interest in the smectic C* phase owing to the discovery of ferroelectricity in this phase⁴ and the advent of a bistable, fast switching electro-optic light - valve⁵ based on this property (for a comprehensive review of ferroelectricity in liquid crystals see ref. 6).

The first observation of ferroelectricity was in 1974 by R.B.Meyer et al.⁴ They experimentally demonstrated the existence of ferroelectricity in smectic C* and H* phases - the H* phase was later identified as I* phase.⁷

The compound studied by them - *p*-decyloxybenzylidene-*p'*-amino-2-methylbutylcinnamate (DOBAMBC)-showed the following sequence of phase transitions.



In the C^* phase just like in the C phase the molecules are arranged in layers with their long molecular axis tilted with respect to the layer normal. In addition to this it is seen that if a particular layer is considered then the tilt directions of the molecules in the layer directly above and below that are turned through small angles in opposite senses with respect to the tilt director of the reference layer (see fig. 7.1). In this way, the tilt directors form a helical distribution on moving from layer to layer. In the I^* phase the molecules are again tilted in their layers but are hexagonally close packed.

The non-chiral C and I phases have monoclinic symmetry for which the symmetry elements are a two-fold rotation axis parallel to the layers and normal to the long molecular axis, a reflection plane normal to the two-fold axis and a centre of inversion. If the materials are composed of chiral molecules, i.e., those which cannot be superimposed on their mirror images, the mirror plane and the centre of inversion are eliminated, which leaves only a two-fold axis.

The absence of a mirror plane results in an arbitrary direction for the molecular dipole moment and hence a component parallel to the two-fold axis thus producing a net polarisation, usually a few Debye per molecule.

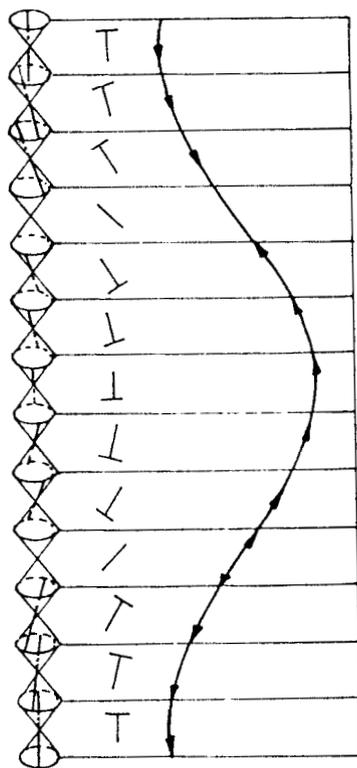


Figure 7.1 Schematic diagram of the C* phase showing the molecular arrangement in different layers (from ref. 8)

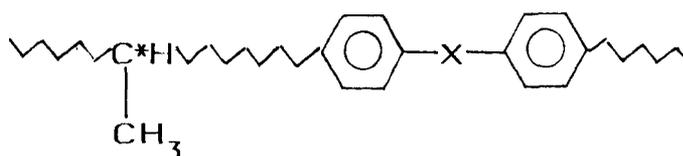
Effects of Pressure on Smectic C Phases

It has long been recognised that the temperature variation of the tilt angle in the C phase depends very much on the type of phase that exists immediately after it at a higher temperature.⁹⁻¹¹ If the high temperature phase is smectic A then the tilt angle would be temperature dependent and goes to zero at the C-A transition. On the other hand, if the C phase precedes a nematic phase then the tilt angle is temperature independent and goes to zero at the C-N transition. Recently, de Vries¹² has observed a third kind of smectic C phase wherein even though the higher temperature phase is a smectic A phase, the tilt angle in the C phase does not change significantly with temperature. In addition to this, the tilt angle remains finite in the A phase also. In order to see whether the pressure behaviour of the C phases is related to the temperature variation of the tilt angle at room pressure, Kalkura et al¹³ carried out pressure studies on three pure compounds, the C phase in each case belonging to a different class mentioned above. In all the cases they found that pressure destabilises the smectic C phase resulting in its suppression. The suppression occurred irrespective of the type of C phase. Even though many of their properties have been extensively investigated,¹⁴⁻¹⁷ there has been only one detailed pressure study¹⁸ on materials exhibiting the C* phase. The results of this study seem to indicate that the C* phase is not destabilised by the application of pressure (we will discuss these results in detail at a later stage). To see if this is true for all liquid crystals exhibiting the C* phase, the author undertook high pressure studies on three such materials (incidentally, all the three compounds are well known ferroelectric liquid

crystals). The results of these studies form the subject matter of this chapter.

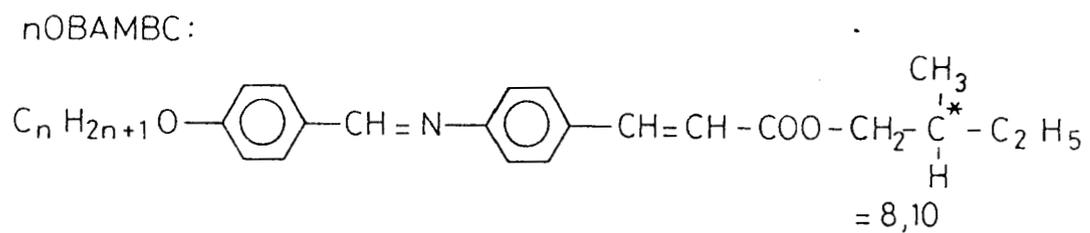
7.2 Materials and Methods

The appearance of C* phase depends highly on the chemical structure of the molecule.¹⁹ The chemical structure of a typical molecule exhibiting C* phase would be



where X is a linkage group like an ester, schiff base etc. C* is the chiral carbon atom (also known as asymmetric carbon atom). It is well known that the presence of a transverse dipole moment enhances the stability of the C phase.²⁰ The chiral phases are obtained by the inclusion of a chiral center within the molecular structure.

The studies that are reported in this chapter have been done on compounds comprised of molecules which have a schiff base (CH=N) as the linkage group. We have studied the eighth and tenth homologues of p-n-alkoxybenzylidene-p'-amino-2-methylbutylcinnamate (OOBAMBC and DOBAMBC) and p-n-hexyloxybenzylidene-p'-amino-2-chloro- α -propylcinnamate (HOBACPC).²¹ It may be recalled here that DOBAMBC was the first liquid crystal pointed out⁴ to be ferroelectric. The molecular structures of all the three compounds studied are given in fig. 7.2; their transition temperatures at atmospheric pressure



HOBACPC

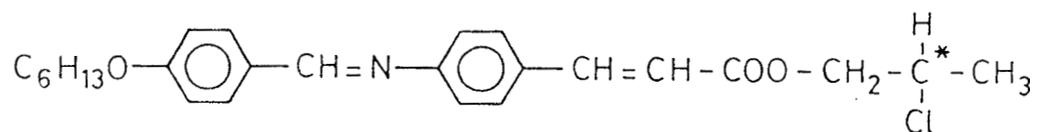


Figure 7.2 Chemical formulae of

1. p-n-alkoxybenzylidene-p'-amino-2-methylbutylcinnamate (nOBAMBC)
2. p-n-hexyloxybenzylidene-p'-amino-2-chloro- α -propylcinnamate (HOBACPC)

are listed in Table 7.1. All the three compounds exhibit smectic A, C* and I* phases. The phase transitions at high pressures were detected using the high pressure optical cell described in chapter II. Pressures were maintained and measured to an accuracy of ± 2 bar while the transition temperature could be determined to better than $\pm 0.5^\circ\text{C}$.

7.3 Results and Discussion

OOBAMBC

The P-T diagram of this compound is shown in fig. 7.3. It is seen that the range of the C* phase which is 27°C at atmospheric pressure decreases at the rate of 15°K/kbar resulting in a complete suppression of this phase at 1.7 kbar and 115°C . At the I*-C*-A triple point the I*-C* phase boundary is collinear with the I*-A phase boundary ($dT/dP = 23^\circ\text{K/kbar}$) while the C*-A line approaches the triple point with a dT/dP of almost zero (see Table 7.2).

DOBAMBC

The global features of the phase diagram of this compound, shown in fig. 7.4 are very similar to that of OOBAMBC:

1. The values of dT/dP for the I*-C* phase boundary at 1 bar as well as at the triple point for this compound are the same as those for OOBAMBC.
2. The C*-A phase boundary has a pronounced curvature towards the pressure

TABLE 7.1

Transition Temperatures (°C) of the Compounds Studied

Compound	K	I*	C*	A	I
OOBAMBC	. 74.5	. (67.0)	. 94.2	. 118.7	
DOBAMBC	. 74.6	. (62.0)	. 94.0	. 117.0	
HOBACPC	. 63.0	. 72.4	. 77.4	. 134.6	

Abbreviations Used

K - Crystal, I* - Chiral Smectic I, C* - Chiral Smectic C,
A - Smectic A, I - Isotropic

The parentheses indicate monotropic transitions

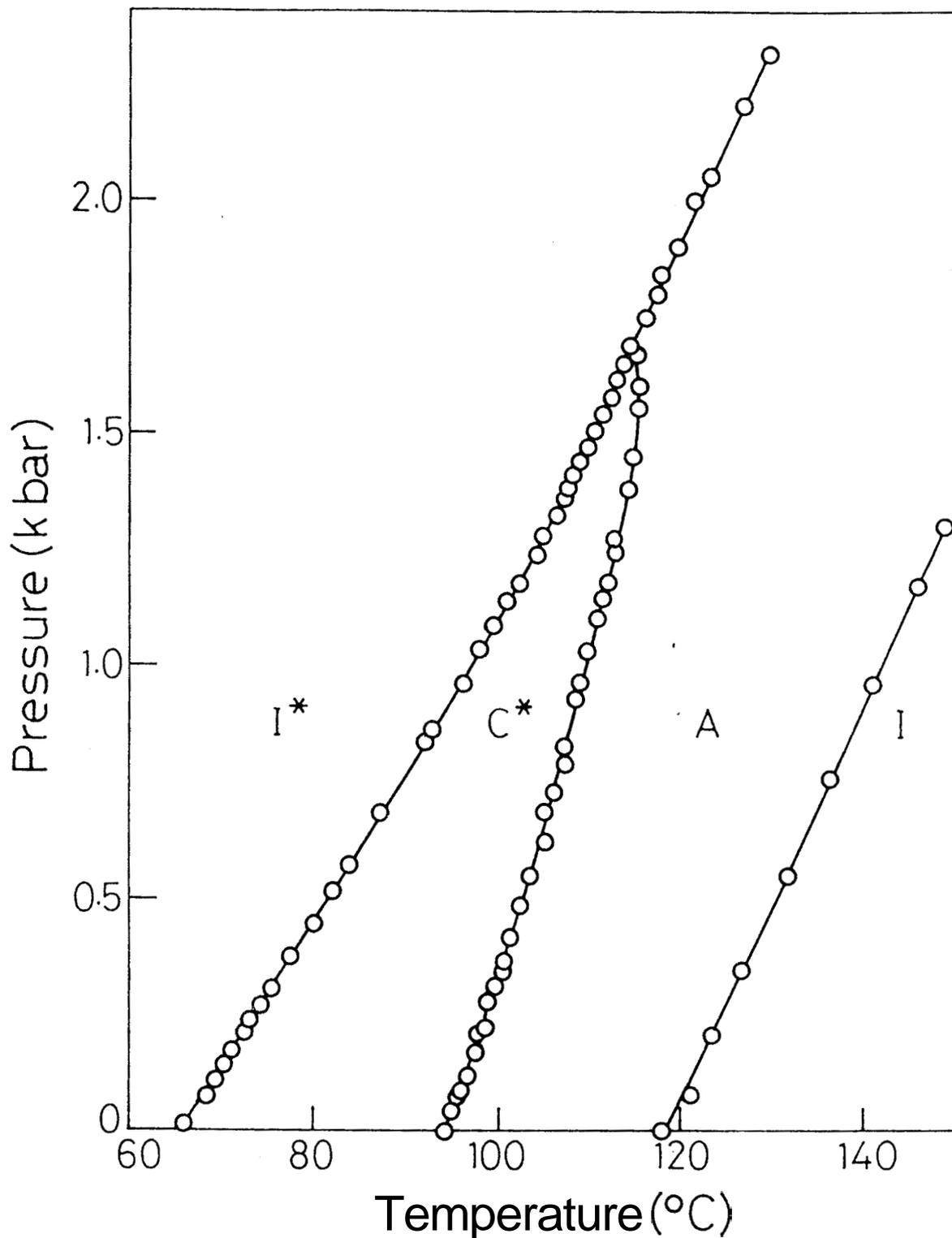


Figure 7.3 P-T diagram of OCIBAMBC showing the I*-C*, C*-A and A-I phase boundaries. The I*-C*-A triple point occurs at 1.7 kbar and 115°C

TABLE 7.2

dT/dP values for the various transitions

Compound	Phase Transition	dT/dP at 1 bar K/kbar	dT/dP at the Triple Point K/kbar
OOBAMBC	I* - C*	32	23
	C* - A	16	0
	A - I	21	
DOBAMBC	I* - C*	32	23
	C - A	23	0
	A - I	26	
HOBACPC	I* - C*	26	
	C* - A	25	
	A - I	-	

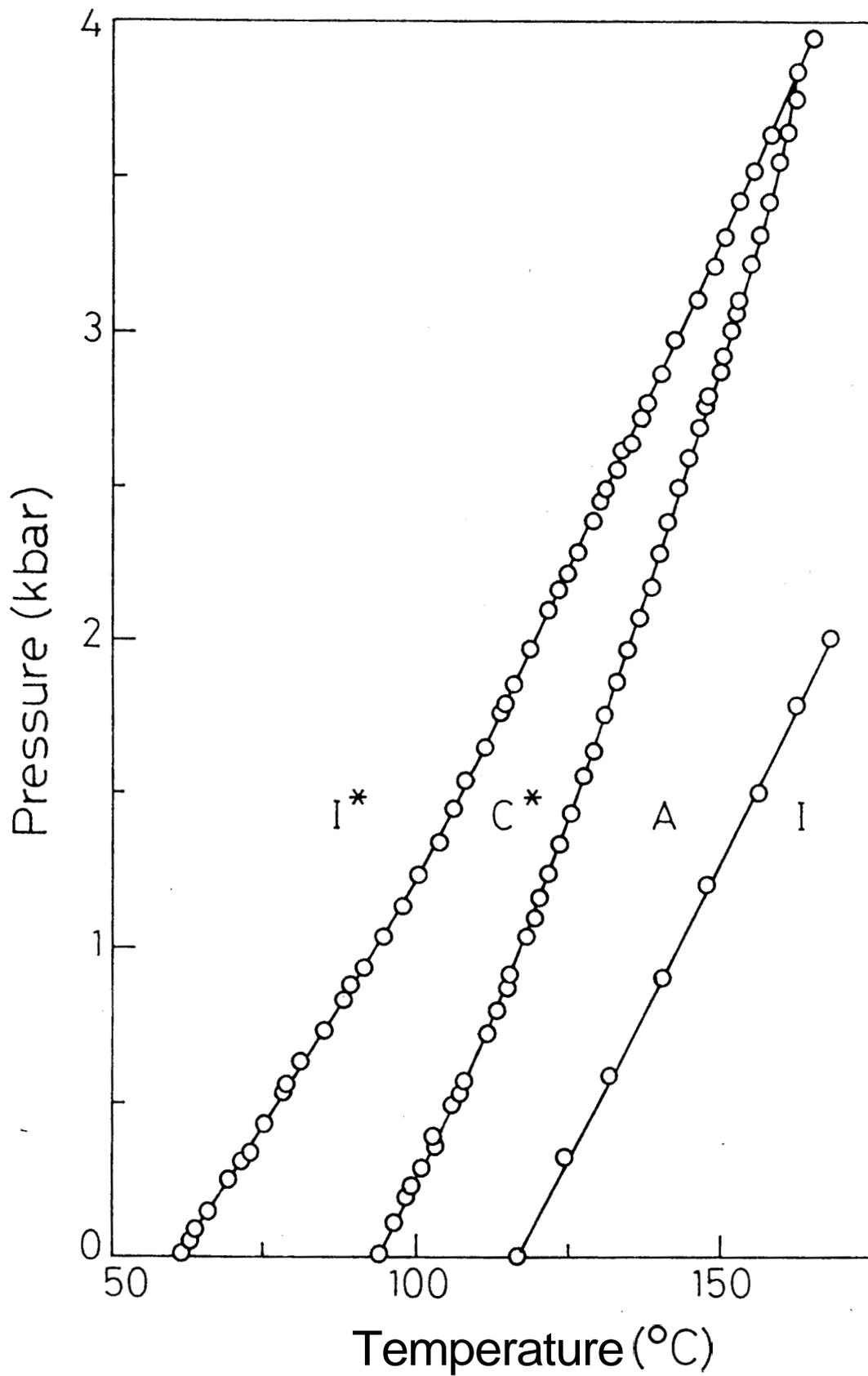


Figure 7.4 P-T diagram of DOBAMBC showing the I*-C*, C*-A and A-I phase boundaries. The I*-C*-A triple point occurs at 3.8 kbar and 162°C

axis.

3. The I^* phase becomes enantiotropic at higher pressures.

However, in DOBAMBC the range of the C^* phase decreases at a much slower rate (about $8^\circ\text{K}/\text{kbar}$). As a consequence the I^*-C^*-A triple point is observed at a higher pressure, viz., 3.8 kbar and 162°C . This somewhat surprising since the transition temperatures at 1 bar for the two compounds are almost exactly the same. The slope of the smectic A - isotropic (A-I) phase boundary is $21^\circ\text{K}/\text{kbar}$ for OOBAMBC and $26^\circ\text{K}/\text{kbar}$ for DOBAMBC. These values are similar to those observed in other smectic compounds.²² It must be mentioned that Guillon et al¹⁸ have also studied DOBAMBC at high pressures.

We shall discuss now their results and then compare their P-T diagram with ours. These authors have measured the layer spacing d as a function of pressure at four constant temperatures in the A, C^* and I^* phases. The variation of layer spacing obtained for one of the temperatures (96°C) is shown in fig. 7.5.

The main features seen which are common at all the four temperatures are

1. d has no variation with pressure in the A phase.
2. In the C^* phase, d exhibits a strong decrease, the rate of decreasing becoming somewhat slower at higher pressures.
3. In the I^* phase, d is either constant or shows a very small increase with increasing pressure.

They also determined the P-T diagram of DOBAMBC by optical microscopic

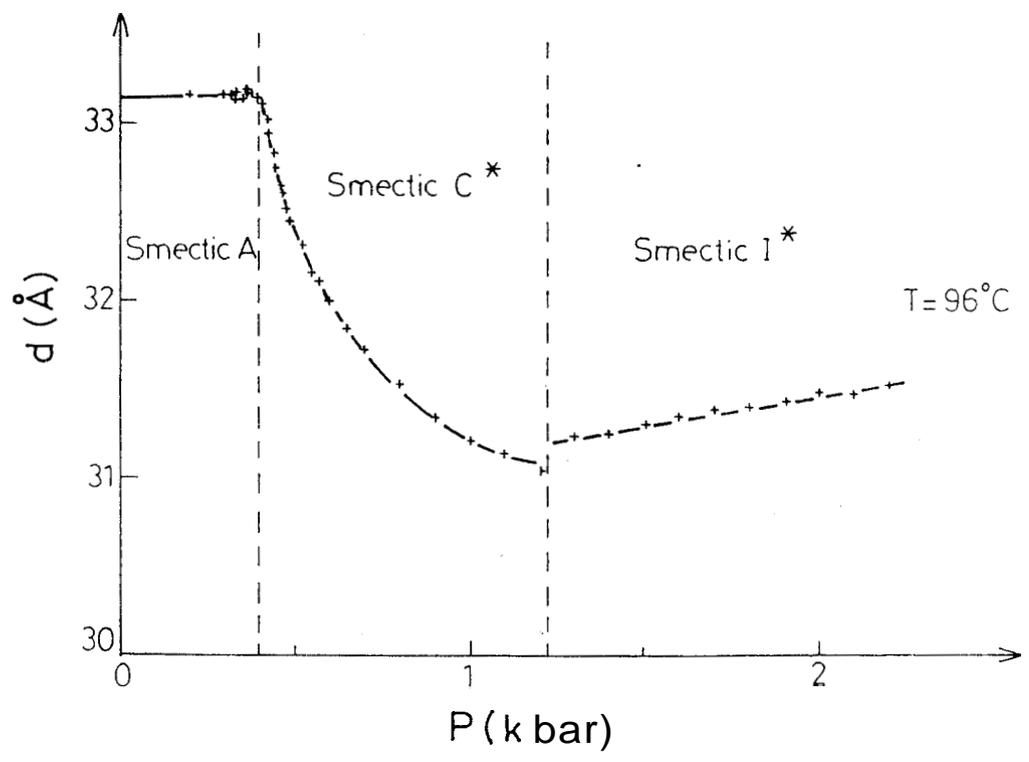


Figure 7.5 Variation of layer spacing as a function of pressure at 96°C for DOBAMBC (from ref. 18)

technique. This diagram is shown in fig. 7.6. It is seen that there is no indication of the suppression of the C* phase seen by us in the same compound. In fact, in the P-T diagram of Guillon et al, there is a slight increase in the range of the C* phase with increasing pressure. To ascertain this discrepancy we computed the P-T diagram of DOBAMBC from the Xray data of Guillon et al.¹⁸ That is, we took the transition pressures for four different temperatures using the d versus pressure curves given by them (fig. 7.5 shows one such curve obtained at 96°C). The phase diagram obtained in this manner is reproduced in fig. 7.7. This phase diagram in fact agrees with ours; the range of the C* phase is seen to reduce with increasing pressure. An extrapolation of the phase boundaries to higher pressures would give a I*-C*-A triple point at about 3.3 kbar. This discrepancy in the P-T diagram of Guillon et al obtained by optical microscopy and Xray scattering methods could be due to the impure samples used in the former study - the C*-A transition temperature at 1 bar of the sample used in the optical study appears (see fig.7.6) to have been more than 10°C lower than that used in the Xray measurements.

HOBACPC

The pressure behaviour of this compound (see fig. 7.8) is very different from that of nOBAMBC. Even though the pressure range of the C* phase is only 5°C at atmospheric pressure, it decreases only very slowly (about 0.5°C/kbar) with increase in pressure. Hence the I*-C*-A triple point in this compound is expected to occur only around 8 kbar, a pressure which is beyond the capability of the pressure cell that was used for the experiments.

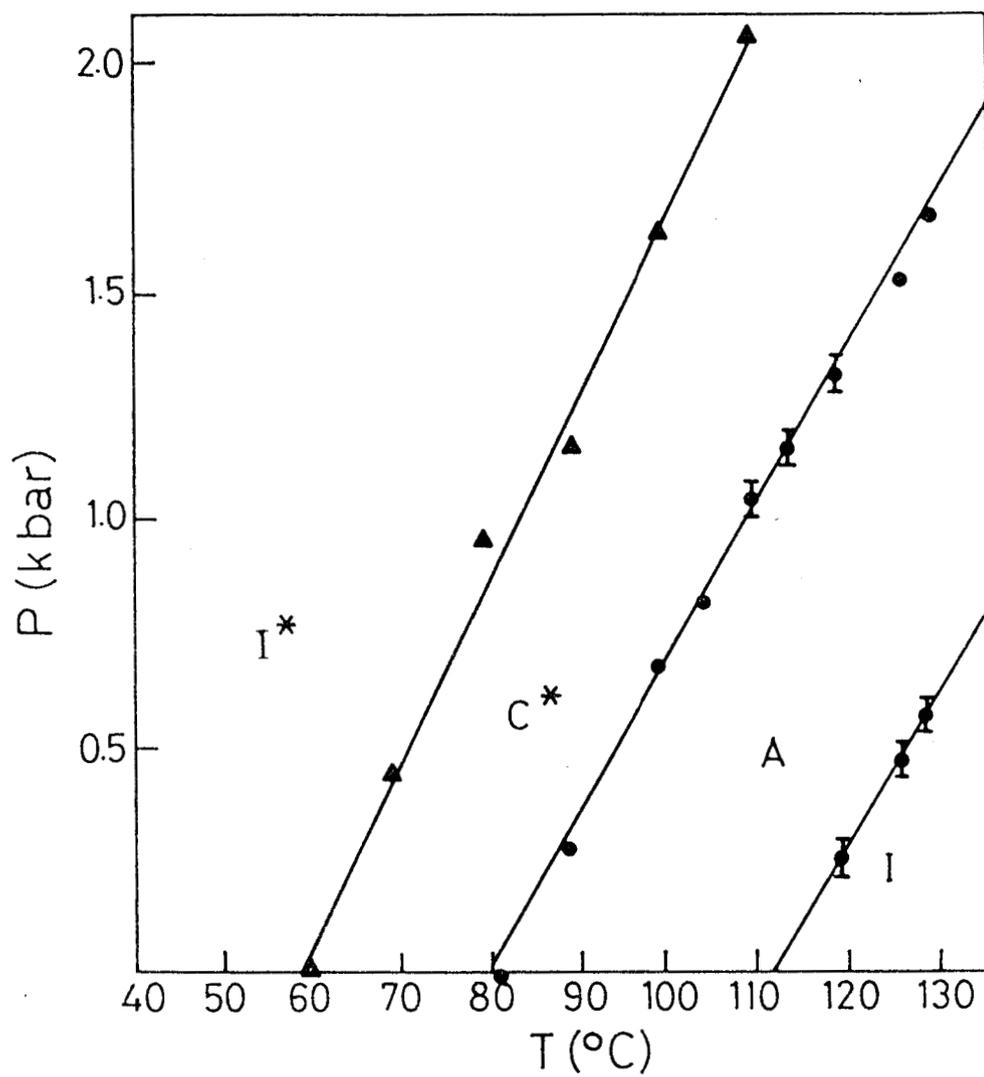


Figure 7.6 P-T diagram of DOBAMBC obtained by Guillon et al (ref. 18) using the optical technique

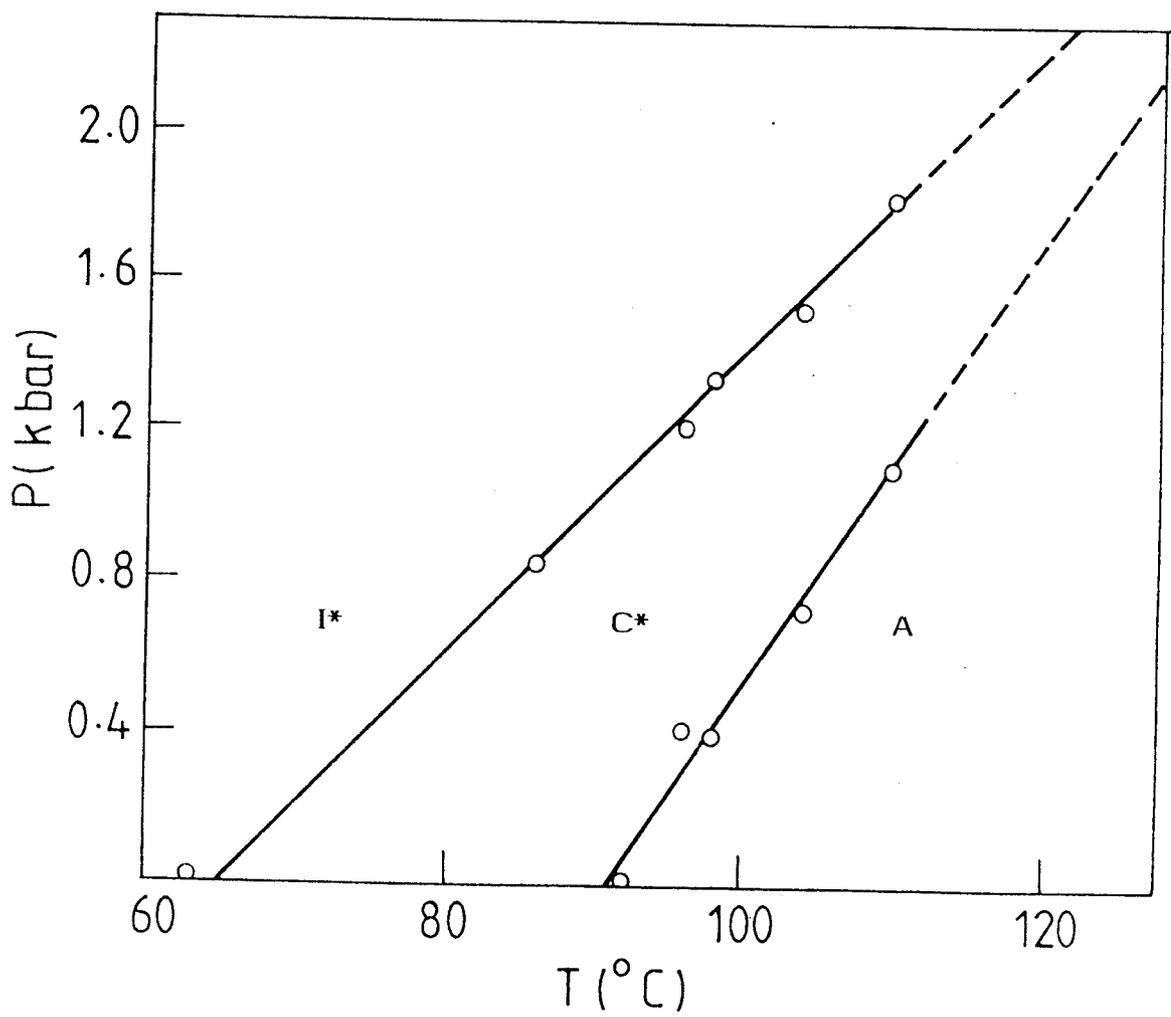


Figure 7.7 P-T diagram of DOBAMBC (Guillon et al.¹⁸). The P-T coordinates are obtained from d versus pressure plots (for details see the text)

The higher stability of the C* phase in this compound as compared to nOBAMBC compounds may be because of the slight enhancement of the transverse dipole moment due to the presence of a chlorine atom in the branch.

It should also be mentioned that the helical axis in HOBACPC used for these experiments is right handed while both nOBAMBC have left handed helix.

The A-I phase boundary could not be determined for this compound since the sample had a tendency to decompose on repeated heating into the isotropic phase. The dT/dP values for the I*-C* and C*-A transitions are listed in Table 7.2.

As already mentioned, Kalkura et al have shown that the non-chiral smectic C phase also gets bounded at high pressure in many materials, regardless of the phases which exist above and below the C phase.¹³ Shashidhar and Chandrasekhar²³ as well as Guillon et al¹⁸ have observed that in the case of 4,4'-bis heptyloxyazoxybenzene, in which the C phase is suppressed above 6.67 kbar, the layer spacing in the C phase is independent of both temperature and pressure.²⁴ Also, Xray studies of Guillon et al¹⁸ on DOBAMBC have shown that the pressure dependence (at constant temperature) of the layer spacing in the C phase of this compound is similar to its temperature dependence at constant pressure. Hence the suppression of the C or C* phase is not directly related to the tilt angle variation.

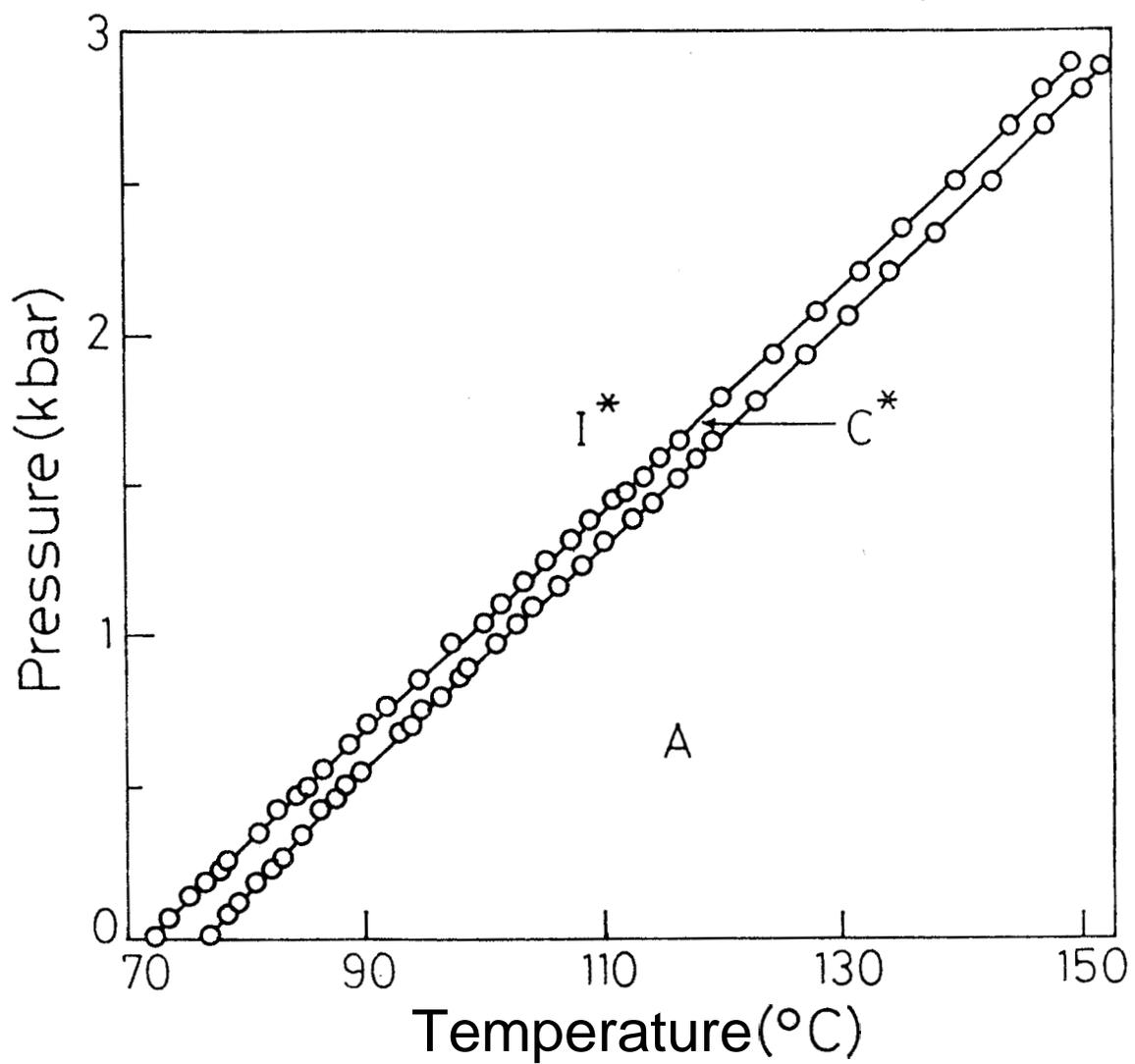


Figure 7.8 P-T diagram of HOBACPC showing the I*-C* and C*-A phase lines

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APPENDIX

HIGH PRESSURE STUDIES OF PHASE TRANSITIONS IN TWO PHOSPHATIDYLCHOLINES

1. Introduction

Lipids form an essential part of biomembranes. Studies of the liquid crystalline properties and phase behaviour of the lipid molecules are useful for an understanding of the structure and dynamics of natural biomembranes.¹

Phosphatidylcholine (lecithin) is a major phospholipid of biomembranes. The chemical structure of a phosphatidylcholine is given in fig.1 (R refers to a hydrocarbon chain). In most naturally occurring membrane lipids, the acyl chains are even numbered. If R is of the form $\text{CH}_3(\text{CH}_2)_{12}$, it is referred to by the prefix di-myristoyl and the molecule is called dimyristoyl phosphatidylcholine (DMPC). The molecule having $\text{CH}_3(\text{CH}_2)_{14}$ chain is called dipalmitoyl phosphatidylcholine (DPPC). DMPC and DPPC are the most widely studied phospholipids, and we shall be concerned only with these two in this chapter.

If one replaces N (CH_3) group at one end of the molecule (see fig. 1) by (NH_3) group the resulting molecule is called phosphatidylethanolamine which is a major phospholipid of bacterial membranes. We will not be dealing with these here. The scheme of presentation is as follows:

A detailed discussion of the different phase transitions exhibited by DMPC - Water and DPPC - Water systems is given followed by a description of the

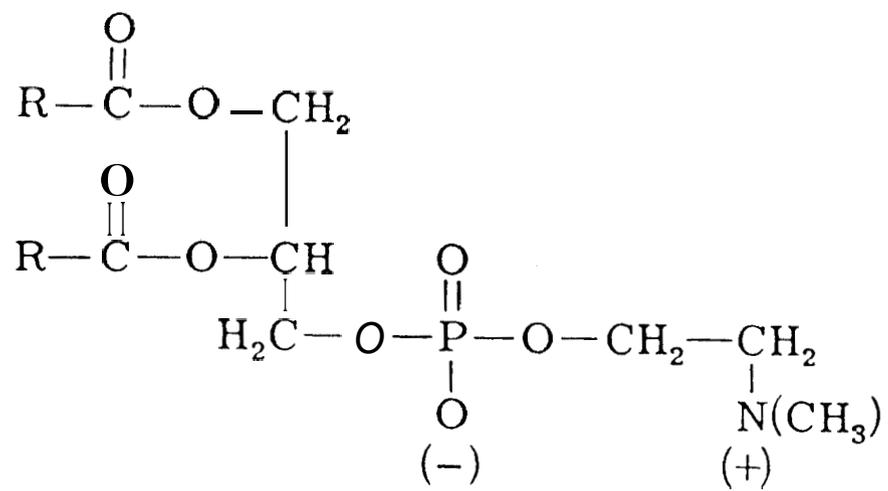


Figure 1 Chemical structure of phosphatidylcholine : R refers to the hydrocarbon chains

structures of these phases as given by the Xray studies of Janiak et al.² Finally, the existing pressure data on these two phospholipids are summarised and then the results of our high pressure studies are discussed in detail.

2 Phase Transitions in DMPC/Water and DPPC/Water Systems

Phosphatidylcholines exhibit rich polymorphism in the presence of water. In the case of DMPC, for water concentrations greater than 20 weight %, two thermal transitions are observed - T_2 , the low enthalpy pretransition and T_3 , the high enthalpy chain melting "Main" transition. For concentrations less than 20% water, T_2 is no longer observed but instead a new transition T_1 is seen prior to T_3 . At still lower concentrations (less than 15% water) T_3 is broadened and shifted to higher temperatures. This transition is now accompanied by an overlapping transition T_4 . The temperature dependence of these transitions (observed by DSC) as a function of hydration is summarised in fig. 2.

3. Characterisation of Phases

Using Xray diffraction in conjunction with DSC, Janiak et al.² characterised the different phases in DMPC. Here a brief account of the classification is given. We will discuss the region where the transitions are independent of composition (greater than 30% water). The phase that exists at temperatures greater than T_3 shows only lamellar reflections together with a diffuse diffraction band in the high angle region. In this phase the acyl chains are

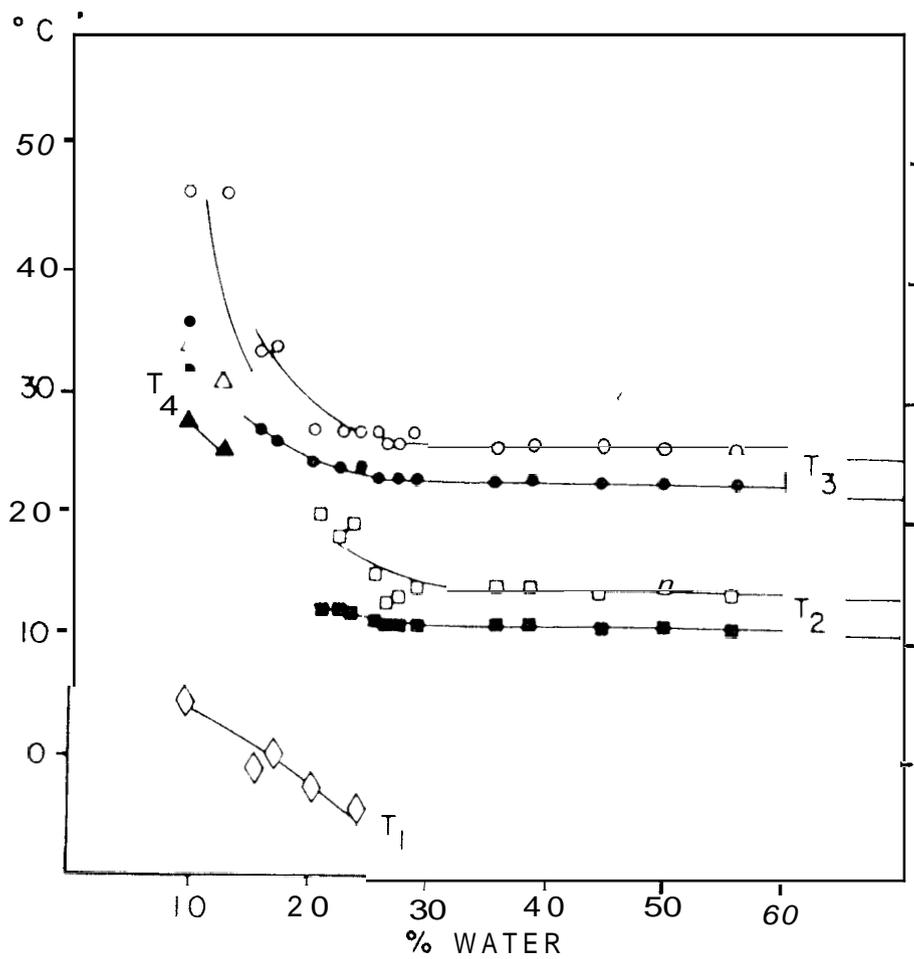


Figure 2 Thermal transitions T_1 (\diamond), T_2 (\square), T_3 (\circ) and T_4 (Δ) observed in hydrated DMPC as a function of composition.

Solid symbols: transition onset temperature

Open symbols: temperature of endotherm (DSC) maxima (from ref. 2)

conformationally disordered and contain a large number of gauche conformers. The interchain steric repulsion is thus higher, due to the larger hard core radii of the chains. This phase is termed as liquid crystalline phase or L_{α} phase.³ A schematic representation of this phase is given in fig. 3a.

Below the liquid crystalline phase (temperature $< T_3$) a "gel" phase exists in which a two-dimensional lattice probably arises from periodic distortion of the lamellae, i.e., the stacked lamellae are distorted by a periodic "ripple" in the plane of the lamellae (fig. 3b). The hydrocarbon chains are in a relatively ordered state and tilted with respect to the bilayer normal and packed in a regular hexagonal lattice. This phase is called Gel I or P_{β} phase.

As the system is further cooled, it undergoes another transition at a temperature T_2 , to a phase termed as L_{β} or Gel II phase. Here the hydrocarbon chains are fully extended and tilted with respect to the plane of the bilayer, but packed in a distorted quasi hexagonal lattice (see fig. 3c). Increasing the temperature results in packing alterations such that the hexagonal lattice becomes less distorted. The average angle of tilt of the hydrocarbon chains decreases with increasing temperature.

Recently, a third transition (Gel II - Gel III) has been observed at -60°C using Raman spectroscopy.⁴ The structure of the Gel III phase is still to be elucidated.

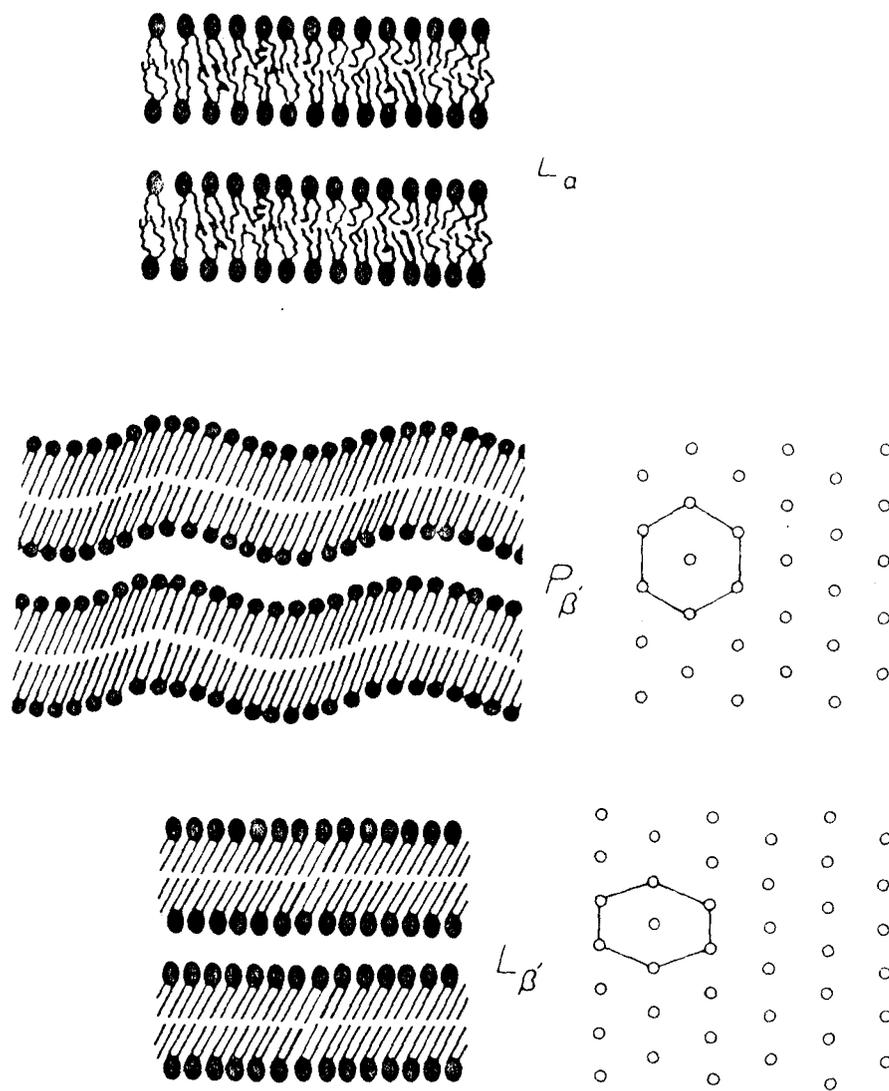


Figure 3 Schematic representation of the structures of the liquid crystal (L_α) Gel I (P_β) and Gel II ($L_{\beta'}$) phases of DMPC/water system (from ref.2)

The phase transitions in DPPC have been similarly identified using calorimetry and Xray diffraction. The so called "main transition" between the liquid crystalline phase and a gel phase and the pre transition between two gel phases have been thermodynamically characterised by Chapman et al⁵ and others.^{6,7} The conformation of the bilayer structures have been studied by detailed Xray diffraction.⁸ Recently, a third phase transition has been observed by Chen et al.⁹ Termed as "sub transition" this phase transition has been characterised by calorimetry and Xray diffraction and P NMR studies.^{10,11} The new phase below the sub transition temperature is given the symbol L_c . From the experiments mentioned above, it appears that the L_c phase adopts a complex hybrid orthorhombic sub cell with precisely defined hydrocarbon chain conformations and mutual orientations. It is probable that the inter bilayer region in the L_c phase is occupied exclusively by tightly bound, H-bonded water molecules providing a coupling between adjacent bilayer polar groups.

4. Earlier Pressure Studies on DMPC and DPPC

There have been some pressure studies on both DMPC - Water and DPPC - Water systems,¹²⁻¹⁶ but all of them (except that of Wong et al¹⁵ in the case of DMPC and Plachy¹⁶ in the case of DPPC) have been concerned with the main transition only. The P-T diagram¹⁴ of three phosphatidylcholines, viz., DMPC, DPPC and DSPC - showing the Gel I - LC boundary - which is typical in all the above mentioned experiments¹²⁻¹⁶ is given in fig. 4. It may be recalled that Wong et al¹⁵ have reported measurements on DMPC

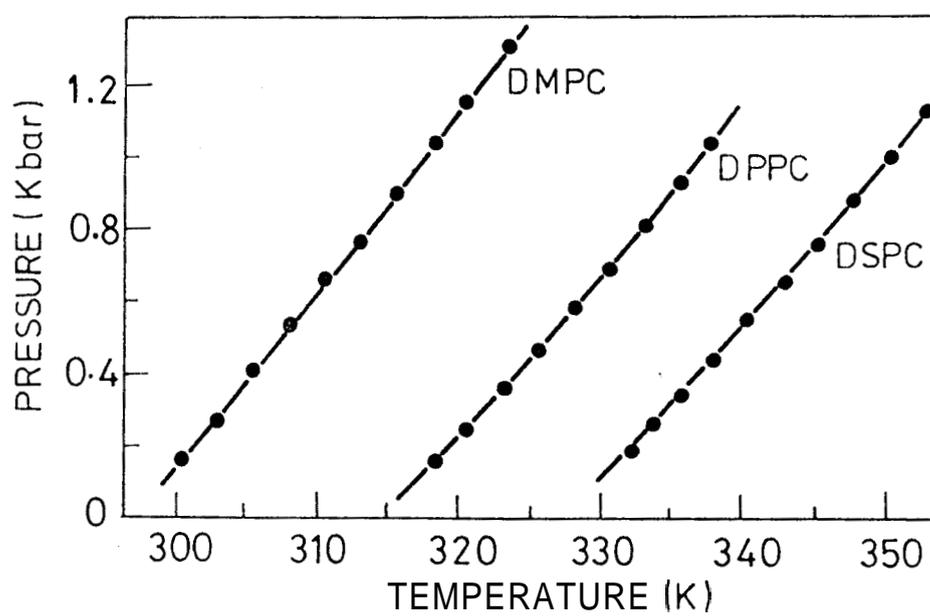


Figure 4 P-T diagram obtained by Russell and Collings¹⁴ for the Gel I-LC transition of three phosphatidylcholines

for all the three transitions, namely, Gel III - Gel II, Gel II - Gel I and Gel I - LC, but the data are not adequate to construct a complete P-T diagram. The P-T diagram obtained by them is given in fig. 5.

We shall now present the results of our detailed pressure studies of the transitions in hydrated DMPC and DPPC (containing 95 weight % of water).

5. Detailed Pressure Studies on DMPC/Water and DPPC/Water Systems

5.1 Experimental

A. Sample Preparation

DMPC and DPPC were purchased from Avanti Polar Lipids, Alabarna and used without further purification. 50 mg of the phospholipid was dissolved in chloroform. The solvent was removed by drying overnight in vacuum (1mm).

The phospholipid was then dispersed in 1cc of 0.1 molar KCl in water, warmed to a temperature slightly above the chain melting transition and agitated gently until the sample became milky white. Both the samples contained 95 wt.% of water. Differential scanning calorimetry runs, particularly of the pretransition, showed that the sample was well homogenised. Also, the transition temperatures at 1 bar agreed very well with those reported in literature.

B. Methods

The phase transitions were detected by the optical transmission technique.

The details of the pressure cell used are described in Chapter II. Pressures were measured to a precision of ± 1.5 bar using a Bourdon type (HEISE) gauge while the temperatures were determined to an accuracy of $\pm 0.05^\circ\text{C}$. Typical runs of the transmitted light intensity obtained for Gel III - Gel II, Gel II - Gel I and Gel I - LC transitions of DMPC are shown in fig. 6. It is known that the change in order at the pretransition is sharp only in the increasing temperature mode while it becomes rather smeared out if one starts from the fluid phase. Sackmann et al¹⁷ associated this with a high defect density existing in freshly formed L_{β} - phase. In order to obtain clear intensity changes we have performed these experiments only in the heating mode.

6. Results and Discussion

A. DMPC

The transition temperatures at 1 bar are given in Table 1. Both the pretransition and the main transition could be followed as functions of pressure starting from atmospheric pressure. However, it was not possible to observe the Gel III - Gel II transition at lower pressures (As mentioned earlier this transition occurs at -60°C at 1 bar). This was because the pressure cell could not be used below 6°C , the 'O' rings used in the cell losing their sealing property below this temperature. However, it was found that by keeping the sample at room temperature and at a pressure of 3 kbar for about 12 hours, the material formed the Gel III phase, and the Gel III - Gel II transition could be clearly observed. Having once observed this transition, the sample had

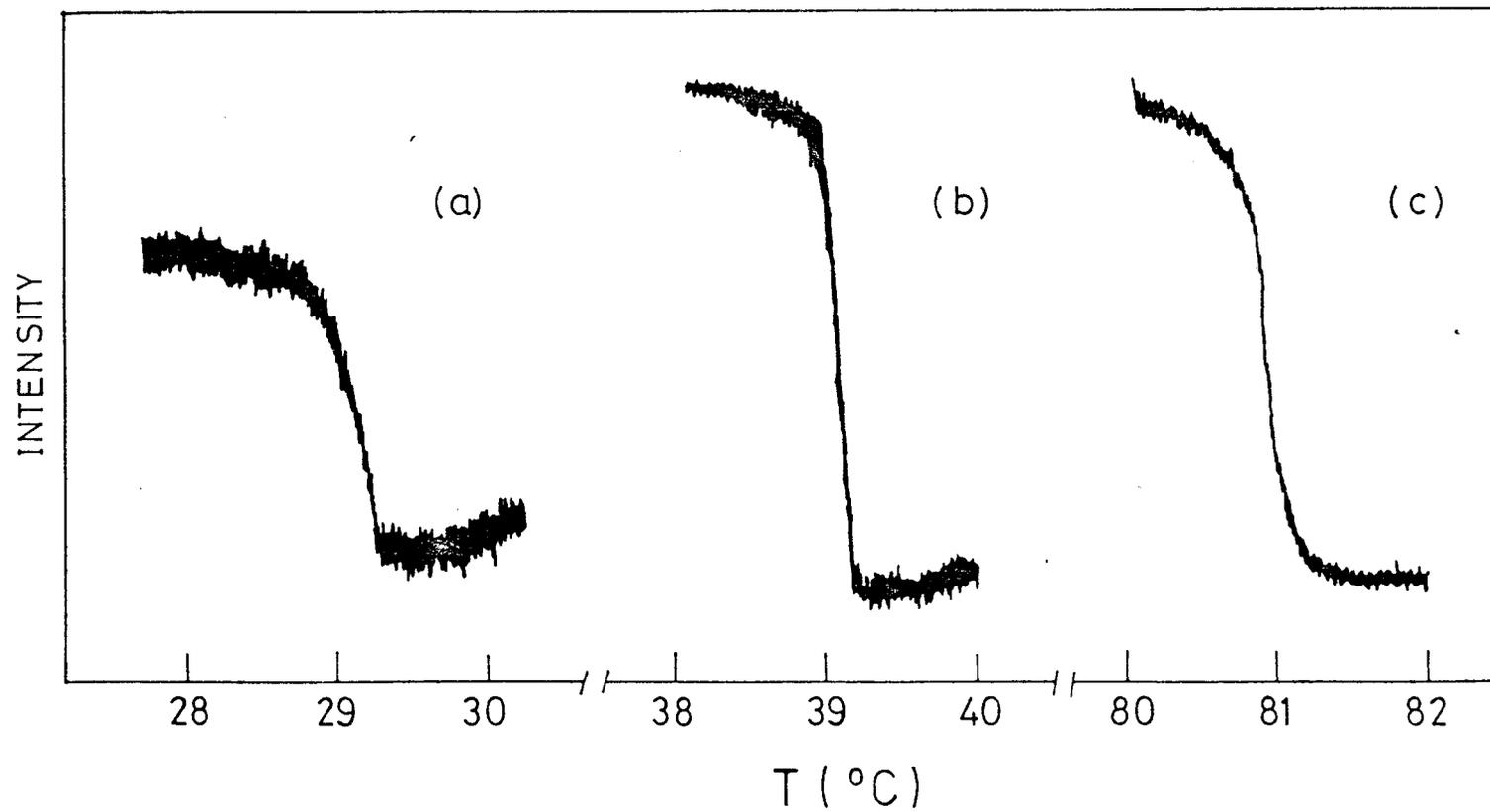


Figure 6 Raw traces showing the change in the transmitted light intensity at the transition in DMPC-water system (a) Gel 111-Gel II, 3.10 kbar, (b) Gel 11-Gel I, 3.10 kbar and (c) Gel I-LC, 3.12 kbar. The intensity scales for (a), (b) and (c) are different

TABLE 1

Transition Temperatures (at 1bar) of hydrated
Dimyristoyl Phosphatidylcholine (DMPC)

Transition	Temperature (°C)
Gel II - Gel I	14.0
Gel I - Liquid Crystal	24.0

to be pressure annealed once again in order to re-observe the transition. Therefore by successive pressure- annealing at different pressures, it was possible to follow the Gel III - Gel II transition for pressures beyond 3 kbar.

The P-T diagram showing all the three phase transitions is given in fig. 7. It is seen that the range of the Gel I phase increases with increasing pressure, showing thereby that the interactions responsible for the formation of the hexagonally ordered Gel I phase are probably stabilised at high pressures. The variation of the Gel I - liquid crystal as well as that of the Gel II - Gel I phase boundaries are linear up to about 12 kbar beyond which there is a small curvature towards the pressure axis, a feature which is commonly observed in thermotropic liquid crystal systems. The dT/dP corresponding to the linear portions of the phase boundaries are $21.4^{\circ}\text{C}/\text{kbar}$ and $10.6^{\circ}\text{C}/\text{kbar}$ respectively. Since the volume change and the enthalpy change at 1 bar for the Gel I - LC transition are known ($\Delta V = 27 \times 10^{-3} \text{ ml/g}^{18}$, $\Delta H = 6\text{kcal/mole}^8$) dT/dP can be calculated from Clausius - Clapeyron equation. The value comes out to be $21.2^{\circ}\text{C}/\text{kbar}$ which compares very well with the experimental value of $21.4^{\circ}\text{C}/\text{kbar}$.

The Gel III - Gel II transition line when extrapolated linearly to atmospheric pressure gives a transition temperature of about -60°C , in agreement with the value reported by Wong and Mantsch.⁴ The Gel II phase decreases in range with increasing pressure and ultimately gets bounded at 3.5 kbar; beyond this pressure Gel III transforms directly to Gel I. We thus have a

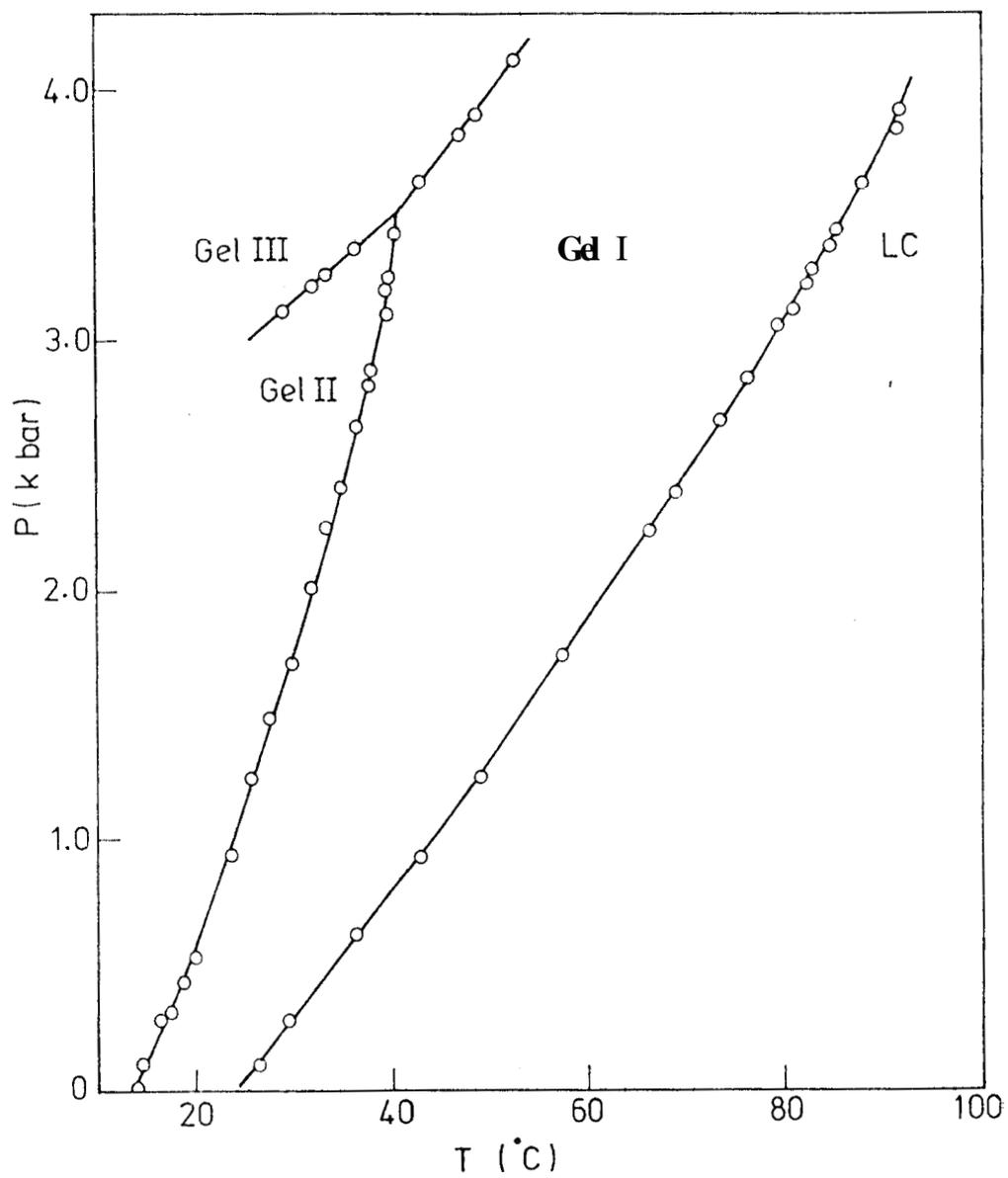


Figure 7 P-T diagram of hydrated DMPC.
 The Gel III-Gel II-Gel I triple point is at 3.5 kbar, 41°C

Gel III - Gel II - Gel I triple point at 3.5 kbar, 41°C. Table 2 gives the dT/dP values for the three boundaries at the triple point. The dT/dP values derived from the initial linear portions of the Gel II - Gel I and Gel I - LC boundaries are also given in the same Table for comparison.

B. DPPC

Like in the case of DMPC, both pre transition and main transition could be followed as functions of pressure right from 1 bar. However, the sub transition could not be obtained even after pressure-annealing the sample.

The transition temperatures at 1 bar are given in Table 3. The P-T diagram of DPPC is given in fig. 8. It is seen that up to about 930 bar there are only two transitions, Gel II - Gel I and Gel I - LC both of which are present at room pressure. Above a pressure of 930 bar, the Gel II phase does not go directly to Gel I, but instead to a new phase (hereafter referred to as X). It may be recalled that Plachy,¹⁶ using ESR technique to obtain the P-T diagram of DPPC, had observed that the pretransition (Gel II - Gel I) becomes undetectable beyond 1 kbar. In our experiments we notice that above the Gel II - X - Gel I triple point, the Gel II - X transition which Plachy might have taken as the Gel II - Gel I transition does become considerably weak. It may also be noted that Russell and Collings¹⁹ have recently found, using adiabatic compression method, that the latent heat of the main transition (Gel I - LC) shows an anomaly around 1 kbar. The value of the latent heat which starts going down from about 300 bar reverses the trend and increases around 900

TABLE 2

dT/dP values (in °C/kbar) for the various
transitions in hydrated DMPC

Transition	dT/dP at 1 bar	dT/dP at the triple point
Gel I - Liquid Crystal	21.4	-
Gel II - Gel I	10.6	5.1
Gel III - Gel II	-	29.2
Gel III - Gel I	-	20.0

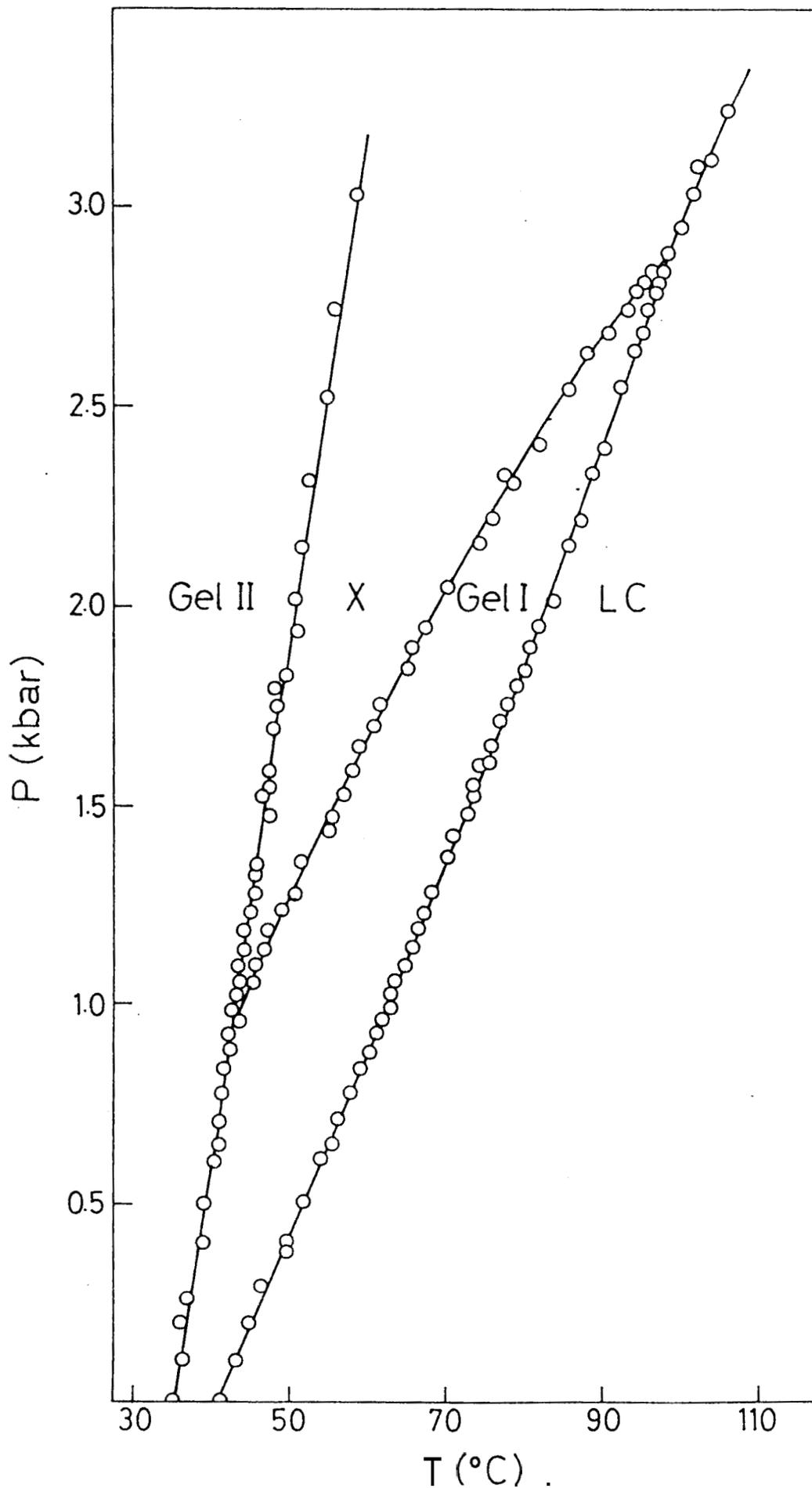


Figure 8 P-T diagram of hydrated DPPC. The Gel II-X-Gel I triple point is at 0.43 kbar, 42.5°C and the X-Gel I-LC triple point is at 2.87 kbar, 98.5°C

TABLE 3

Transition Temperatures (at 1bar) of hydrated
Dipalmitoyl Phosphatidylcholine (DPPC)

Transition	Temperature (°C)
Gel II - Gel I	35.2
Gel I - Liquid Crystal	41.1

bar. In our opinion, this change may be due to the effect of molecular ordering that is happening at lower temperatures. Indeed such effects are known to occur in non-amphiphilic systems.^{20,21}

At pressures above the triple point, the phase boundary involving Gel II phase (i.e. Gel II - X) continues to have practically the same slope (dT/dP), viz., about $8^{\circ}\text{C}/\text{kbar}$, as at lower pressures. The range of the Gel I phase which increases with increasing pressure at lower pressures (i.e., below the Gel II - X - Gel I triple point) shows a dramatic decrease at higher pressures and finally at 2.87 kbar, 98.5°C the Gel I phase gets suppressed. Thereafter the induced phase X directly goes to the LC phase, leading to the observation of another triple point X - Gel I - LC. The dT/dP values for the various transitions at 1 bar as well as at the two triple points are given in Table 4.

Thus the pressure-temperature diagram of DPPC has a remarkable topology. The salient features of this diagram - all of which have been observed probably for the first time in lecithins - are summarised below:

- i) An induced phase between Gel II and Gel I.
- ii) Suppression of the Gel I phase.
- iii) Existence of two triple points, viz., Gel II - X - Gel I and X - Gel I - LC.

TABLE 4

dT/dP values (in °C/kbar) for the various
transitions in hydrated DPPC

Transition	dT/dP at 1 bar	dT/dP at TP1	dT/dP at TP2
Gel I - LC	21.5	-	18.0
Gel II - Gel I	8.5	8.5	-
Gel II - X	-	8.0	-
X - Gel I	-	23.0	30.0
X - LC	-	-	22.0

TP1 refers to Gel II - X - Gel I triple point

TP2 refers to X - Gel I - LC triple point

As regards the observation of a new phase X in DPPC, it may be noted that Strenk et al,²² using deuterium NMR spectroscopy, found evidence for the possible existence of a ripple-ripple phase transition. According to them, this transition found in aqueous dispersions of DMPC at low levels of hydration, can be explained in terms of a spatial modulation in the orientational order of the water brought on by the ripple structures in the lipid bilayer. At this transition, they observed that the values of the ratio of the amplitude to the periodic length of the ripple (A/Λ) as well as the temperature dependence of A/Λ change discontinuously from one ripple structure to the other.

Ruppel and Sackmann,²³ using freeze-fracture electron microscopy as a tool observed that two different types of ripple phases coexist within the $P_{\beta'}$ phase. These two coexisting phases, according to them, are clearly distinguished by (i) the distance between the ripples (wavelength Λ or $\Lambda/2$), (ii) the form and symmetry of the microscopic surface profiles and (iii) the defect structure of the surface texture. A characteristic feature of the Λ phase is the appearance of dislocations in the ripple pattern of strength $S = +1/2$ and $S = -1/2$. In contrast the $\Lambda/2$ phase is characterised by the formation of wall-defects (two regions of ripples of opposite orientation meet at the wall).

In the light of the two observations mentioned above, we feel that the induced phase "X" may be arising because of a ripple-ripple transition in the $P_{\beta'}$ phase. Perhaps, as pressure increases the range of one of the ripple phases grows at the expense of the other. High pressure Xray studies on DPPC can throw light on the structural details of this pressure induced phase.

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