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Pressure Effects on the Phase Transition of Urea Adducts with *n*-Paraffins and Polyethylene

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Abstract. The decomposition of urea adducts with hydrocarbons is treated as a first-order phase transition and the pressure dependence is studied up to 0.7 GPa for several kinds of adducts. The thermodynamic quantities at the decomposition of the adduct can be analysed as a sum of those quantities of the component materials. The transition from the orthorhombic to the hexagonal form of the adduct with polyethylene is also investigated by X-ray diffraction and the pressure dependence of the lattice parameters is measured for the adducts. The results are compared with the phase transition in the pure paraffin.

Key words: Clathrate, urea-paraffin adducts, phase transition, thermodynamic analysis, X-ray diffraction, high pressure.

1. Introduction

A urea-paraffin complex (urea adduct) decomposes into paraffin and urea at a temperature called the decomposition temperature, T_d. The decomposition temperatures are higher than the melting points of pure paraffins by about 100 K, due to the effect of the urea lattice formed by hydrogen bonding. When the number of carbon atoms of the guest molecule is less than 20, the T_d of the adduct becomes lower than the melting point of pure (tetragonal) urea, T_m^u and the adduct decomposes into liquid paraffin and solid tetragonal urea. When the number of carbon atoms of the guest paraffin is larger than 20, the adduct decomposes into liquid paraffin and liquid urea. These two types of decompositions are not thermodynamically identical and different pressure dependences can be expected. In the first part of the present work, the pressure dependences of T_d's are examined for different kinds of adducts with shorter and longer paraffins than $C_{20}H_{42}$.

The structure of the urea adduct with a paraffin at room temperature has been reported by Smith [1]. The crystal structure is hexagonal and hydrocarbon molecules (guest molecules) are enclosed in the hexagonal channels formed by urea molecules (host molecules). This hexagonal structure changes to the orthorhombic phase on cooling [2, 3]. In the hexagonal phase of the adducts, the guest molecules are considered to rotate in the cage of the urea lattice on the basis of several experiments: ESR [4, 5], NMR [6, 7] and dielectric measurements [8].

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On the other hand, *n*-paraffins with some definite chain lengths exhibit a structural change at the temperature close to the melting point. This transition has been known as the 'rotational phase transition', where the paraffin molecules rotate around their chain axes, and the crystal structure changes to hexagonal or pseudo-hexagonal. Recent publications have studied this phenomenon in detail [9, 10], and this transition is known to be more complicated than previously thought. However, the main feature of the molecular motion is not altered very markedly.

These two types of transitions in paraffins and urea-hydrocarbon adducts may have a common characteristic. If we assign the orthorhombic-hexagonal transition of adducts to the rotational phase transition, i.e., to the molecular motion of guest molecules, it may be identical with the transition in *n*-paraffins. Since the transition temperature in the adduct is lower by *ca.* 100 K, it may be caused by weaker interaction between guest molecules in the adducts.

The enthalpy of transition of a paraffin is large [11] and the volume change is discrete so that this transition is known as a first-order transition. However, in the case of adducts, the transition enthalpy is far less and the endothermic peak in DTA is rather broad. Parsonage and Pemberton [3, 12] investigated this transition and noticed the importance of longitudinal interaction between guest paraffin molecules in the same channel, i.e., it might be considered as a second-order transition. Because of this, the difference in the mechanism of the two cases should also be clarified, as should the similarity between them. More detailed experimental data are, therefore, necessary on both the thermodynamic quantities and the structural parameters. The second part of the present work deals with the characteristics of the transition.

2. Experimental Procedures

Polycrystalline samples of urea adducts with several kinds of *n*-paraffins, C_nH_{2n+2}, $(11 < n < 32)$, were obtained by adding a xylene solution of the paraffin to a saturated methanol solution of urea. (Hereafter, these adducts are abbreviated as A_P.) The powdered sample thus obtained was dissolved in an excess of methanol. As the solvent slowly evaporated, a single crystal of A_P was obtained. This can also be obtained by slowly cooling the saturated solution at higher temperatures. The adduct with polyethylene (abbreviated as A_{PE}) was obtained by adding urea to a concentrated xylene solution of Sholex 6009 ($M_n = 1.4 \times 10^4$, $M_w = 11.4 \times 10^4$) and keeping the solution at 120°C for several days [13].

The sample cell used for differential thermal analysis under high pressure has been previously reported [14]. About 6 mg of a sample is inserted in a high pressure cell in order to measure T_d. The heating rate is about 10°C/min, and pressures are measured by a calibrated manganin gauge. The pressure-transmitting fluid is silicone oil. In the case of the measurement of T_t (ortho-hex transition point) of A_{PE}, 40 mg of the sample material is necessary and the heating rate is 40°C/min., since the latent heat of the transition is very small.

The ortho-hex transition temperature increases with the chain length of the guest molecule and in the case of A_{PE}, T_t is about 8°C. Since the high pressure cell used is difficult to cool below room temperature, temperature and pressure changes of the crystal structure of the adduct are examined only on A_{PE}.

X-ray diffraction under high pressure was done with Mo$K\alpha$ radiation using a diamond anvil-type cell, but Cu$K\alpha$ radiation was used for the investigation of a single crystal of A_P under atmospheric pressure.

3. Pressure Dependence of Decomposition Temperatures

In the course of heating A_P, two kinds of decomposition processes are observed, depending on the pressure and the number of carbon atoms of the guest paraffin.

When the number of carbon atoms is less than 20, T_d is lower than the melting point of pure (tetragonal) urea, T_m^u, under relatively low pressures, and the adduct decomposes into tetragonal (solid) urea and liquid paraffin (type-1 reaction). Two peaks – decomposition and melting of urea – are thus observed in the thermogram. Only one peak is observed in the case of adducts with guest molecules longer than $C_{20}H_{42}$ or when the pressure is higher than some definite value, P_c, which depends on the chain length of the guest molecules (type-2 reaction). The results obtained are shown in Figure 1.

The pressure dependence of T_m^u is smaller than that of T_d of $A_{C\text{-}11}$ (adduct with $C_{11}H_{24}$), so that the T_d–P curve shows a discontinuity at 0.15 GPa: i.e., the type of reaction changes

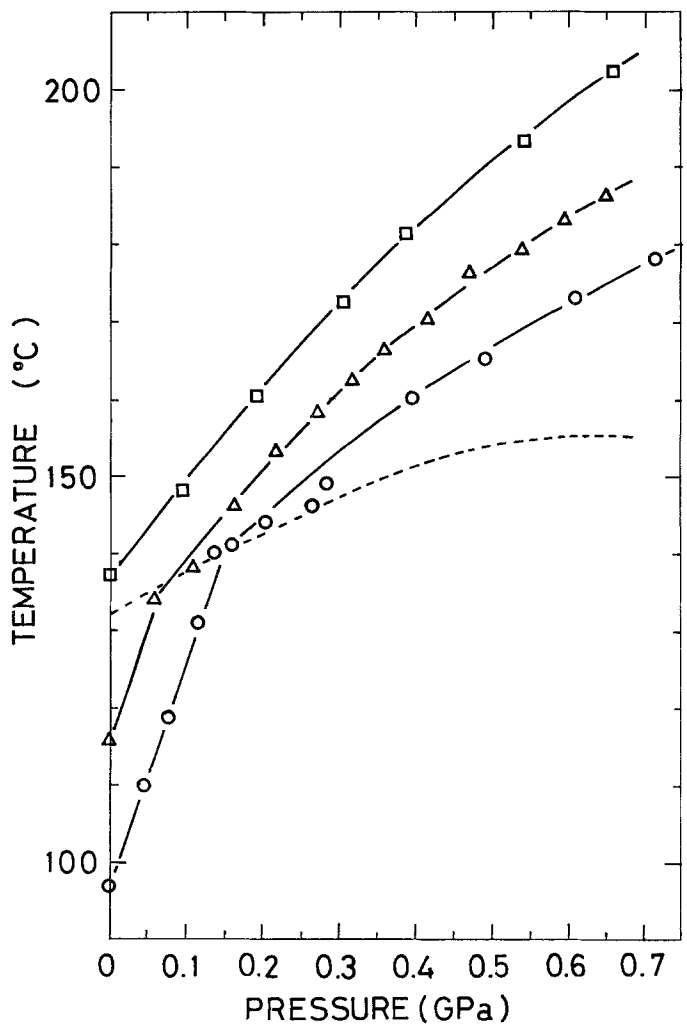

Fig. 1. Pressure dependence of T_d of three kinds of adducts; □: urea adduct with $C_{32}H_{66}$; △: with $C_{15}H_{32}$; ○: with $C_{11}H_{24}$. The dotted curve is the melting point of urea.

from type 1 to type 2 on passing through the critical pressure, P_c. The slope dT_d/dP of A_P is a little bigger in the case of type-1 reactions compared with dT_m/dP of pure paraffins but smaller in the case of type-2 reactions, where T_m^p is the melting point of paraffin (Figure 2).

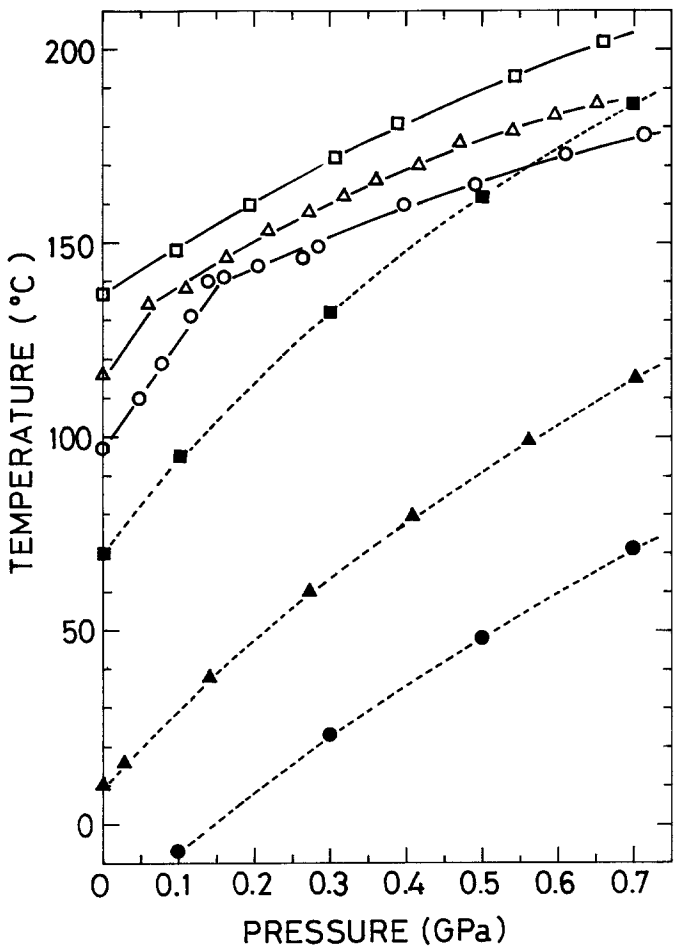

Fig. 2. Pressure dependence of T_d of adducts (full curve) and T_m^p of the *n*-paraffin (dotted curve). Open symbols □, △ and ○ are the same as in Figure 1. Closed symbols ■, ▲ and ● are melting points of the *n*-paraffins, $C_{32}H_{66}$, $C_{15}H_{32}$ and $C_{11}H_{24}$, respectively [15].

Though the decomposition is not reversible, we may assume that the Clausius–Clapeyron relation will hold and the decomposition is treated as a first-order phase transition. Assuming the additive law that the thermodynamic quantities of urea-paraffin adducts are the sum of those of urea and paraffin, we get the following equation.

$$dT_d/dP = \Delta V^a/\Delta S^a \approx (\Delta V^u + \Delta V^p)/(\Delta S^u + \Delta S^p) \quad (1)$$

where ΔV is the volume change and ΔS is the entropy change in the transition, and the superscripts *a*, *p* and *u* correspond to adduct, paraffin and urea, respectively.

In the type-1 decomposition, we take into account the entropy change only of the paraffin neglecting the entropy change from urea in the adduct to tetragonal urea; $\Delta S^u \approx 0$. Since adducts have a hexagonal structure in the temperature range concerned, the configurational entropy of a guest molecule in this phase will be almost the same as that of pure paraffin in the hexagonal phase. Therefore, ΔS^a at T_d will be assumed to be nearly equal to the entropy change of the paraffin at T_m^p, ΔS^p.

The volume of a unit cell of the adduct is about 2.5% smaller than that occupied by the same number of urea molecules in the tetragonal form and one molecule in the solid hydrocarbon [1], so that ΔV^a will be a little larger than ΔV^p for the same number of moles of paraffin, if we assume that the fraction of molar volume in an adduct crystal occupied by paraffins is equal to the molar volume of the solid paraffin crystal. Consequently,

$$dT_d/dP > dT_m^p/dP \quad \text{(type 1)}. \tag{2}$$

In the case of type-2 reactions, urea and paraffin melt simultaneously at T_d; ΔS^u is not negligible. Since $dT_m^u/dP < dT_m^p/dP$ as shown in Figures 1 and 2, we get the following inequality,

$$\Delta V^u/\Delta S^u < \Delta V^p/\Delta S^p. \tag{3}$$

Combining Equation (1) and inequality (3),

$$dT_d/dP < dT_m^p/dP \quad \text{(type 2)}. \tag{4}$$

The relations (2) and (4) explain well the observed results (Figures 1 and 2). Since dT_d/dP is almost constant in the narrow pressure range for the type-1 reaction (Figure 1), the following equation is obtained

$$T_d(P) \approx T_d(0) + P\Delta V(0)/\Delta S^a. \tag{5}$$

This relation can also be deduced from thermodynamics as the first approximation. For adducts with $C_{11}H_{24}$ the observed $\Delta T(\equiv T_d(P) - T_d(0))$ is 21 K for $P = 0.1$ GPa (Figure 1). Since the measured values in the present work are $\Delta H_d = 1.53 \times 10^5$ J/kg and $T_d = 99°C = 372$ K, $\Delta S_d = 412$ J/kg · K. Utilizing the reported value for ΔV^a corrected for thermal expansion, 8.6×10^{-5} m^3/kg, we get 20.9 K for $\Delta T(P)(\equiv P\Delta V^a/\Delta S^a)$ at $P = 0.1$ GPa. The agreement is satisfactory.

Consequently, the decomposition of urea adducts can be treated as first-order phase transitions and the thermodynamic quantities related to this transition can be attributed to those of the components of the system.

This conclusion is reasonable, since the interactions between guest and host molecules in an adduct are weak van der Waals interactions. It will be noticeable that a clear understanding of the decomposition is established from the present experimental results.

4. The Ordered Arrangement of Guest Molecules in the Urea Lattice and the Ortho-Hex Transition of Adducts

On cooling, the crystal structure of an adduct changes from hexagonal to orthorhombic and the transition temperature, T_t, is about 100 K lower than that of the pure paraffin of the same chain length. In the hexagonal phase, it is ascertained that the movement of guest paraffin molecules, such as rotational motion around their long chain axes, is very active compared with that in the low-temperature orthorhombic phase previously mentioned. The thermal

motion along the chain direction will also be active; the degree of longitudinal movement is estimated through the temperature factor of the Bragg reflection [16].

Since the high-temperature phases of adducts and pure paraffins are both hexagonal or pseudo-hexagonal, we can assume that the entropy change at this transition, ΔS_t, will be nearly equal for both materials. On the other hand, the enthalpy change, ΔH_t, is far less in the case of the adduct, as mentioned above and the interaction between guest molecules is reduced appreciably due to their separation by host molecules. Generally, the periodicity in the c-direction of urea lattices is incommensurate with the chain length of the guest molecules and the guest-host interaction will be, on average, smeared out. Parsonage and Pemberton [12] calculated the longitudinal and lateral interactions between guest-guest and guest-host molecules, and discussed the possibility of a phase transition based on the mechanism equivalent to the three-dimensional Ising model. On the other hand, there may be another possibility where each guest molecule interacts through the host urea molecules, e.g., through the distortion of the urea lattice. Positive evidence supporting this idea has not yet been reported, but each urea lattice is distorted from the hexagonal symmetry at a low temperature, according to the orientation of the respective guest molecule included [2].

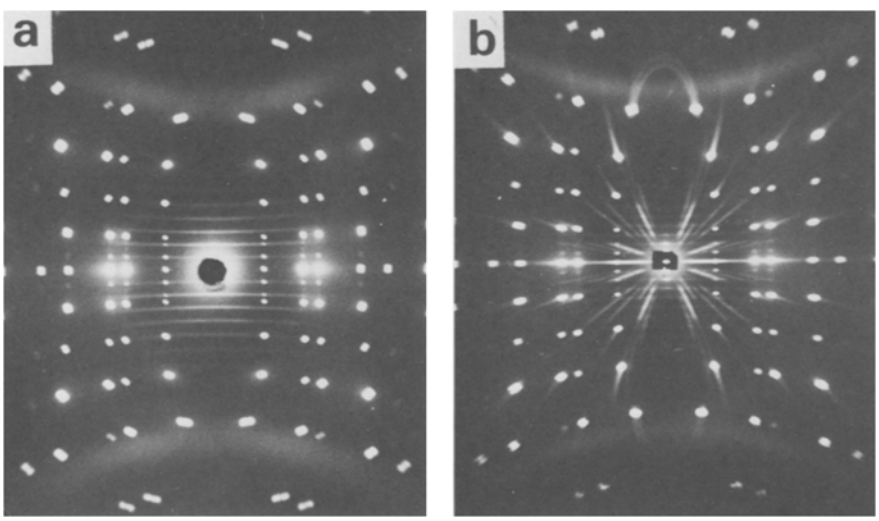

Fig. 3. X-ray photographs of single crystals of adducts. The axis of rotation is the c-axis (vertical). Bragg reflections on layer lines are due to the periodicity of guest paraffin molecules, $C_{20}H_{42}$ (a) and $C_{29}H_{60}$ (b). In (a) monochromatic Cu$K\alpha$ was used with a graphite crystal.

Bragg spots with streaks are observed in X-ray observations of single crystals of adducts (Figure 3). The presence of both streaks and Bragg spots implies the existence of a mean ordered array of guest molecules and the existence of a random positional disorder around the mean position. Since the streaks are confined to the layer lines corresponding to the chain length of guest molecules, the guest molecules in a urea channel are packed close to each other along their chain axes. From the absence of equatorial streaks, the positional disorder is caused by the displacement of the guest molecules along the c-axis.

Bragg spots are observed, even in the cases where the chain length is not commensurate with the periodicity of the urea lattice (c = 11.005 Å) and distinct Bragg spots are clearly seen

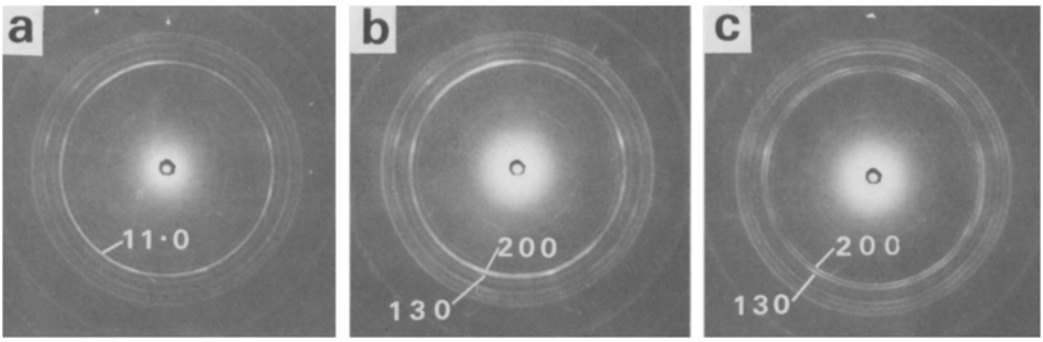

Fig. 4. Powder photographs of the adduct with polyethylene under different pressures (a) P = 1 atm. (b) 0.28 GPa (c) 0.91 GPa.

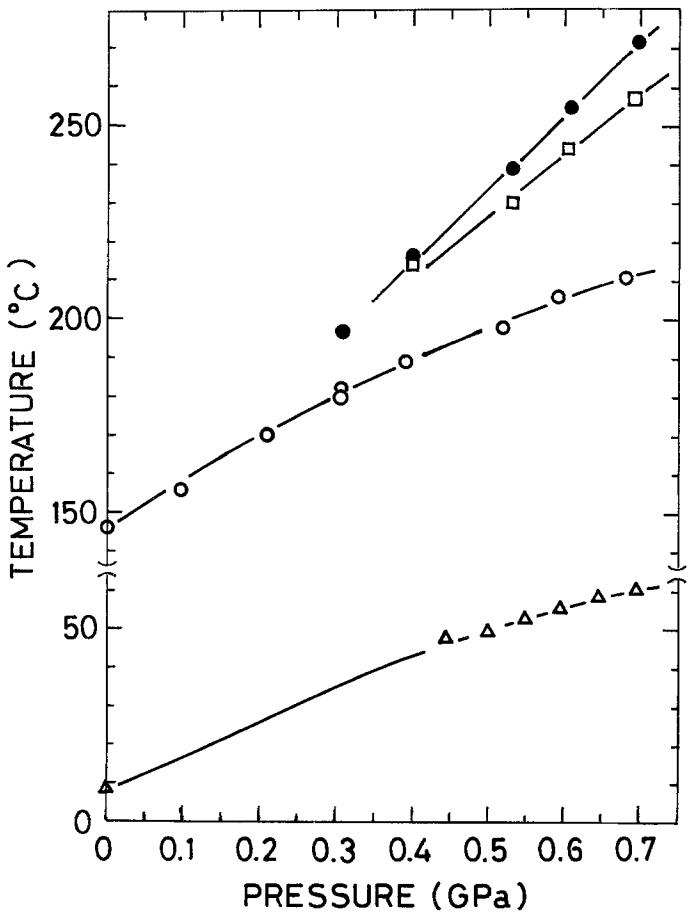

Fig. 5. Pressure dependences of T_t (△) and T_d (○) of A_{PE} and T_t (□) and T_m^p (●) of polyethylene.

for adducts with $C_{20}H_{42}$ (l = 27.485 Å) and $C_{29}H_{60}$ (l = 38.727 Å). It is not clear why such three-dimensional ordering is developed. It may be due to the ordering process in the crystallization of the adducts. However, we measured the intensity change of these Bragg reflections, (00l), compared with temperature and found that the change is reversible [16]. This ordered arrangement of guest molecules will correspond to a free-energy minimum in the adduct crystals.

5. Structural Change of A_{PE} Under High Pressure

When the pressure is hgher than about 0.3 GPa, A_{PE} decomposes into liquid urea and solid (orthorhombic) polyethylene at its T_d (type-3 reaction). Polyethylene itself transforms into the hexagonal phase and melts at a higher temperature as reported previously [17]. The transition temperature, T_t, of the adduct increases with the chain length of the guest molecule [2, 3] and in the case of polyethylene adducts, A_{PE}, T_t is about 281 K [18]. Transition temperature

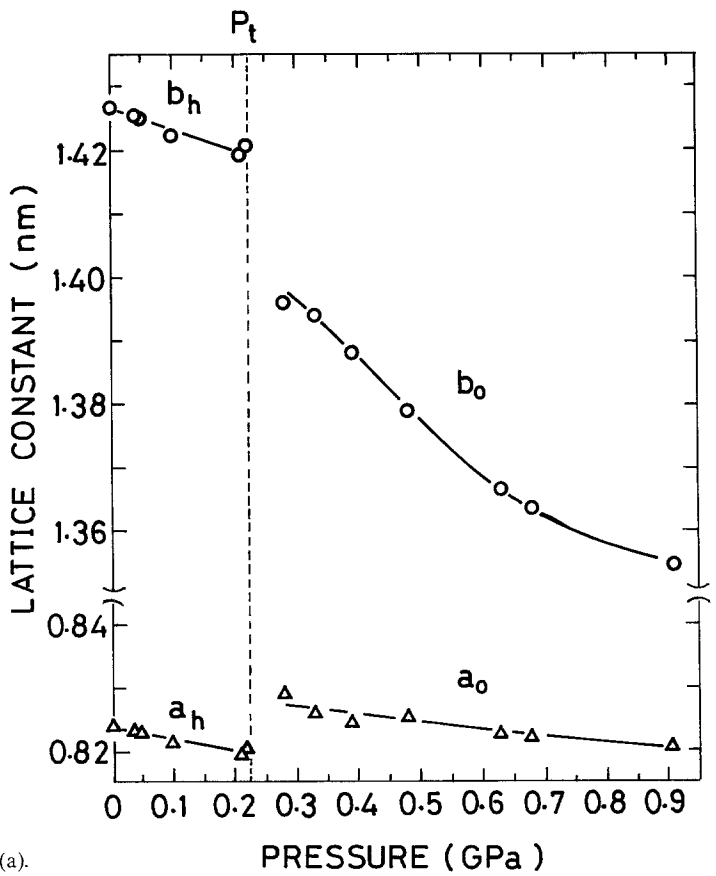

Fig. 6(a).

Fig. 6. (a) Pressure dependences of the lattice parameters of A_{PE}, referring to the orthorhombic reference lattice. Suffices h and o indicate hexagonal and orthorhombic phases, respectively. (b) Pressure dependence of b/a. The orthorhombic unit cell is also taken for the hexagonal phase. (c) Change in the cross-sectional area of the unit cell of A_{PE} with pressure. $S = a \cdot b$. Since the dimension of the c-axis changes little in the pressure range studied, the volume V is proportional to S.

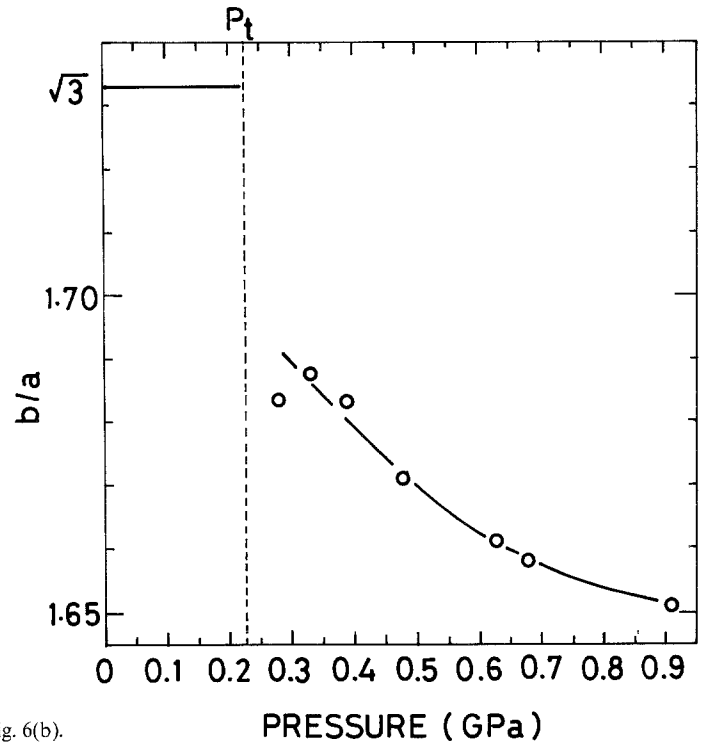
Pt
√3
1.70
1.65
b/a
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9
PRESSURE (GPa)

Fig. 6(b).

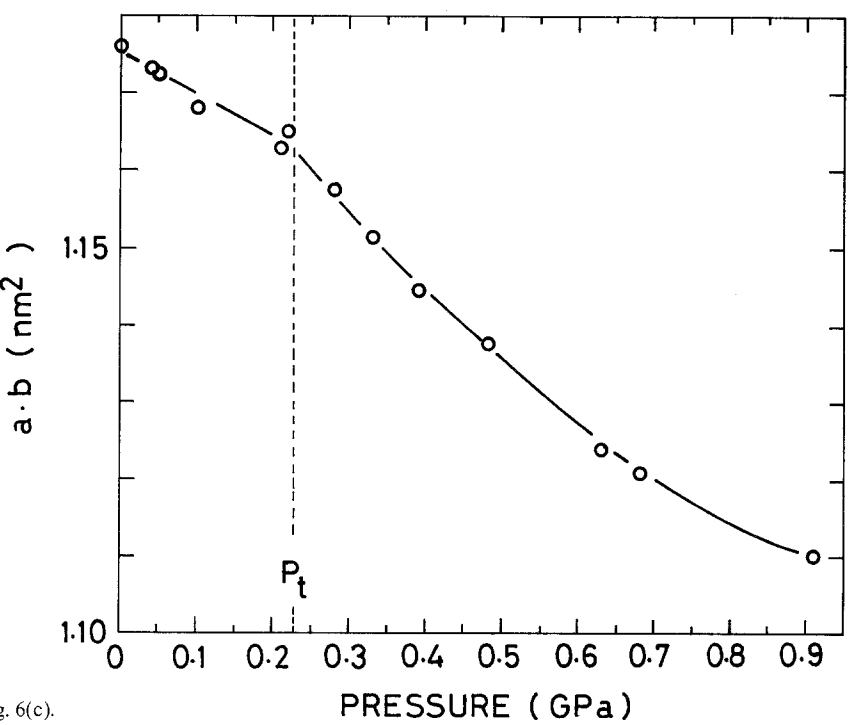
1.15
1.10
a·b (nm2)
Pt
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9
PRESSURE (GPa)

Fig. 6(c).

increases with pressure, so that a pressure-induced phase transition from hexagonal to orthorhombic should be observed at room temperature (*ca.* 25 °C). Actually, this structural change is confirmed by X-ray diffraction at about 0.2 GPa (Figure 4). The transition pressure P_t increases with a rise in temperature. The phase diagram of A_{PE} thus determined by high-pressure DTA is shown in Figure 5 and the changes in lattice parameters at room temperature are shown in Figure 6a and b. As seen in Figure 4, the 130 and 200 reflections of the orthorhombic phase develop with the 11.0 reflection of the hexagonal phase with decreasing pressure, therefore, the detailed information in the pressure range close to P_t cannot be obtained on account of the limit of separation of the diffraction rings. However, if we extrapolate the values of the spacings to P_t, abrupt changes in the lattice parameters are recognized to occur at P_t. The volume change ΔV in the transition is too small to detect experimentally (Figure 6c) but this fact itself does not always deny that the transition is first order. The entropy change ΔS in the transition is small but has a definite value: *ca.* 7.1 J/kg · K [18]. The value for dT_t/dP obtained from Figure 5 is about 8.7×10^{-8} K · m^2/N. Therefore, ΔV in the transition is estimated at 6.2×10^{-7} m^3/kg. This value is only 0.75×10^{-3} of the specific volume of the adducts: 8.2×10^{-4} m^3/kg.

Consequently, this transition is first order, although a discrete volume change is not observable in the present work and the transition has the common feature with the high-temperature transition of solid paraffin concerning the molecular motion. A detailed model on molecular motion in the hexagonal phase of polyethylene adducts cannot be proposed at present, but X-ray investigations on A_P will be published in the near future. It will be interesting to clarify the nature of the molecular motion of a long chain in such a restricted space and under isolated conditions.

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