A disk-like vessel formed with *n*-heptadecane low-pressure phase filmy crystals epitaxially growing during its high-pressure phase growth in the mixed liquid of *n*-pentadecane and *n*-heptadecane

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Abstract

While we optically observed the pressure-induced transformation between the solid phases of SII and SI of *n*-heptadecane, of which *p*–*T* diagram has a parallel and wide gap between the coexistence lines between liquid–SI and between SI–SII (the same as that of *n*-pentadecane), we found that the SII crystal of *n*-heptadecane is stable even below the coexisting line between the SI and liquid, as is that of *n*-pentadecane. Fortunately, we can easily distinguish the SI crystal, of which morphology shows a hexagonal thin plate with very round corners, from the SII crystal, of which morphology shows a long and narrow pillar-like form in the liquid. Here, we report on the epitaxial growth of SI filmy crystals of *n*-heptadecane on its SII crystal in the *p*–*T* condition of 40 MPa and 30 °C. Although we could not observe the epitaxial growth of *n*-pentadecane, we could observe the clear epitaxial growth of *n*-heptadecane in the mixed liquid of *n*-pentadecane and *n*-heptadecane. Growth suppression by *n*-pentadecane brings about clear crystal shapes. Moreover, the epitaxially growing SI filmy crystals of *n*-heptadecane form a disk-like vessel which put its pillar-like SII crystal between the filmy crystals. If several billion years ago this vessel had been formed in a mixed drop of normal alkanes drifting about above the bottom of a deep sea, where the *p*–*T* condition was 40 MPa and 30 °C, the vessel might be seen as a cradle of primitive life.

Keywords Pressure induced crystal growth · Liquid phase epitaxy · Organic compounds · Normal alkanes · Self-organization

1 Introduction

A few odd normal alkanes provide a pair of polymorphism structures in their solids. These phases are the low-pressure and high-temperature solid phase SI (disordered, hexagonal), and the high-pressure and low-temperature solid phase SII (ordered, orthorhombic) (Fig. 1) [1–3]. As the order–disorder transformation between the SI and SII is of great interest to us, we carried out the observations of the growths and transformations of *n*-tridecane and *n*-pentadecane [4–6].

Both polymorphism and order–disorder transformation are the peculiarities of molecular crystals which include

not only odd normal alkanes but also carbon tetrachloride [9] and cyclohexane [10]. These peculiarities are brought about by the following features of molecular crystals: very weak intermolecular forces, which are the bonding forces of the crystals, very stable conformations of the molecules, which are formed by the covalent bonds between C–C, C–H, and C–Cl atoms.

The weak intermolecular forces bring the crystals and their liquids small inner energies *U*s. The stable molecules present small differences of entropy *S* between liquid and solid phases, and the specific volume *V* variation depending on pressure *p*, as discussed later. Due to these thermodynamic properties, the differences of Gibbs free energy

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Fig. 1 The orthorhombic and hexagonal unit cells of *n*-heptatadecane [1–3]. The SII phase is orthorhombic, and the SI phase is hexagonal. **(a)** A projection of the orthorhombic unit cell onto *a*-plane. **(b)** A projection of the orthorhombic unit cell onto *c*-plane. **(c)** A projection of the hexagonal unit cell onto *a*-plane. **(d)** A projection of the hexagonal unit cell onto *c*-plane. A rectangle in **b** with thick black lines is a projection of the unit cell onto *c*-planes. The lattice constants of the orthorhombic unit cell are $a=0.497$ nm, $b=0.748$ nm, and $c=4.703$ nm. In all panels, an *n*-heptatadecane molecule was denoted only with a zigzag C–C bond chain, where a thick and short black stick shows a C–C bond. In the orthorhombic unit cell shown in **a** and **b**, the planes defined by the C–C bond chains are fixed. In the hexagonal unit cell shown in **c** and **d**, the planes can rotate partially hindered along their chain axes within blue circles indicated in **d** [7, 8]. The C–C bond chains of *n*-heptatadecane, which rotate partially hindered in the hexagonal unit cell, are slightly displaced perpendicularly to the chain axes and thus cease the rotations for denser packing of the orthorhombic unit cell

$G(\equiv U - TS + pV)$ between liquid and solids phases are also small.

In particular, the G differences of odd normal alkanes are very small, and will be discussed later. As a result, the SI and SII phases of odd normal alkanes simultaneously coexist with the liquids. Of course, if one solid phase was stable, another solid would be slightly metastable. Small variation of temperature or pressure alternates the stable and metastable phases. The small G differences of

odd normal alkanes motivate us to research their transformations and crystal growth.

As pressure dependence on G is important for our research on odd normal alkanes, we adopted pressure control to observe the transformations and the growths of the solid phases from the liquids. Moreover, pressure fortunately varies very quickly and distributes uniformly in fluids. A diamond anvil cell (DAC) was used, and optimized for optical microscopy to generate high pressure [11].

In our research on odd normal alkanes, we first reported the epitaxial growth of the *n*-tridecane filmy SI crystal along the edge of its thick-pillar-like SII crystal in the liquid [6]. We also reported that the reason why the SI crystal can grow on the SII crystal in the liquid is that the metastable area of SII spreads widely below the SII–SI coexistence line in the p – T diagram of *n*-tridecane [5].

When the SII crystals of *n*-pentadecane first crystallized in the liquid, we found the non-destructive transformation from SII to SI crystals of *n*-pentadecane in the liquid to be the same as that of *n*-tridecane. Moreover, we grew an SII crystal in the liquid, completely filling the gasket hole (specimen vessel) of the DAC. After we compressed the gasket hole, the transformation to SI crystals started. When we compressed the hole further, it was filled completely with the SI crystal. When we finally compressed the hole, all the SI crystal transformed again to the SII crystal [4].

We thus thermodynamically elucidated and concluded that the SII crystal of *n*-pentadecane, which coexisted with the liquid, was a stable phase and that the stable region of the SII solid is separated by that of the SI solid into two areas in the p – T diagram of *n*-pentadecane. From the conclusions regarding *n*-pentadecane, the SII crystal of *n*-tridecane would also be stable even below the coexisting line between the SI and liquid. However, we could not observe the epitaxial growth of the *n*-pentadecane filmy SI crystal along the edge of its thick, pillar-like SII crystal in the liquid.

We continued the research on odd normal alkanes, and decided on *n*-heptadecane as the next research subject. This is because the p – T diagram of *n*-heptadecane has a parallel and wide gap between the coexistence lines between SI–liquid and between SI–SII, as is that of *n*-pentadecane (Fig. 2a). We could observe the SII crystal of *n*-heptadecane coexisting with the liquid over 50 °C. We could not observe the phase transition from the SII to SI phases of *n*-heptadecane through compression, as observed in *n*-pentadecane. Only the phase transition from the SI to SII phases of *n*-heptadecane occurred through compression. Moreover, we could not observe the epitaxial growth of the *n*-heptadecane filmy SI crystal along the edge of its thick, pillar-like SII crystal in the liquid.

Fig. 2 **a** Temperature dependences of SII-SI, SI-liquid, and SII-liquid equilibrium pressures for *n*-tridecane [5], *n*-pentadecane [4] and *n*-heptadecane. The equilibrium pressures of *n*-tridecane and *n*-pentadecane between SII-SI and SI-liquid phases were measured by both CPM and RFT. The equilibrium pressures of *n*-heptadecane measured by RFT are shown in **(b)**. Those between SII and liquid phases were measured by only RFT. **b** Temperature dependences of SII-SI, SI-liquid, and SII-liquid equilibrium pressures for *n*-heptadecane. The equilibrium pressures between SII-SI and SI-liquid phases were measured by both CPM and RFT. Those between SII and liquid phases were measured by only RFT. However, the equilibrium pressures of *n*-heptadecane between SII-SI, SI-liquid and SII-liquid phases were measured by RFT only in the temperature range of 40–60 °C, because the equilibrium pressures between 25 and 40 °C are too small to be measured by RFT

In parallel, we examined the dissolution between *n*-alkane liquids by mixing them with volume ratios 1/9, 1/3, 1/1, 3/1 and 9/1. The *n*-hexadecane and *n*-heptadecane liquids could not form a uniform solution in any volume ratio; they kept separating into two liquid phases. The *n*-tetradecane and *n*-hexadecane, the *n*-octane and *n*-hexadecane, and the *n*-pentadecane and *n*-heptadecane mixed liquids could form a uniform solution in all volume ratios.

Owing to the difference of the orientations of the methyl bases on both the normal alkane terminals, mixed liquid of normal alkanes will separate into mixed liquid of even normal alkanes and that of odd normal alkanes. From

the unexpected feature of mixed liquid of normal alkanes, if the mixed liquid were put the bottom of a deep sea, the liquid would separate into mixed liquid of even normal alkanes and odd normal alkanes.

As for the typical and simple mixed liquid of odd normal alkanes, we prepared the mixed liquid of *n*-pentadecane and *n*-heptadecane with a volume ratio 1/1. In the *p*-*T* condition where *n*-heptadecane crystal can grow, odd normal alkane crystals of carbon number larger than seventeen already crystalized. The adherent power of *n*-pentadecane on the growing interface of *n*-heptadecane is the larger than those of any odd normal alkane crystals of carbon number lower than fifteen. Therefore, the mixed liquid of *n*-pentadecane and *n*-heptadecane can be a typical and simple mixed liquid of odd normal alkanes for the growth of *n*-heptadecane crystals.

We then examined the growth of the SI and SII crystals of *n*-heptadecane in the mixed liquid. When *n*-heptadecane crystal grows in the mixed liquid, the molecule of *n*-pentadecane adheres on the growing interface of *n*-heptadecane and prevents the growth of *n*-heptadecane crystal. As the adherence of *n*-heptadecane molecule on the growing interface of *n*-heptadecane is larger than that of *n*-pentadecane, *n*-pentadecane molecule, which adheres to the interface, finally detaches from the interface. We thus observe the crystal growth of *n*-heptadecane under the growth suppression of *n*-pentadecane molecule in the mixed liquid.

As a result, we could observe clearly the epitaxial growth of the *n*-heptadecane filmy SI crystals along the edges of its thick, pillar-like SII crystal in the liquid. The parallel-arranged pair of SI filmy crystals, which interposed the SII thick, pillar-like crystal resembling a backbone, could grow further, and the filmy crystals would attach their peripheries together. Finally, the SI filmy crystals form a stable, thin disk-like container with the backbone of a thick pillar-like SII crystal.

2 Experimental apparatus and procedure

We used *n*-pentadecane and *n*-heptadecane of analytical grade (purity > 99%) made by Merck Schuchardt OHG. They were used as-supplied without further purification, and were directly drawn from the sample bottles using a disposable micro-syringe to prevent unnecessary contamination. They were mixed in volume ratio 1/1, and the mixed liquid was left alone over a two-week period with shaking for a few minutes each day. The sample densities of *n*-pentadecane and *n*-heptadecane are 767.1 kg/m³ and 778.3 kg/m³ at 22 °C respectively. The molecular weights of *n*-pentadecane and *n*-heptadecane are 0.21242 kg/mol

and 0.24048 kg/mol respectively. Thus, the molar ratio of *n*-pentadecane/*n*-heptadecane = 1.116/1.000.

We measured the phase transition pressures and temperatures of *n*-heptadecane by the cylinder-piston method (CPM), as previously reported [5]. We simultaneously measured the pressure dependences of the liquid, SI and SII of the *n*-heptadecane densities by CPM. Please see Ref. 5 for a detailed description of the measurement apparatus and procedure of the CPM.

The sample volume in the cylinder, which was varied by the translation of the plug inserted into the cylinder moving with a piston rod, was calculated from the plug position measured by a dial gauge (resolution: 1 μm). The initial sample volume was 3.146 cm^3 . The sample completely filled the cylinder at 22 $^{\circ}\text{C}$. The sample mass capsulated in the cylinder was 2.449 g. We could easily obtain the pressure dependence of the molar volume of the sample.

We used the DAC for pressure generation and optical observation of the crystal growth [12]. We confined a small amount of the mixed liquid of *n*-pentadecane and *n*-heptadecane in the hole (diameter: 0.6 mm) of a Pt-5%Au gasket (thickness: 0.5 mm), interposed between the upper and lower diamond faces of the DAC. A ruby ball (diameter: 0.134 mm) was enclosed together with the mixed liquid for pressure measurement by the ruby fluorescence technique (RFT) [13, 14]. We improved the pressure measurement with a precision of less than ± 0.01 GPa using a reference light of a Ne spectrum peak [10]. Please see Ref. 8 for a detailed description of the measurement apparatus procedure of the RFT.

We directly observed the *n*-heptadecane crystals in the DAC, where the crystals coexist with the mixed liquid, using an inverted optical microscope [11]. After partial solidification of the mixed liquid by compression, many needle-like crystals appeared. A single crystal then survived after several pressure adjustments, and which was used for our observation.

3 Results

Figure 2a shows the temperature dependences of the SII–SI, SI–liquid, and SII–liquid equilibrium pressures for *n*-tridecane (20–45 $^{\circ}\text{C}$) [5], *n*-pentadecane (20–40 $^{\circ}\text{C}$) [4] and *n*-heptadecane (25–40 $^{\circ}\text{C}$). Those of SII–SI and SI–liquid of *n*-heptadecane were measured by both CPM and RFT, which were in correspondence. That of SII–liquid was measured by only RFT. It should be noted that the dependences of SII–liquid of *n*-tridecane and *n*-pentadecane settled down below those of SI–liquid. In other words, the SII phases were stable even below the equilibrium pressures between SI and liquid, where the SI phases were no longer stable.

The SII–SI and SI–liquid equilibrium pressures for *n*-pentadecane measured by RFT agreed well with those by CPM. However, the SI–liquid equilibrium pressures for *n*-heptadecane measured by RFT in the temperature range 25–40 $^{\circ}\text{C}$ dispersed widely. Moreover, the SII–liquid equilibrium pressures for *n*-heptadecane measured by RFT dispersed more widely than the SI–liquid equilibrium pressures because of the very low SII–liquid equilibrium pressure.

Figure 2b shows the temperature dependences of the SII–SI and SI–liquid equilibrium pressures for *n*-heptadecane (25–40 $^{\circ}\text{C}$) measured by CPM, and those of the SII–SI, SI–liquid, and SII–liquid equilibrium pressures of *n*-heptadecane (40–60 $^{\circ}\text{C}$) by only RFT. In the high temperature region (40–60 $^{\circ}\text{C}$), the equilibrium pressures of *n*-heptadecane measured by RFT could be measured stably because of the high pressure. They agreed with the extrapolated equilibrium pressures measured by CPM.

Figure 3a shows the pressure dependences of the SII, SI, and liquid densities of *n*-heptadecane at the temperatures from 25 to 40 $^{\circ}\text{C}$ with 5 K intervals measured by CPM.

Fig. 3 **a** Pressure dependences of the SII, SI, and liquid densities of *n*-heptadecane at temperatures from 25 to 40 $^{\circ}\text{C}$ with 5 K interval measured by PCM. The explanatory marks of the dependences at the temperatures are the same as those in (b). **b** Pressure dependences of molar volumes (*v*-*p* diagrams) of the SII, SI, and liquid phases of *n*-heptadecane at temperatures from 25 to 40 $^{\circ}\text{C}$, calculated from the pressure dependences of the densities shown in (a)

Figure 3b shows the pressure dependences of the molar volume of the SII, SI, and liquid of *n*-heptadecane.

Figure 4 shows the alternating growth of an SII thick, pillar-like crystal and SI filmy crystals of *n*-heptadecane in the DAC while maintaining the sample temperature at 29.1 °C. The alternating growth was brought about by the pressure variation across the coexistence line between liquid and SI, which was actually the second coexistence line between SI–SII, and under that between liquid and SII lay.

An SII crystal and the SI crystals, which grew from the edges of the SII crystal, ceased from growing in (a). The final pressure in (a) would be on the actual second coexistence line between SI and SII of *n*-heptadecane in the mixed liquid of *n*-pentadecane and *n*-heptadecane. Because of the growth suppression of *n*-pentadecane in the mixed liquid, the pressure would be larger than that in pure *n*-heptadecane liquid shown in Fig. 3b. The

compression just before (a) increased the pressure above the coexistence line between SI and SII, and thus the SI filmy crystals grew. The growth of the SI crystals decreased pressure to the coexistence line.

The SI crystals were growing again after compression, although the SII crystal slightly dissolved (b). The large amount of the growth of SI crystals slightly decreased pressure again under the coexistence line. Thus, the SI crystals stopped to grow, and the SII crystal were growing (c).

The pressure was kept again on the coexistence line. However, the temperature variation within 0.1 K for 3 h (the interval from (c) to (d)) brought about slight growth of SI crystals. The SI crystals were growing slightly and the SII crystal ceased from growing (d).

As the final pressure of the successive and alternating growth was 41 MPa, the *p*–*T* condition of 41 MPa and

Fig. 4 Sequential images of the alternating growth of an SII thick, pillar-like crystal and SI filmy crystals of an *n*-heptadecane in the mixed liquid kept in the gasket hole of the DAC. A large bright circle in each panel is the gasket hole. The numbers at the upper left corner indicate the date and time of photographing, and the numbers after “T” at the upper right corner indicate the temperatures of the DAC, which are fixed at 29.1 °C. The round blurred shadow at the middle right side of the gasket hole is a ruby ball enclosed for the pressure measurement. The scale bar at the lower left corner in (a) indicates 0.1 mm. The slightly slanting and horizontally very long rectangle in the center of the gasket hole in each panel was the SII crystal. The horizontally long direction of the crystal was the *a*-axis, the upper and lower surfaces were the *c*-planes, and

the very long side surfaces were the *b*-planes. Interference fringes appeared between the lower *c*-plane and the lower diamond surface in (a), (b) and (c). The SI filmy crystals epitaxially grew on the *b*-plane edges between the *c*-planes and the *b*-planes. Two pairs of the filmy crystals grew from the upper and lower edges of the two *b*-planes. Two pairs of filmy crystals could be seen clearly in (b) and (c). **a** The crystals started to grow just before compression. **b** The SI filmy crystals were growing and the SII thick, pillar-like crystal slightly dissolved, 10 min 41 s later from (a). **c** The SI filmy crystals stopped to grow and the SII thick, pillar-like crystal was growing, 14 min 21 s later from (b). **d** The SI filmy crystals were growing and the SII thick, pillar-like crystal stopped to grow, 2 h 57 min 56 s later from (c). The final pressure of the growth was 41 MPa

29.1 °C was on the coexistence line between SI and liquid of *n*-heptadecane in the p - T diagram of the mixed odd normal alkanes. It is important to remember that the SII stable region stretched below the coexistence line. Namely, the p - T condition was also the coexistence condition of SI and SII of *n*-heptadecane.

4 Discussion

First, we would like to discuss the small differences of entropy S and Gibbs free energy G between the SI solid and liquid of *n*-heptadecane, as noted in the Sect. 1.

The density difference between the SI solid and liquid of *n*-heptadecane is 8%, as shown in Fig. 3a. As the value of 8% is as small as that of metals, of which structures of liquid and solid are interpreted as the dense packings of sphere-like atoms, the liquid of *n*-heptadecane has a dense-pack structure. The dense-pack structure is the only parallel arrangement of straight molecules of *n*-heptadecane (molecule of random C-C bond chain cannot exist in the liquid). The parallel arrangement of straight molecules of *n*-heptadecane brings low entropy as a liquid. On the other hand, as the SI solid of *n*-heptadecane has a disorder part in the solid structure (the hindered rotation of the plane of the straight C-C bond chain is allowed), the SI solid has high entropy as a solid. Thus, the difference of entropy S between the SI solid and liquid is small.

The SI crystal has a larger compressibility than that of liquid; in particular, the compressibility of the low-pressure side near the liquid stable region varies larger than that of the high-pressure side near the SII stable region with decreasing pressure (Fig. 3b). A large volume V reduction of *n*-heptadecane with increasing pressure p causes small variation of pV . As a result, the Gibbs free energy G difference between the SI solid and liquid of *n*-heptadecane has small variation in the SI stable region, which is bounded by the coexistence lines between SI-liquid and between SI-SII in the p - T diagram of the mixed odd normal alkanes.

Although we could not observe the SII crystal of *n*-heptadecane first crystallized in the liquid at the temperature range of 25–40 °C, and reasonably we could not observe the phase transition from the SII to SI phases through compression at the temperature range, the SII-Liquid equilibrium line would be expected to situate slightly below the SI-Liquid equilibrium line, from the following two facts.

1. The SII crystal first crystallized in the liquid at the temperature range of 50–55 °C and the pressures are lower than the equilibrium pressures between the SI and liquid phases (Fig. 2b).
2. The large compressibility of the SI crystal brings the Gibbs free energy of the SI phase a slight decreasing

with increasing temperature and with decreasing pressure [4]. As a result, the SII stable region is separated by the SI stable region into two areas in the p - T diagram of *n*-heptadecane.

The relative arrangement of SII-SI, SI-Liquid and SII-liquid equilibrium lines of *n*-heptadecane in the mixed liquid between *n*-pentadecane and *n*-heptadecane will not vary. The arrangement will be only translated to high pressure and low temperature sides. In addition to the translation of the lines, we can expect the growth suppression effect of *n*-pentadecane on the *n*-heptadecane crystals. Although we could not determine the eutectic point of the mixed binary system between *n*-pentadecane and *n*-heptadecane, the system would be eutectic, and the eutectic point would locate in the high concentration area of *n*-pentadecane. We have now a further subject to reveal the 3D p - T - c phase diagram of the binary system between *n*-pentadecane and *n*-heptadecane (c : the mixing ratio between these odd normal alkanes).

We could thus simultaneously observe the SII and SI crystals in the mixed liquid at the pressure of 40 MPa and the temperature of 30 °C (Fig. 4). The p - T condition, which is located in the SI stable region bounded by the SII-SI and SI-liquid equilibrium lines in the p - T diagram of *n*-heptadecane, will be on the SI-liquid equilibrium line of *n*-heptadecane in the mixed odd normal alkane system.

The parallel-arranged pair of SI filmy crystals of *n*-heptadecane provided sharp round peripheries due to the growth suppression effect of *n*-pentadecane (Fig. 4a). We should remember that the filmy crystals of *n*-tridecane have the waving or zigzag peripheries [5, 6]. The SII thick, pillar-like crystal also had sharp planar surfaces due to the growth suppression effect of *n*-pentadecane.

After small compression, the SI filmy crystals of *n*-heptadecane grew and the SII thick, pillar-like crystal slightly dissolved (Fig. 4b). This is because the p - T condition was located in the SI stable region, where the SII crystal is unstable, beyond the SI-Liquid equilibrium line.

As the pressure was decreased by the growth of the SI filmy crystals, the SI filmy crystals ceased to grow and the SII thick, pillar-like crystal started to grow (Fig. 4c). This is because the p - T condition was located in the SII stable region below the SI-liquid equilibrium line.

The alternating growth of an SII thick, pillar-like crystal and SI filmy crystals of *n*-heptadecane bring about a stable arrangement of the crystals (Fig. 4d). Finally, the p - T condition was located on the SI-liquid equilibrium line. The parallel-arranged pair of SI filmy crystals epitaxially grew on the edges of the SII thick, pillar-like crystal. The SI filmy crystals thus formed a stable, thin disk-like container with the backbone of a thick, pillar-like SII crystal.

5 Conclusions

The thin, disk-like container bounded by the SI filmy *n*-heptadecane crystals could grow in the mixed liquid of 30 °C in temperature and 40 MPa in pressure. These temperature and pressure conditions could exist near the spouting holes of hot water at the bottom of a deep ocean, even several billion years ago.

Therefore, the carbon number of the alkane bases of the fatty acid constituting phospholipids is seventeen. Needless to say, phospholipids form the bimolecular lipid membrane, which works as the universal basis of cell membrane. The container may be seen as a cradle of primitive life.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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