

# Crystal Lattice Size and Stability of Type H Clathrate Hydrates with Various Large-Molecule Guest Substances

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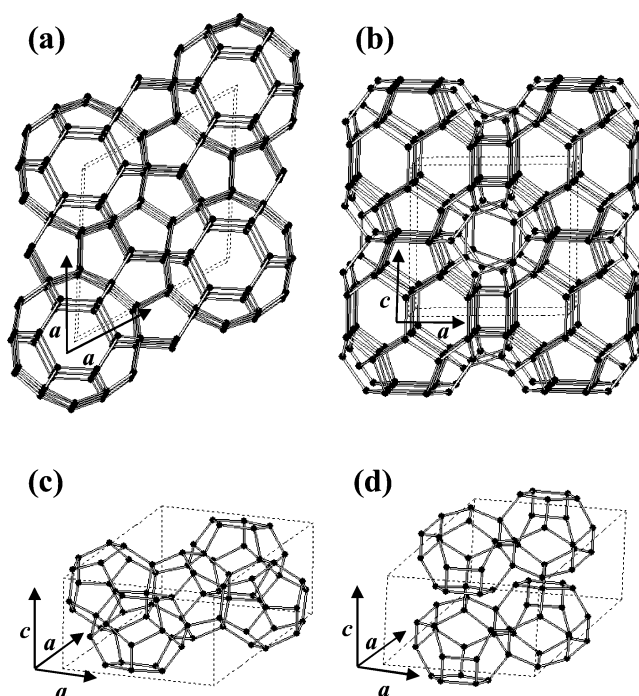
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To gain a better understanding of the effects of guest molecules on the lattice and stability of type H hydrates, we performed powder X-ray diffraction (PXRD) measurements and semiempirical molecular orbital calculations. The unit cell parameters and cohesive energies of various type H hydrates that contain methane ( $\text{CH}_4$ ) were analyzed. PXRD measurements indicated that an increase in the large-molecule guest volume caused the unit cell volume to increase. It was also indicated that a large-molecule guest substance caused the  $a$ -axis-direction of the unit cell to increase with little decrease in the  $c$ -axis direction. Calculations of cohesive energy by means of a semiempirical molecular orbital method indicated that the functional group and configuration of large-molecule guest substances affects the stability of type H hydrates. It was concluded that the icosahedron ( $5^{12}6^8$ ) cages do not easily increase in length along the  $c$ -axis direction when larger guest molecules are used to form the hydrate, but the  $5^{12}6^8$  cage and the layer of dodecahedron ( $5^{12}$ ) cages can easily increase in length along the  $a$ -axis direction due to interactions of the guest–host molecule.

## Introduction

Clathrate hydrates are inclusion compounds consisting of hydrogen-bonded crystals of water molecules with cages that contain a guest molecule.<sup>1</sup> They crystallize mainly under high-pressure and low-temperature conditions. The particular crystallographic structure of the hydrate depends on the guest substance and is categorized according to the size of the guest molecule.<sup>1</sup> These structures include the following types: type I, which has a unit cell consisting of two dodecahedron ( $5^{12}$ ) and six tetrakaidecahedron ( $5^{12}6^2$ ) cages with space group  $Pm3n$  (ref 2); type II, which has a unit cell of sixteen  $5^{12}$  cages and eight hexakaidecahedron ( $5^{12}6^4$ ) cages with space group  $Fd3m$  (ref 3); and type H, which has a unit cell of three  $5^{12}$  cages, two irregular dodecahedron ( $4^35^66^3$ ) cages, and an icosahedron ( $5^{12}6^8$ ) cage with a space group  $P6/mmm$  (ref 4). The structure of type H is shown in Figure 1. Type H hydrate is unique as it always forms with two different guest substances, one being a large-molecule guest substance having a molecular size of  $\sim 8$  Å and the other being a small-molecule guest substance having a molecular size of  $\sim 4$  Å, such as xenon (Xe) or methane ( $\text{CH}_4$ ).

The storage of natural gas in type H hydrates has been studied for industrial applications because this hydrate structure can hold large amounts of natural gas.<sup>5</sup> The amount of guest gas contained in 1  $\text{m}^3$  of the hydrate may exceed 120  $\text{m}^3$  at standard temperature and pressure,<sup>6,7</sup> which is equivalent to compressed



**Figure 1.** Ball-and-stick representation of a type H hydrate: (a) projection perpendicular to the layer of  $5^{12}$  cages (basal plane projection); (b) projection along the layer of  $5^{12}$  cages (i.e., along the  $c$  axis); only  $5^{12}$  and  $4^35^66^3$  cages in the type H hydrate are shown in (c) and (d), respectively. The dotted line in each figure expresses the unit cell of a type H hydrate, and each arrow indicates the axis of the unit cell.

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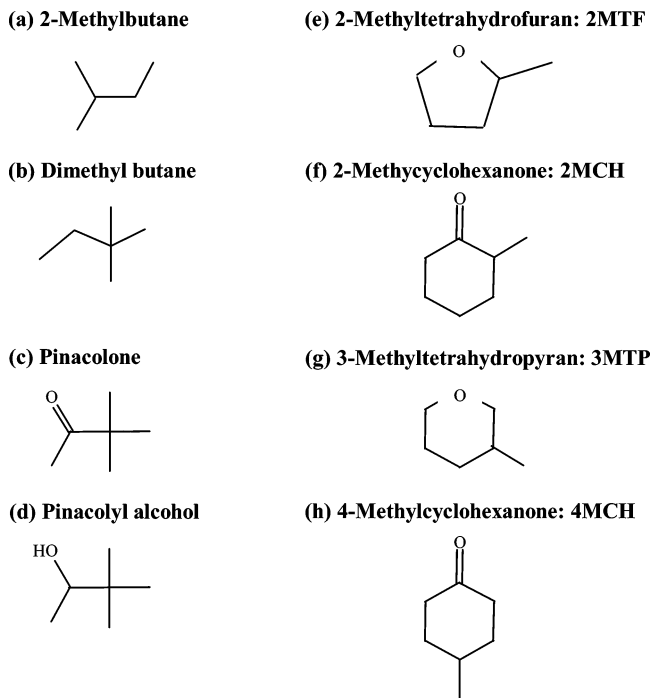
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gas under a pressure of 12 MPa. Because type H hydrate has a lower formation pressure than types I and II (which can also store natural gas<sup>5</sup>), type H hydrates are a promising way to store



**Figure 2.** Structures of the large-molecule guest substances.

and transport natural gas, even though the hydrate must contain a large molecule such as adamantane ( $C_{10}H_{16}$ ) in addition to the  $CH_4$ . Accordingly, thermodynamic properties of several type H hydrates have been investigated experimentally and theoretically.<sup>5,8–13</sup> Recent studies have shown that even a slight difference in the configuration of the large-molecule guest substance has a significant influence on hydrate equilibrium conditions.<sup>14–16</sup> On the other hand, a recent study has made it clear that lattice expansion of a type I hydrate of a binary system can be caused by differences in guest–host interactions.<sup>17</sup> However, it is not clear how the guest substances affect the hydrate stability and the lattice structure.

We describe here the change in lattice size of type H hydrates due to changes in the large-molecule guest substances, based on results from powder X-ray diffraction (PXRD) experiments. Calculations of cohesive energies using the semiempirical molecular orbital method, which reflect equilibrium conditions of type H hydrates, are also described, to understand the change in lattice size of type H hydrates.

## Experimental Section

Eight hydrate crystal samples were synthesized in a high-pressure vessel from mixtures of distilled water,  $CH_4$  (99.99%; Takachiho Chemical Industrial, Co., Ltd.), and one of the following large-molecule guest substances: 2-methylbutane ( $C_5H_{12}$ ), also known as isopentane; dimethylbutane ( $C_6H_{14}$ ), also known as neohexane; pinacolone ( $C_6H_{12}O$ ), pinacolyl alcohol ( $C_6H_{14}O$ ), 2-methyltetrahydrofuran ( $C_6H_{12}O$ ), hereafter referred to as 2MTF; 3-methyltetrahydropyran ( $C_6H_{12}O$ ), hereafter referred to as 3MTP; 2-methylcyclohexanone ( $C_7H_{12}O$ ), hereafter referred to as 2MCH; and 4-methylcyclohexanone ( $C_7H_{12}O$ ), hereafter referred to as 4MCH. The structures of these large molecules are shown in Figure 2 and their certified purities are summarized in Table 1. Because all hydrates in this study contain  $CH_4$ , we refer to the large-molecule guest substance as simply the guest molecule.

Hydrate crystal samples for powder X-ray diffraction measurements were prepared with liquid water, a liquid guest

substance, and  $CH_4$  gas using a high-pressure cylinder. The vessel was a stainless steel cylinder with inner dimensions 80 mm in diameter and 40 mm in height and was equipped with a magnetic stirrer to agitate the fluids and hydrate crystals inside the vessel.<sup>14</sup> In each experimental run, the vessel was first charged with liquid water and each large-molecule guest substance. We used 35 cm<sup>3</sup> of liquid water and 20 cm<sup>3</sup> of each large-molecule guest substance. The vessel containing the liquids was then immersed into a bath equipped with a PID-controlled cooling/circulating unit. The temperature inside the vessel was kept at 274 K. The air was purged from the vessel by repeating the procedure of pressurization with  $CH_4$  to 1.5 MPa and depressurization to atmospheric pressure three times. The  $CH_4$  gas was then supplied from the high-pressure  $CH_4$  cylinder through the pressure regulating valve, thereby setting the pressure inside the vessel at 2.5 MPa in all of the experiments except for the experiment with 2MTF. This temperature–pressure condition was set outside type I  $CH_4$  hydrate formable conditions to avoid the possible formation of type I  $CH_4$  hydrate. In the experiment with 2MTF the pressure was set at 3.5 MPa at 274 K. This temperature–pressure condition is inevitably set in the range of type I  $CH_4$  hydrate formation conditions because the phase-equilibrium conditions in the 2MTF system are quite close to those in the  $CH_4$  + water system without any large-molecule guest substances. The line connecting the test vessel and the high-pressure  $CH_4$  cylinder was opened during the hydrate formation in the vessel to keep the pressure constant by continuously supplying  $CH_4$  gas to compensate for pressure reduction in the vessel due to hydrate formation, so that a sufficient amount of hydrate crystals would be stored in the cell. Pressure and temperature were kept constant for over 50 h with continuous agitation in the vessel at 400 rpm after nucleation of the hydrate. The vessel was subsequently taken out of the temperature-controlled bath and then immediately immersed into a liquid nitrogen pool in a stainless steel container. We allowed 20 min for  $T$  to decrease to below  $\sim 100$  K and then disassembled the vessel to remove the hydrate crystals inside under a nitrogen ( $N_2$ ) gas atmosphere below 100 K. Lacteous and massive hydrate samples were removed from the vessel.

For the PXRD measurements, the hydrate samples were ground under a  $N_2$  gas atmosphere at a temperature below 100 K to avoid their dissociation. Fine-powdered hydrate samples were placed in a quartz glass capillary tube (Hilgenberg; 2.0 mm, 0.01 mm thick) and then put on top of a goniometer of the X-ray diffraction apparatus (50 kV, 200 mA; Rigaku model Rint-2000). The measurements were done using Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å) at 113 K and atmospheric pressure. The temperature of the sample during the measurements was kept constant within 1.0 K by blowing cold, dry  $N_2$  gas around the capillary tube. During PXRD measurements, the temperatures of samples were calibrated by using temperature measurements performed with a K-type thermocouple in advance of the PXRD measurements. The PXRD measurements were done in  $2\theta$  step scan mode with a step width of 0.02° in the  $2\theta$  range of 5–70°. To eliminate the possible effects of preferred orientations, the sample capillary cell was rotated at 60 rpm during each measurement.

The unit cell parameters of the hydrate samples were determined from their diffraction patterns using a full-pattern profile fitting method via RIETAN-2000.<sup>18</sup> Because the hydrate has a hexagonal structure, there are two unit cell parameters,  $a$  and  $c$ , to be determined. To determine them, we used diffraction from hexagonal ice as a standard by assuming that the  $a$  and  $c$

TABLE 1: Calculated Properties of the Large Guest Molecules and Their Type H Hydrates

| large guest molecule    | vol of molecule (Å <sup>3</sup> ) | max van der Waal diameter (Å) | source                       | dissociation pressure at 275 K (MPa) | unit-cell parameter <i>a/c</i> (Å) | vol of unit cell (Å <sup>3</sup> ) | cohesive energy per H <sub>2</sub> O (kJ/mol) |
|-------------------------|-----------------------------------|-------------------------------|------------------------------|--------------------------------------|------------------------------------|------------------------------------|---|
| isopentane              | 95                                | 8.0                           | Aldrich Chemical, 99%        | 2.52 <sup>8</sup>                    | 12.15(9)/10.031(8)                 | 1282(2)                            | −41.6691                                      |
| neohexane               | 111                               | 8.0                           | Tokyo Chemical Industry, 99% | 1.41 <sup>14</sup>                   | 12.150(9)/10.009(3)                | 1287.9(6)                          | −41.8667                                      |
| pinacolone              | 114                               | 8.0                           | Aldrich Chemical, 99%        | 1.41 <sup>14</sup>                   | 12.192(2)/9.981(8)                 | 1285.2(2)                          | −41.8152                                      |
| pinacolyl alcohol       | 119                               | 8.0                           | Aldrich Chemical, 99%        | 1.87 <sup>14</sup>                   | 12.251(3)/9.966(3)                 | 1295.5(6)                          | −41.7469                                      |
| 2-methyltetrahydrofuran | 93                                | 8.2                           | Aldrich Chemical, 99%        | 3.10 <sup>16</sup>                   | 12.141(3)/10.018(3)                | 1278.8(5)                          | −41.5858                                      |
| 2-methylcyclohexanone   | 110                               | 8.2                           | Aldrich Chemical, 99%        | 1.68 <sup>15</sup>                   | 12.171(4)/10.023(5)                | 1286.2(8)                          | −41.8337                                      |
| 3-methyltetrahydropyran | 111                               | 7.5                           | Aldrich Chemical, 99%        | 1.50 <sup>16</sup>                   | 12.126(3)/10.040(3)                | 1278.4(6)                          | −41.6085                                      |
| 4-methylcyclohexanone   | 120                               | 8.0                           | Aldrich Chemical, 99%        | 1.86 <sup>15</sup>                   | 12.157(5)/10.068(5)                | 1288.8(9)                          | −41.8478                                      |

values for ice were 4.49734 and 7.32160 Å, respectively. (These values were extrapolated from the results of Röttger et al.<sup>19</sup> to 113 K.)

### Calculations

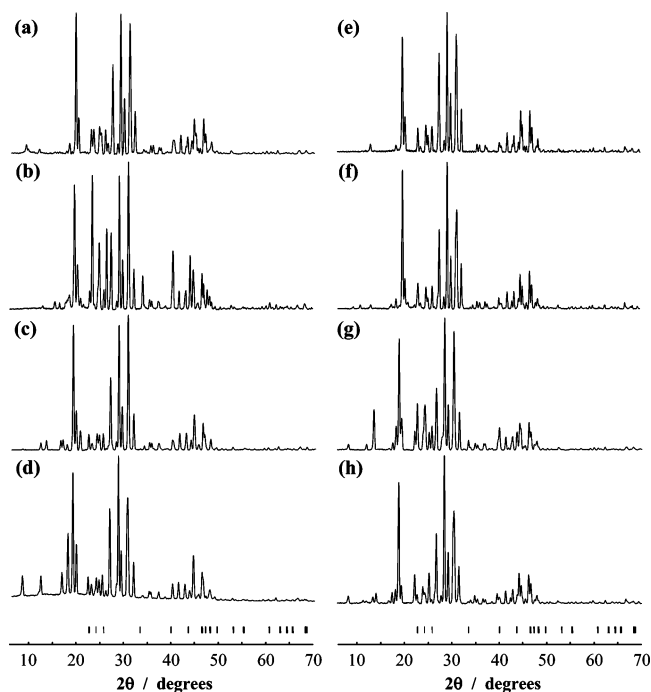
Semiempirical molecular orbital calculations for the type H hydrates of various guest molecules were performed to estimate cohesive energy using MOPAC2002<sup>20,21</sup> with PM3 parametrization<sup>22</sup> under the periodic boundary condition. In this study, the cohesive energy was defined as the difference between the heat of formation of hydrate crystal and that of the constituent.

The lattice structure data of a type H hydrate of Ar reported by Manakov et al.<sup>23</sup> were used as the initial structure for our molecular orbital calculations. In the geometry optimization calculations of that method, all atomic positions of the host lattice and guest molecules in the unit cell were fully optimized with periodic boundary conditions. During the geometry optimization calculations for the type H hydrates, the unit cell axis was not fixed to be 120°, which corresponds to orthorhombic symmetry, because the MOPAC2002 program does not allow fixing of the unit cell axis angle. Nevertheless, the resultant axis angles of 120.0(8)° were almost the same as the initial value of 120.0°, which suggested that the optimized structures were consistent with that of a type H hydrate.

### Results and Discussion

X-ray diffraction profiles at 113 K show that the crystal structures are type H (see Figure 3). Some peaks in the plots are from hexagonal ice that was transformed from interstitial water. These profiles were used to determine the unit cell parameters, *a* and *c*. Each X-ray profile of type H hydrate shows similar relative peak intensities. The differences in peak intensities for 2θ below about 20° would suggest a different type of guest molecule and a different distribution of guest molecules in the host lattice.

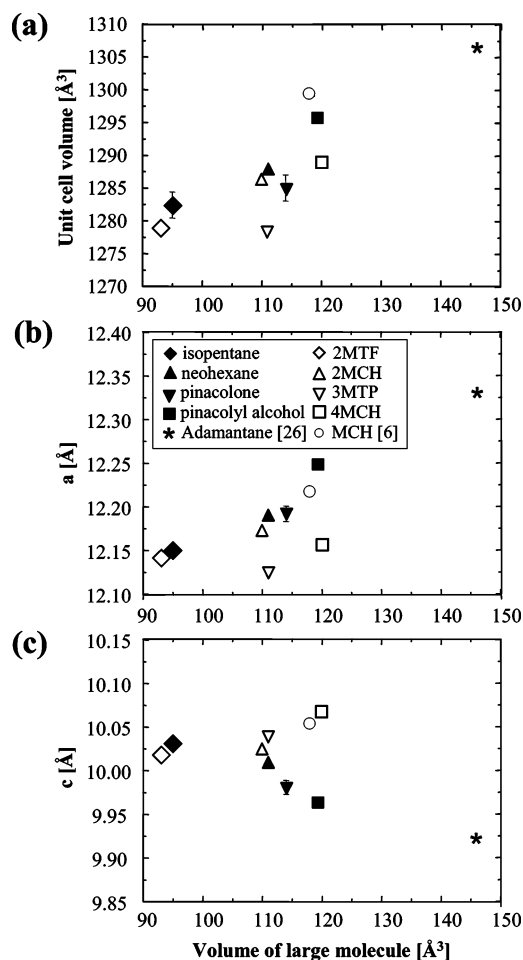
One way to distinguish the various guest molecules is by their molecular volumes. To estimate these volumes, we used the Winmster program.<sup>24,25</sup> In the cases of isopentane, neohexane, pinacolone, and pinacolyl alcohol, the functional groups, methyl (−CH<sub>3</sub>), carbonyl (C=O), and hydroxyl (−OH) are another way to distinguish guest molecules. The resulting trends in the unit cell parameters are shown in Figure 4. Resultant unit cell volumes have a general dependence on the volume of the guest molecule for all types of guest molecules used in this study (Figure 4a). This trend in the volume of the unit cell is consistent with experimental results for a type II hydrate.<sup>6</sup> However, Figure 4b shows that, on average, the unit cell parameter *a* increases with an increase in the guest volume. In contrast, the unit cell parameter *c* decreases on average for an increase in the guest



**Figure 3.** X-ray diffraction patterns of the type H hydrates at 113 K: (a) CH<sub>4</sub> + isopentane hydrate; (b) CH<sub>4</sub> + neohexane hydrate; (c) CH<sub>4</sub> + pinacolone hydrate; (d) CH<sub>4</sub> + pinacolyl alcohol hydrate; (e) CH<sub>4</sub> + 2MTF hydrate; (f) CH<sub>4</sub> + 2MCH hydrate; (g) CH<sub>4</sub> + 3MTP hydrate; and (h) CH<sub>4</sub> + 4MCH hydrate. The curves in each pattern represent the observed intensities. The line marks below each pattern show the calculated peak positions for hexagonal ice.

volume (Figure 4c). In the cases of 2MCH, 3MTP, and 4MCH, the results in Figure 4 show that the unit cell parameters do not have an obvious dependence on the volume of the guest molecule even though their volumes are larger than those of 2MTF and isopentane.

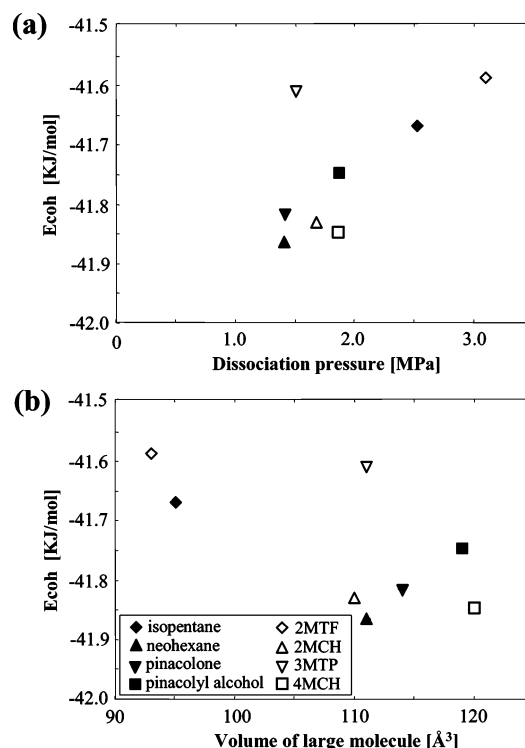
Udachin et al. and Kirchner et al. performed single-crystal structural analysis of a type H hydrate made with CH<sub>4</sub> and methylcyclohexane (C<sub>7</sub>H<sub>14</sub>), the latter referred to as MCH, at 173 K and adamantane (C<sub>10</sub>H<sub>16</sub>) + CH<sub>4</sub> hydrate at 123 K.<sup>6,26</sup> The single-crystal analysis results at different temperatures were then converted to unit cell parameters at 113 K using thermal expansion coefficient of type H hydrate,<sup>27</sup> which is the same temperature that we used in this study for comparison of unit cell parameters of type H hydrate. The unit cell parameters with values converted to 113 K are also shown in Figure 4 for comparison. The converted unit cell parameters of adamantane, as measured by single-crystal structural analysis, seem to overlap with the trend for isopentane, neohexane, pinacolone, and pinacolyl alcohol. The converted unit cell parameters of MCH measured by single-crystal analysis seem to overlap with the trend for 2MTF, 2MCH, 3MTP, and 4MCH.



**Figure 4.** Unit cell parameters for the H hydrates with various guest molecules: (a) unit cell volume; (b) *a*-axis; (c) *c*-axis. The values are based on the PXRD results at 113 K. Results from refs 6 and 26 were converted to their estimated values at 113 K using the results of Tse.<sup>27</sup> The error bars of all parameters are smaller than the symbols.

These anisotropic unit cell parameter results suggest that the type of guest molecule in the 5<sup>12</sup>6<sup>8</sup> cages differs in its effect on the host lattice of the type H hydrate structure. Here it should be noted again that the unit cell parameter *c* decreased on average when the guest molecular volume increased in the case of isopentane, neohexane, pinacolone, and pinacolyl alcohol. This puzzle may be partly resolved by performing structure refinement on type H hydrate, including the positions of each guest molecule in the cage structures using full-pattern profile fitting of PXRD patterns.

Instead, we used a simpler consideration for the previous results, as follows. For the type H hydrate, the unit cell parameter *a* is determined by the layers of 5<sup>12</sup> cages (Figure 1c), whose vacant sites are occupied by 5<sup>12</sup>6<sup>8</sup> cages (Figure 1d). The unit cell parameter *c* of type H hydrate is equal to the length of the 5<sup>12</sup>6<sup>8</sup> cage in the *c*-axis direction, as shown in Figure 1b. It has been reported that the thermal expansion of the unit cell parameter *a* in type H hydrates is larger than that of the unit cell parameter *c*.<sup>27</sup> This suggests that the 5<sup>12</sup> cage layer expands easily and that the 5<sup>12</sup>6<sup>8</sup> cage expands mainly in the *a*-axis direction, not the *c*-axis direction. Here, taking into account the anisotropic expansion of the unit cell parameters *a* and *c* of type H hydrate with the types of guest molecules used in this study, the following conclusion is obtained: When guest molecules enter the hydrate, the 5<sup>12</sup>6<sup>8</sup> cages have enough space in the *c*-axis direction and the cages just become more spherical



**Figure 5.** Calculated cohesive energies of the hydrates: (a) in terms of the dissociation pressures; (b) in terms of the guest molecular volumes.

(increase in *a*-axis length and decrease in *c*-axis length) to make more space. However, shrinking of the 5<sup>12</sup> cage is not as easy because it has a CH<sub>4</sub> molecule inside. So the 5<sup>12</sup> cage also expands to make space for the 5<sup>12</sup>6<sup>8</sup> cage expansion in the *a*-axis direction, otherwise the 5<sup>12</sup> cage would have to shrink. As a result, the unit cell parameter *c* decreases with an increase in the unit cell parameter *a*.

The cohesive energies per water molecule of the type H hydrate were calculated by a semiempirical molecular orbital calculation. This information is useful for estimating the phase equilibrium curves of the pure hydrate system, as has been shown for the case of a type I hydrate.<sup>28</sup> To better understand how the guest substances affect their hydrate stabilities, we calculated the cohesive energies per water molecule for the type H hydrates. In the calculations, the 5<sup>12</sup> and 4<sup>3</sup>5<sup>6</sup>6<sup>3</sup> cages are occupied by a CH<sub>4</sub> molecule and the 5<sup>12</sup>6<sup>8</sup> cage is occupied by one of the following: isopentane, neohexane, pinacolone, pinacolyl alcohol, 2MTF, 3MTP, 2MCH, or 4MCH. The results are listed in Table 1.

The calculated cohesive energies were compared with the dissociation pressure of each hydrate. Figure 5a shows that, on average, the calculated cohesive energy increases as the dissociation pressure of hydrate crystals is increased. In fact, except for the case of 3MTP, the energy–pressure relation is nearly linear. These results suggest that the cohesive energies of type H hydrates calculated using semiempirical calculations are reasonable for estimating their stabilities.

In general, it is suggested that hydrate stability increases with the volume of the guest molecule, from the equilibrium conditions. We compared the cohesive energies to the molecular volumes. Figure 5b also shows that on average, the calculated cohesive energy increases as the molecular volume increases. In addition, Figure 5b shows the effects of functional groups on the cohesive energy for neohexane, pinacolone, and pinacolyl alcohol. For these three guest molecules, the larger the molecular



volume, the greater the destabilization of the hydrate structure. This suggests that the hydroxyl ( $-\text{OH}$ ) group and the carbonyl ( $\text{C}=\text{O}$ ) group make the hydrate structure more unstable than hydrocarbon groups do. These results are consistent with previously reported phase equilibrium data.<sup>14–16</sup> They imply that these functional groups interact with the host lattice or other guest molecules in the hydrate. Hence, the type of functional group and configuration of the guest molecule affect the equilibrium conditions of a type H hydrate. These interactions between guest–host molecules would cause anisotropic changes in the unit cell parameters as measured by means of PXRD.

In this study, anisotropic crystal lattice change due to large-molecule guest substances was shown, based on experimental results obtained using PXRD. The effects of guest molecules on the host lattice of type H hydrate were also indicated by the calculation using a semiempirical molecular orbital method. In general, one should calculate the absolute values of total energy from first principle calculations; however, when starting from first principle calculations, much greater computer resources and longer times are required than for semiempirical calculations. Therefore, in this study we used semiempirical calculations to compare the relative stabilities of hydrates with various guest compositions. Further study, such as comparison of atomic parameters refined by experimental results using diffraction methods and optimized structures by calculation methods, will be useful to improve our understanding of the effects of large molecules on the stability of type H hydrates.

## Conclusions

We used PXRD and a semiempirical molecular orbital calculation method to analyze the structure and equilibrium conditions of type H hydrates containing  $\text{CH}_4$  and one of the following molecular types: isopentane, neohexane, pinacolone, 2MTH, 3MTP, pinacolyl alcohol, 2MCH, and 4MCH. The PXRD results showed that the unit cell volumes have a dependence on the volume of large-molecule guest substances. It was also shown that an increase in the guest molecule volume and differences in functional groups caused the unit cell parameter  $a$  to increase on average but parameter  $c$  to slightly decrease on average. The calculation results by means of a semiempirical molecular orbital method indicated that the calculated cohesive energy increases as the dissociation pressure of type H hydrate is increased, which suggests that the calculated cohesive energy is a reasonable reflection of the stability of a type H hydrate. The calculation results indicate that the stabilities of type H hydrates depend on the functional group and the configuration of the large-molecule guest substance. Differences in these would cause a change in the interaction with guest–host molecules. Taking into account the type H hydrate lattice structure which consists of three types of cage structures, the following conclusion was obtained: The  $5^{12}6^8$  cages do not easily increase in length along the  $c$ -axis direction when larger

guest molecules are used to form the hydrate, but the  $5^{12}6^8$  cages and the layer of  $5^{12}$  cages can easily increase in length along the  $a$ -axis direction due to interactions with the guest–host molecule.

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