Phase Transitions

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# Phase Transition of a Structure II Cubic Clathrate Hydrate to a Tetragonal Form

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***Abstract:*** *The crystal structure and phase transition of cubic structure II (sII) binary clathrate hydrates of methane ($CH_4$) and propanol are reported from powder X-ray diffraction measurements. The deformation of host water cages at the cubic–tetragonal phase transition of 2-propanol + $CH_4$ hydrate, but not 1-propanol + $CH_4$ hydrate, was observed below about 110 K. It is shown that the deformation of the host water cages of 2-propanol + $CH_4$ hydrate can be explained by the restriction of the motion of 2-propanol within the $5^{12}6^4$ host water cages. This result provides a low-temperature structure due to a temperature-induced symmetry-lowering transition of clathrate hydrate. This is the first example of a cubic structure of the common clathrate hydrate families at a fixed composition.*

Clathrate hydrates, also known as gas hydrates, are host–guest compounds that are crystalline materials consisting of water molecule frameworks. The host water cages of clathrate hydrate are hydrogen-bonded and encage guest molecules inside via van der Waals interactions.[1] Each guest molecule is encaged into different types of cages ordered in three-dimensional structures according to the size of the guest molecule. Three different crystal structure of clathrate hydrate are well known depending on type of guest molecules; cubic structure I (sI) with space group $Pm\bar{3}n$, cubic structure II (sII) with space group $Fd\bar{3}$m, and hexagonal structure H (sH) with space group $P6/mmm$.[2] These host structures are analogues of the semiconducting Group 14 clathrates[3] and silica clathrates (so-called clathrasils).[4]

Natural-gas or methane hydrate is now seen as a possible global source of methane,[5,6] and the capability of gas hydrates to store large amounts of gas has opened up possibilities for potential industrial applications such as hydrogen[7,8] and ozone[9,10] storage. Physical properties of gas hydrates are attributed to host–guest interactions such as rattling motions[11] or hydrogen bonding[12,13] of guest molecules. Host–guest interactions also play a crucial role, as gas hydrate structures are thermodynamically stable only when a minimum number of cages are occupied by the guest molecules, depending on their nature.

Phase changes of clathrate hydrates are known to take place with pressure, and cubic clathrate structures, sI and sII, at ambient pressure transform to hexagonal sH or a structure closely related to it at pressure above 0.5 GPa.[14] Up to now, however, few examples of the phase change with temperature have been reported in the common clathrate hydrate structural families sI, sII, and sH at constant composition.[15,16] On the other hand, clathrasils have a variety of polyhedral cages and show temperature-induced phase changes.[17] Given the analogy between oxygen linking tetrahedral atoms in silicate framework structure in clathrasils and hydrogen bonds linking oxygen atoms in clathrate hydrates,[18,19] there is a great interest in determining whether lower symmetry clathrate hydrates are indeed realized from cubic clathrate structures with changes in temperature.

Herein, we present the results of X-ray crystal structure analysis of binary hydrates of 1-propanol + $CH_4$ and 2-propanol + $CH_4$. Alcohol molecules are soluble in water, and do not form pure clathrate hydrates at higher temperatures. They were thought to be inhibitors of gas hydrate formation due to host–guest hydorogen bonding, but it has been recently reported that alcohols, such as methanol,[20] ethanol,[21] propanols,[22–25] and butanol,[26] form gas hydrates in the presence of a help gas such as $CH_4$. Because the OH group of these molecules may modify the host–guest interactions,[27] a detailed comparison of the structures and dynamics of guest molecules may lead to further insights into the guest dynamics and the host–guest interactions in these inclusion compounds.

Binary hydrates of $CH_4$ + 1-propanol and $CH_4$ + 2-propanol were formed from solution of liquid water and 1-propanol or 2-propanol at a molar ratio of 17:1 (that is, 0.0556 mole fraction 1-propanol or 2-propanol aqueous solution) by pressurizing up to 2.2 MPa with $CH_4$ at 268.3 K. The crystal structure of both 1-propanol + $CH_4$ hydrate and 2-propanol + $CH_4$ hydrate was cubic sII, as expected. Interestingly, in the case of 2-propanol + $CH_4$ hydrate, the powder diffraction profile showed that regular cubic sII transformed into a different crystal structure with a lower symmetry below about 110 K, some diffraction peaks being split (see Figure 1), whereas the crystal structure of 1-propanol + $CH_4$ hydrate did not change at temperatures between 93 K and 200 K. It was also revealed that the phase transition was reversible and the phase transformed back to sII form upon heating.

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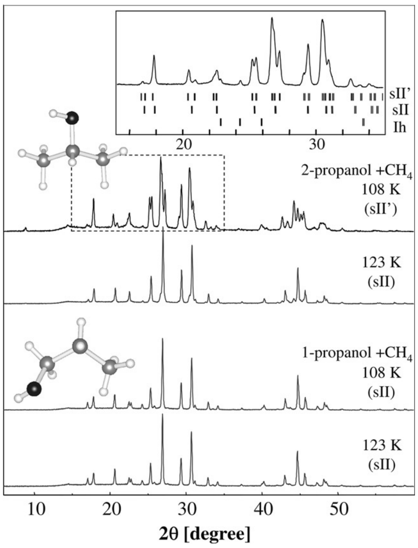

*Figure 1.* Powder X-ray diffraction (PXRD) patterns of 1-propanol + $CH_4$ and 2-propanol + $CH_4$ hydrates. At 123 K, crystal structure of these two hydrates were sII. Inset: the peak splitting at 108 K due to the phase transition from the sII hydrate (middle tick marks) to sII′ hydrate (upper tick marks). Here, the calculated peak positions for hexagonal ice Ih (lower tick marks) which coexists within the hydrate sample are also shown.

The PXRD profile of 2-propanol + $CH_4$ hydrate at 93 K (sII′) was indexed by the software Materials Studio X-Cell of BIOVIA, Corp.[28] Its lattice was determined to be tetragonal with a space group of $I4_1/amd$ (no.141), $I\bar{4}2d$ (no.122), $I4_1md$ (no.109), $I4_122$ (no.98), $I4_1/a$ (no.88), $I\bar{4}$ (no.82), $I4_1$ (no.80), or $I4$ (no.79) from the extinction rule. $I4_1/amd$ was found to be the best that can successfully form the host cage structure. While the high-temperature unit cell of sII described as $16D{\cdot}8H{\cdot}136H_2O$ (D ($5^{12}$) cage having 12 pentagonal faces and H ($5^{12}6^4$) cage having 12 pentagonal faces and four hexagonal faces), the low-temperature unit cell, sII′, becomes $8D'{\cdot}4H'{\cdot}68H_2O$ (D′ ($5^{12}$) cage and H′ ($5^{12}6^4$) cage) as shown in Figure 2a.

The unit-cell parameters of sII 1-propanol + $CH_4$ hydrate and 2-propanol + $CH_4$ are at almost the same size (see Figure 2b), even though these unit-cell parameters generally depend on compositional ratios and cage occupancies. This trend also fits the n-butane and iso-butane($C_4H_{10}$) + $CH_4$ hydrates owing to their similarity of molecular conformations. The host structure of 2-propanol + $CH_4$ hydrate shrank about 1.0% along the $c$ direction and expanded about 1.3% along the $a$ direction owing to the phase transition into the sII′ structure by temperature lowering. Interestingly, the cell volume of 16 $5^{12}$ cages and 8 $5^{12}6^4$ cages for the sII′ phase of 2-propanol + $CH_4$ hydrate was larger than that of sII by about 1.4% with decreasing temperature (Figure 2c).

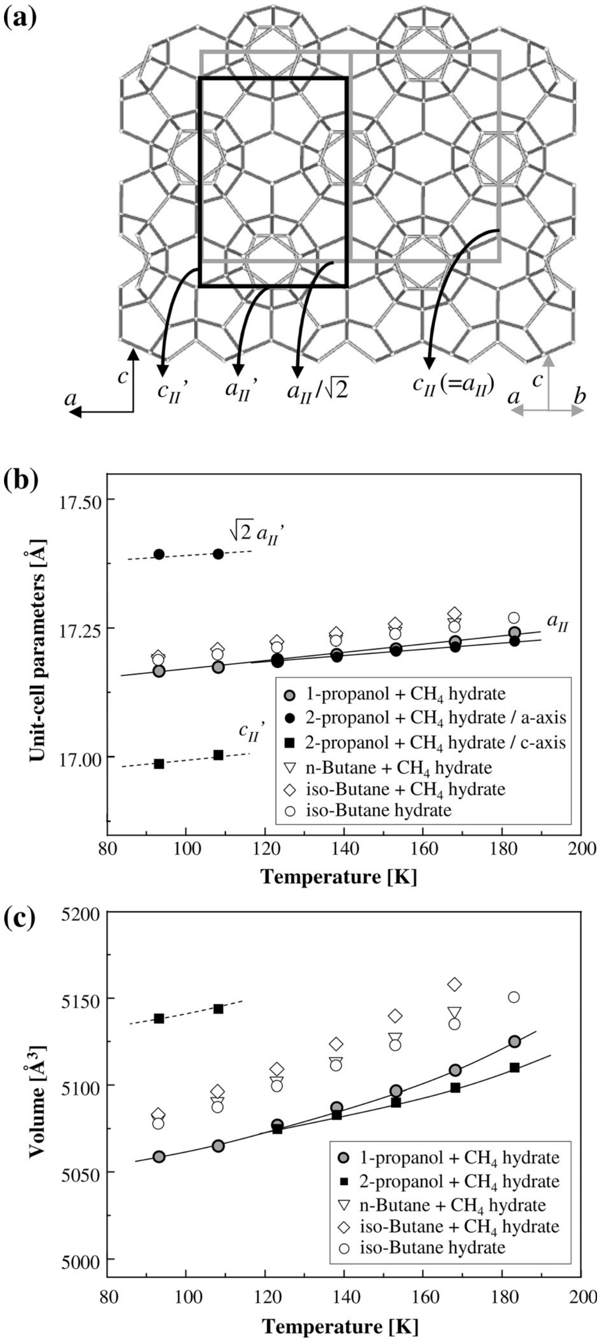

*Figure 2.* a) Unit cell of the low-temperature form (sII′; dark gray) and the high-temperature form (sII) of 2-propanol + $CH_4$ hydrate (light gray). b), c) Temperature dependence of the b) unit-cell parameters and c) cell volumes for 1-propanol + $CH_4$ and 2-propanol + $CH_4$ hydrate. The solid lines correspond to the cubic cell parameters. Dotted lines represent tetragonal cell parameters, which are corrected for comparison. The volumes corresponds to the cell volume of 16 $5^{12}$ cages and 8 $5^{12}6^4$ cages for cubic and tetragonal structures. Unit-cell parameters of butane hydrates[29] are also shown for comparison.

Structure refinements using PXRD data for these hydrates provided us with absolute cage occupancies and the distribution of guest molecules in the host water cages as well as the distortion of the host water cages.[30] Analysis of the distortion of the host water cages depending on the guest molecular species may provide information on the interaction between host and guest molecules. Crystallographic data obtained are summarized in Table 1 and powder diffraction data for structure analysis are shown in the Supporting Information, Figures S1–S4. For these analyses, the relative cage occupancies for the $CH_4$ molecule in the small and large cages of the 1-propanol + $CH_4$ and 2-propanol + $CH_4$ hydrate

***Table 1:*** X-ray crystallographic data depending on type of guest molecules and temperature.

| | 2-propanol + $CH_4$ | 2-propanol + $CH_4$ | 1-propanol + $CH_4$ | 1-propanol + $CH_4$ |
|---|---|---|---|---|
| Temperature [K] | 153(1) | 93(1) | 153(1) | 93(1) |
| Crystal system, space group | cubic, *Fd*$\bar{3}$*m* | tetragonal, *I*4$_1$/*amd* | cubic, *Fd*$\bar{3}$*m* | cubic, *Fd*$\bar{3}$*m* |
| Unit cell parameters [Å] | *a*: 17.1973(1) | *a*: 12.2904 (3)<br>*c*: 16.9841 (6) | *a*: 17.1979(3) | *a*: 17.1657(2) |
| Volume Unit cell [Å$^3$] | 5086.0(1) | 2565.5 (1) | 5086.5(1) | 5058.1(1) |
| Volume D/H cage [Å$^3$] | 163/314 | 167/310 | 164/313 | 162/311 |
| Cage occupancies | | | | |
| $CH_4$(H)/Propanol(H) | 0.219/0.781 | 0.219/0.781 | 0.218/0.782 | 0.218/0.782 |
| $CH_4$(D) | 0.650 | 0.650 | 0.880 | 0.880 |
| Density [g cm$^{-3}$] | 0.986 | 0.978 | 0.991 | 1.011 |
| $R_w$ | 0.102 | 0.093 | 0.122 | 0.100 |

were estimated from the Raman spectra (Supporting Information, Figure S5). The main effect on the host structure by the phase transition for 2-propanol + $CH_4$ hydrate was found on the oxygen–oxygen (O−O) distance within the host water lattice (see Figure 3). The O−O distance, denoted $Wa_{11}$—$Wa_{11}$ in the low-temperature sII′ phase of 2-propanol + $CH_4$ hydrate, is 2.99 Å, which distance is about 0.2 Å longer than other O−O distance in the sII phase and the equivalent O−O distance denoted $Wa_1$–$Wa_1$ in the cubic sII phase (Supporting Information, Tables S5 and S6). As a result, the large H′ cages in the sII′ phase of 2-propanol + $CH_4$ hydrate has expanded in its equatorial plane within the (001) plane, and the diameter of the small cage also has expanded. The longest diameter (maximal distances between the centers of oxygen atoms composing the cavity) of the H′ cage within the (001) plane is 9.58 Å and the mean diameter of the D′ cage is 7.83 Å for sII′ of 2-propanol + $CH_4$ hydrate at 93 K, and these diameters for 1-propanol + $CH_4$ hydrate are 9.35 Å and 7.75 Å, respectively. Each cage volume for 1-propanol + $CH_4$ and 2-propanol + $CH_4$ hydrate was also calculated at 93 K and at 153 K. The H′ cage of the low-symmetry structure at 93 K in sII′ is deformed, but the cage volume is equivalent to the H cage for sII of 1-propanol + $CH_4$ hydrate at 93 K. On the other hand, the cage volume of the D′ cage for $CH_4$ + 2-propanol hydrate is larger than that of the D cage for 1-propanol + $CH_4$ hydrate at 93 K. This suggests that the volume of the H′ cage remains constant, but the volume of the D′ cage was enlarged owing to the phase transition when 2-propanol and $CH_4$ were the guests.

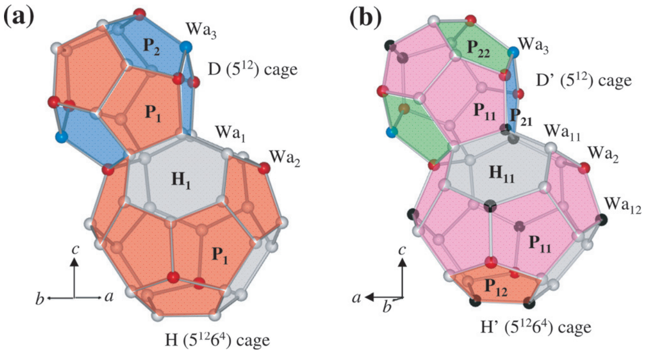

***Figure 3.*** Detailed polyhedral small ($5^{12}$) and large ($5^{12}6^4$) cage for a) sII and b) sII′. Each symbolic number of the virtual chemical species corresponds to those shown in Tables S1–S4 in Supporting Information.

The distribution of guest molecules and the cage occupancies of these hydrates were also analyzed along with the structure refinement using rigid-body constraints for the guest molecules. Here, for 1-propanol, a *gauche* conformation refined by single structure analysis of $CH_4$ + 1-propanol hydrate was used.[23] As shown in Figure 4 a,b and the Supporting Information, Figure S6, the 1-propanol is distributed over the 6 equivalent positions that lie about the symmetry axis of the H cage. These results of $CH_4$ + 1-propanol hydrate are in good agreement with the reported value from single-crystal structure analysis.[23] The resultant structure in Figure 4 c,d show that the distribution or dynamical disorder of guest molecules associated with the reorientation of 2-propanol guest changed along with the crystal phase as temperature is reduced. The difference in the H′ and H cages is reflected in the distribution of the 2-propanol molecules within the cages. In the low-symmetry phase of 2-propanol + $CH_4$ hydrate, the favored position of 2-propanol is along the stretched dimension of the cage within the (001) plane, whereas the guest is disordered over four positions in the sII phase. Thus, we may speculate that the transition of ordering of guest motions for 2-propanol will result in one of the four equivalent positions in the large cage being occupied, and once this happens the cage distorts to optimize the host–guest interactions. The transition can be then considered to be driven by the restriction of the motion of a tightly fitting large guest molecule, thus distorting the H cage. In contrast to the H cage, host–guest interactions should be small in the D cage when $CH_4$ is the guest. As a result, the small D′ cages, as interspatial cavities for the large H′ cages, may expand in order to fill the space between the H′ cages.

The intermolecular distance between the propanol hydroxy oxygen and the closest host water oxygen 1-propanol oxygen atom at a distance of 2.70 Å (at 153 K) and 2.85 Å (at 93 K) were obtained (Supporting Information, Figure S7). These distances are compatible with host–guest hydrogen bonding. The distance between the propanol hydroxy oxygen and the closest host water oxygen 2-propanol oxygen atom is at a distance of 3.19 Å (at 153 K) and 3.16 Å (at 93 K), which is equal to the sum of the van der Waals radii of oxygen (1.5 Å) and carbon (1.7 Å). The formation of temporary (ca. 100 ps) hydrogen bonds of the OH function of both 1-propanol and 2-propanol with host water molecule with the presence of $CH_4$ have been reported by molecular dynamics (MD) simulations.[27] Thus, it is still unclear whether the resultant distributions of 1-propanol and 2-propanol within H

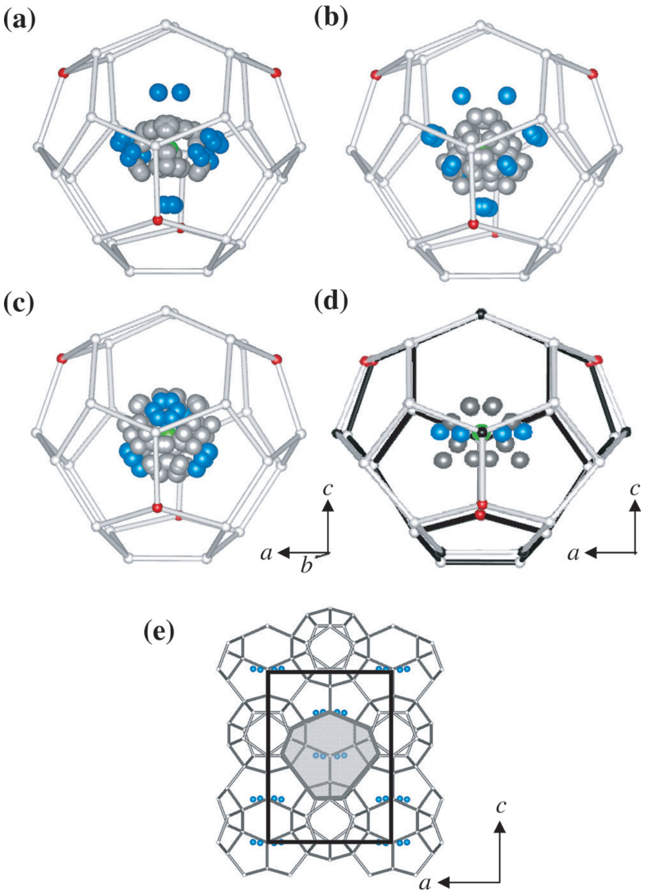

*Figure 4.* View of guest molecules in $5^{12}6^4$ cage with full symmetry. a), b) 1-Propanol molecule in the sII large ($5^{12}6^4$) cage at a) 153 K and b) 93 K. c), d) 2-Propanol molecule in the sII large ($5^{12}6^4$) cage at c) 153 K and in the sII′ large ($5^{12}6^4$) cage at d) 93 K. Here, the propanol hydroxy oxygen is shown in blue and the virtual chemical species, $-CH_2$ and $-CH_3$, are shown in gray. The virtual chemical species of $CH_4$ is shown in green. d) Comparison of distorted sII′ large ($5^{12}6^4$) cage (gray) enclathrating 2-propanol and sII large cage (black line). The cage deformations are slightly exaggerated for clarity. e) Distribution of propanol hydroxy oxygen within the unit-cell of sII′ hydrate.

and H′ cages reflect the occurrence of intermolecular hydrogen bonding or not. Further studies taking into account conformational changes of these propanol molecules[31–34] are necessary.

In the case of *n*-butane + $CH_4$ or *iso*-butane + $CH_4$ hydrates, it is shown that enclathration of *n*-butane or *iso*-butane expands the unit-cell size, but disorder of *iso*-$C_4H_{10}$ and *gauche*-*n*-butane are spherically extended within the large $5^{12}6^4$ cages in the same temperature range as this study.[29] *n*-Butane + $CH_4$ or *iso*-butane + $CH_4$ hydrates do not show phase transitions in the same temperature range as this study, while the conformations of *n*-butane and *iso*-$C_4H_{10}$ are analogous to 1-propanol and 2-propanol, respectively. Dipole ordering of the guest molecule is observed in the sI hydrate of trimethylene oxide,[35] and a phase change with temperature was reported in this system even though the detailed crystal structure are not known.[36] It can be concluded that the phase transition of 2-propanol + $CH_4$ hydrate was caused by the synergistic effect of host–guest interaction of 2-propanol in $5^{12}6^4$ cage, such as host–guest hydrogen bonding,[23,27] and the relatively tight confines of the large $5^{12}6^4$ cage.

In conclusion, we studied the sII binary clathrate hydrates of $CH_4$ and propanol with powder X-ray diffraction analysis. The difference of configuration between 2-propanol and 1-propanol leads to a phase transition, but this situation may not be unique for this particular guest in the 2-propanol + $CH_4$ system. In fact, a clathrasil[37,38] encaging tetrahydrofuran (THF) as guest transform into tetragonal structures at lower temperatures. Moreover, some clathrasils show progressive symmetry-lowering as the temperature is lowered due to the coupling between restricted guest dynamics and symmetry lowering of the host lattice. Determining more general guidelines for the phase transition of clathrate hydrates at lower temperatures taking into account the analogy between clathrate hydrates and clathrasils will be the topic of future studies. Furthermore, this work will provide an additional understanding for various host–guest compounds and their weak host–guest interactions besides clathrate hydrates and clathrasils.

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**Keywords:** clathrates · gas hydrates · inclusion compounds · phase transitions · powder X-ray diffraction

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