Clathrate Hydrates

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Lattice Expansion of Clathrate Hydrates of Methane Mixtures and Natural Gas**

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Clathrate hydrates are inclusion compounds consisting of a hydrogen-bonded crystal of water molecules with cages that contain a guest molecule. The crystal structures of types I, II, and H are well known,[1] and two other types of clathrate hydrate have recently been reported.[2] Guest–host interactions play a crucial role in the crystal structure, and thus clathrate hydrates are thermodynamically stable only when guest molecules are encaged in the host cages. The relation between structural type of clathrate hydrate and guest molecule is categorized according to the size of the guest molecule.[3] However, the use of these categories is not clear when applied to mixed hydrates; for example, a structural transition in methane (CH_4) + ethane (C_2H_6) mixed-gas hydrates from type I to II was observed, even though pure CH_4 and C_2H_6 each form type I.[4,5] There is not much difference between the molecular size of CO_2 (ca. 5.1 Å) and C_2H_6 (ca. 5.5 Å) with respect to the cavities of the hydrate cages, but their effect on hydrate structure may be completely different. Additionally, recent studies have shown that even pure CH_4 and pure CO_2 form type I and type II hydrates in coexistence. It has been shown that the correlation of guest size and formed structure type is not straightforward for pure systems, too.[6]

The structural transitions of mixed-gas clathrates are interesting not only from a fundamental point of view but also from the practical viewpoint of natural gas resources and technology.[7] For instance, natural gas clathrate hydrates in oceanic sediments and permafrost, also called natural gas hydrate, are recognized as an alternative natural fuel resource because they contain significant amounts of natural gases. The main gas in the hydrates is CH_4, but they also contain CO_2, C_2H_6, and small amounts of other gases. In addition, CH_4+CO_2 mixed-gas hydrates have been studied as a medium to remove CO_2 from air; in particular, natural gas hydrates can be converted to CO_2 hydrate, and thus a fuel is obtained and an unwanted combustion byproduct is removed.[8]

We present here our measurements of the lattice expansion of CH_4+CO_2 and $CH_4+C_2H_6$ hydrates as a function of mixed-gas composition. This is important because lattice expansion plays a crucial role in thermodynamic modeling of hydrate systems.[5,9] Data for natural gas hydrate from the sediments of Lake Baikal are also reported to examine the effect of small amounts of other gases and the kinetic effect under natural conditions on their crystal structures.

X-ray diffraction (XRD) patterns of CH_4+CO_2 hydrate identified it as type I, which is composed of two 12-hedra and six 14-hedra with space group *Pm*3*n* (Figure 1). The crystal structure of $CH_4+C_2H_6$ hydrate changed from type I to type II with increasing C_2H_6 content in the mixed-gas hydrate, in agreement with previous studies.[4,5] (The type II structure (Figure 1) is composed of sixteen 12-hedra and eight 16-hedra with space group *Fd*3*m*.) Since the type I and type II hydrates have cubic structures, only one unit-cell parameter—the lattice constant *a*—need be determined.

The lattice constants are plotted in Figure 2. The lattice constant of CH_4+CO_2 hydrate is roughly independent of gas composition, and this suggests that changes in the occupancy of CH_4 or CO_2 in the cages of the mixed-gas hydrate do not affect the lattice size of type I hydrate. In the case of $CH_4+C_2H_6$ hydrate, a large increase in the lattice constant occurs at approximately 60 to 80% CH_4 content, which corresponds to the structural transition from type I to type II. In the region of high CH_4 content in $CH_4+C_2H_6$ hydrate, from approximately 80 to 100%, the lattice constants of type I hydrate are almost the same as that of pure CH_4 hydrate. In the region of low CH_4 content in $CH_4+C_2H_6$ hydrate, from approximately 0 to 40%, the lattice constants of type I hydrate are same as that of pure C_2H_6 hydrate and are approximately 0.07 Å larger than that of the high-CH_4 region. The deviation of the lattice constant of type I $CH_4+C_2H_6$ hydrate corresponds to 0.6% of the value for a pure CH_4 hydrate crystal. This deviation may not seem large, but it corresponds to a pressure difference of several hundred megapascals, in accordance with the bulk modulus of CH_4 hydrate.[13]

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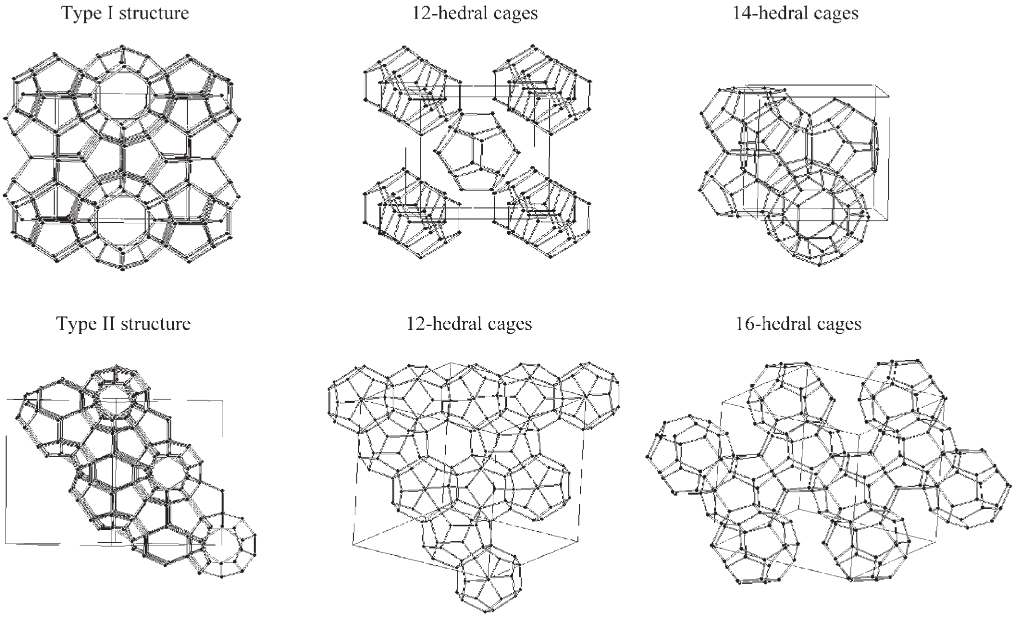

Figure 1. Ball-and-stick representations of the host lattices of types I and II clathrate hydrates. Only oxygen atoms are drawn and solid lines indicate the unit cell of each structure. Middle and right figures show only the small and large cages, respectively, of each structure.

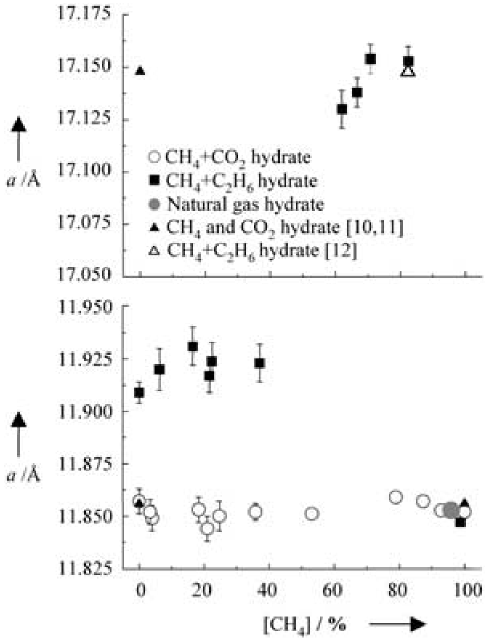

Figure 2. Variation of lattice constants of clathrate hydrates at 113 K as a function of CH_4 gas content in the hydrates. Lattice constants of CH_4+CO_2 hydrate, $CH_4+C_2H_6$ hydrate, and natural gas hydrate are from this study. Lattice constants of CO_2 hydrate (CO_2+D_2O), deuterated methane hydrate (CD_4+D_2O), and $CH_4+C_2H_6$ hydrate (CH_4/C_2H_6 82:18; $CH_4+C_2H_6+D_2O$) were determined at different temperatures and converted to values at 113 K.

The results also suggest that a change in the occupancy of CH_4 or C_2H_6 in the cages of the mixed-gas hydrate does not affect the lattice size of type I hydrate. On the other hand, the lattice constant of type II hydrate seems to increase as the CH_4 occupancy in the $CH_4+C_2H_6$ hydrate increases. This difference between type I and type II hydrates implies a major difference in guest–host or guest–guest interactions due to their different crystal structures. Differences in the properties of CO_2 and C_2H_6 molecules in the hydrate are also suggested. For example, the 12-hedral small cage has a large (ca. 71%) CO_2 occupancy but a small (ca. 5%) C_2H_6 occupation in pure CO_2 and C_2H_6 hydrate, respectively.[10,14] Also, different locations of disordered CO_2 and C_2H_6 molecules in 12-hedral and 14-hedral cages in pure CO_2 hydrate and C_2H_6 hydrate have been shown by assuming that each molecule rotates about the cage symmetry axis at a constant angle to the equatorial plane.[10,14] There may be several factors that affect the change of lattice constants of mixed gas hydrates.

We also analyzed the crystal structure of natural gas hydrate from the sediments of Lake Baikal (Figure 3). Using gas chromatography, we found that the gas content of the natural gas hydrate was 95.9% CH_4, 4.1% CO_2, and less than 500 ppm of C_2H_6 and C_3H_8. The XRD profile showed that the crystal structure of the natural gas hydrate in the sediment sample was type I (Figure 4). Also, the ^{13}C NMR spectrum of

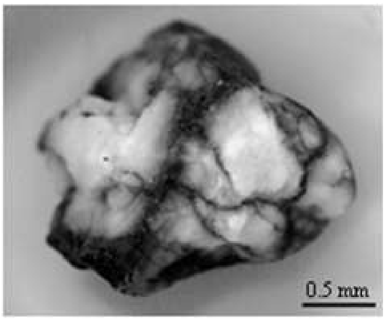

Figure 3. Hydrate-bearing sample from the sediment of Lake Baikal. The white regions are a mixture of natural gas hydrate and ice, and the black regions are sediment.

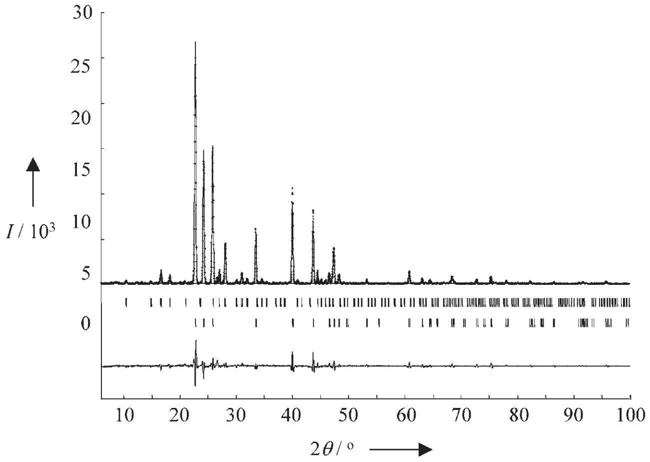

Figure 4. X-ray diffraction profiles of a sample from the sediment of Lake Baikal at 113 K. The dot marks are the observed intensities, and the solid line was calculated from the best-fit model of the Rietveld refinements. The upper tick marks represent the calculated peak positions for the type I gas hydrate, and the lower tick marks those for hexagonal ice. The bottom curve is the difference between the observed and calculated intensities. The sample was 18% hydrate and 82% hexagonal ice by mass, whereby some of the ice came from trapped lake water that froze during cooling.

the natural gas hydrate showed that CH_4 is encaged in the gas hydrate with a large-cage occupancy of 0.94 and a small-cage occupancy of 0.99. CO_2, C_2H_6, and C_3H_8 were not detected by ^{13}C NMR spectroscopy. We used this ^{13}C NMR data in the Rietveld refinement of the XRD profile.[15] Thus, the lattice constant of the natural gas hydrate was estimated to be 11.8527(6) Å, and its density was calculated to be 0.948 $g\,cm^{-3}$ at 113 K. The lattice constant of the natural gas hydrate is consistent with those of the artificially formed mixed-gas hydrates (see Figure 2), even though the differences in cage occupancies between artificial and natural gas hydrates is suggested experimentally to be due to differences in their formation conditions.[16] This also shows that the small amounts of C_2H_6 and C_3H_8 did not influence the structural transition or the lattice expansion. This result suggests that the knowledge of artificial clathrate hydrate structures can be applied to natural gas hydrates.

In the present study, the effect of guest molecules on the lattice constant of mixed-gas hydrates was measured for the first time. The dependence of lattice expansion on gas occupancies differs for different guest molecules. For instance, lattice expansion of $CH_4+C_2H_6$ hydrate depends on the composition of the guest molecules, whereas no lattice expansion of CH_4+CO_2 hydrate was observed. Even a small deviation of the lattice constant corresponds to a large pressure difference at constant temperature, and thus crystal structure data should be considered in detail for optimal thermodynamic modeling. However, the guest molecules are difficult to locate because of their rotational disorder and nonstoichiometry due to their random occupancy in each cage, even though the clathrate hydrate lattice may be well defined. Therefore, further analysis of the guest molecules in the hydrate cages will be required for a better understanding of mixed-gas hydrates.

Experimental Section

Mixed-gas hydrate samples were synthesized by our previously reported method.[5] Sediment samples containing natural gas hydrate were recovered by gravity coring at gas-vent fields in Lake Baikal in June 2002.[17] The samples are from the lake bottom at a water depth of 1393 m, and the site had latitude 51° 55.203′ N and longitude 105° 38.080′ E. After the cores were brought up, the gas hydrate-containing samples were immediately stored at about 100 K in an atmosphere of nitrogen gas to prevent hydrate dissociation.

For the XRD measurements, finely powdered hydrate samples were put in a quartz glass capillary cell (Hilgenberg; 2.0 mm, 0.01 mm thick) and then mounted on the goniometer of the XRD apparatus. The XRD measurements were performed with $Cu_{K\alpha}$ radiation (50 kV, 200 mA; Rigaku model Rint-2000) at 113 K and atmospheric pressure. Lattice constants were determined at 113 K by using a two-phase Rietveld refinement method with RIETAN-2000.[18] For this analysis, the lattice constant of hexagonal ice was fixed at 4.4793 Å for the a axis and 7.3216 Å for the c axis.[19]

For the natural gas hydrate sample, ^{13}C NMR spectroscopy was used to determine the composition of the encaged gas molecules in the cages. Powdered samples of natural gas hydrate were put in a tube-shaped zirconium sampler that was then placed in the NMR probe (100 MHz; JEOL model JNM-AL400 FT). CP-MAS ^{13}C NMR spectra were recorded at 183 K on an NM-AL40/BU spectrometer at a frequency of 100 MHz. Chemical shifts were then determined by assuming that the polydimethylsilane (PDMS) peak was at 0 ppm.

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[1] a) H. R. Müller, M. von Stackelberg, *Naturwissenschaften* **1952**, 39, 20; b) M. von Stackelberg, H. R. Müller, *Naturwissenschaften* **1951**, 38, 456; c) J. A. Ripmeester, J. S. Tse, C. I. Ratcliffe, B. M. Powell, *Nature* **1987**, *325*, 135.

[2] a) K. A. Udachin, J. A. Ripmeester, *Nature* **1999**, *397*, 420; b) K. A. Udachin, C. I. Ratcliffe, J. A. Ripmeester, *Angew. Chem.* **2001**, *113*, 1343; *Angew. Chem. Int. Ed.* **2001**, *40*, 1303.

[3] E. D. Sloan, Jr., *Clathrate Hydrate of Natural Gases*, 2nd ed., Marcel Dekker, New York, **1998**.

[4] a) S. Subramanian, R. A. Kini, S. F. Dec, E. D. Sloan, Jr., *Chem. Eng. Sci.* **2000**, *55*, 1981; b) S. Subramanian, A. L. Ballard, R. A. Kini, S. F. Dec, E. D. Sloan, Jr., *Chem. Eng. Sci.* **2000**, *55*, 5763; c) S. Takeya, Y. Kamata, T. Uchida, J. Nagao, T. Ebinuma, H. Narita, *Can. J. Phys.* **2003**, *81*, 479.

[5] T. Uchida, S. Takeya, Y. Kamata, I. Y. Ikeda, J. Nagao, T. Ebinuma, H. Narita, O. Zatsepina, B. A. Buffett, *J. Phys. Chem. B* **2002**, *106*, 12426.

[6] a) D. K. Staykova, W. F. Kuhs, A. N. Salamatin, T. Hansen, *J. Phys. Chem. B* **2003**, *107*, 10299; b) J. M. Schicks, J. A. Ripmeester, *Angew. Chem.* **2004**, *116*, 3372; *Angew. Chem. Int. Ed.* **2004**, *43*, 3310.

[7] E. D. Sloan, Jr., *Nature* **2003**, *426*, 353.

[8] a) Yu.-T. Seo, H. Lee, *J. Phys. Chem. B* **2001**, *105*, 10084; b) H. Lee, Y. Seo, Yu.-T. Seo, I. L. Moudrakovski, J. A. Ripmeester, *Angew. Chem.* **2003**, *115*, 5202; *Angew. Chem. Int. Ed.* **2003**, *42*, 5048.

[9] a) L. A. Ballard, E. D. Sloan, Jr., *Chem. Eng. Sci.* **2000**, *55*, 5773; b) Y. Koyama, H. Tanaka, K. Koga, *J. Chem. Phys.* **2005**, *122*, 074503.

[10] K. A. Udachin, C. I. Ratcliffe, J. A. Ripmeester, *J. Phys. Chem. B* **2001**, *105*, 4200.

[11] C. Gutt, B. Asmussen, W. Press, M. R. Johnson, Y. P. Handa, J. S. Tse, *J. Chem. Phys.* **2000**, *113*, 4713.

[12] C. J. Rawn, A. J. Rondinone, B. C. Chakoumakos, S. L. Marshall, L. A. Stern, S. Circone, S. H. Kirby, C. Y. Jones, B. H. Toby, Y. Ishii, *Proc. 4th Int. Conf. Gas Hydrate*, Yokohama, **2002**, p. 595.

[13] H. Hirai, T. Kondo, M. Hasegawa, T. Yagi, Y. Yamamoto, T. Komai, K. Nagashima, M. Sakashita. , H. Fujihisa, K. Aoki, *J. Phys. Chem. B* **2000**, *104*, 1429.

[14] K. A. Udachin, C. I. Ratcliffe, J. A. Ripmeester, *J. Supramol. Chem.* **2002**, *2*, 405.

[15] H. M. Rietveld, *J. Appl. Crystallogr.* **1969**, *2*, 65.

[16] Z. Huo, K. Hester, D. Sloan, Jr., *AIChE J.* **2003**, *49*, 1300.

[17] J. Klerkx, T. I. Zemskaya, T. V. Matveeva, O. M. Khlystov, B. B. Namsaraev, O. P. Dagurova, L. P. Golobokova, S. S. Vorob'eva, T. P. Pogodaeva, N. G. Granin, G. V. Kalmychkov, V. A. Ponomarchuk, H. Shoji, L. L. Mazurenko, V. V. Kaulio, V. A. Solov'ev, M. A. Grachev, *Dokl. Earth Sci.* **2003**, *393A*, 1342.

[18] F. Izumi, T. Ikeda, *Mater. Sci. Forum* **2000**, *321–324*, 198.

[19] K. Röttger, A. Endriss, J. Ihringer, S. Doyle, W. F. Kuhs, *Acta Crystallogr. Sect. B* **1994**, *50*, 644.