Gas Hydrates

DOI: 10.1002/ange.200703718

Dissociation Behavior of Clathrate Hydrates to Ice and Dependence on Guest Molecules**

*Satoshi Takeya and John A. Ripmeester**

Clathrate hydrates are crystalline ice-like inclusion compounds consisting of hydrogen-bonded water molecules that form host cages which contain small guest molecules. Three different crystal structural families are known; the structure depends on the nature of the guest molecules: structure I with space group *Pm*3*n*, structure II with space group $Fd\bar{3}m$, and structure H with space group *P6/mmm*.[1] Host–guest interactions play a crucial role, as hydrates are thermodynamically stable only when guest molecules occupy the host cages to a certain minimum level. Even for hydrate growth, the interaction energy and dynamics of the host and guest molecules are also important. Hydrate formation starting from amorphous solid water (ASW) with enclosed guest molecules at low temperatures is an example: H_2O molecules phase-separate from the amorphous phase to form cubic ice (Ic) initially, then they form the appropriate hydrates with an increase in temperature.[2] The dissociation of clathrate hydrates has also been studied, but the mechanism is still not well understood. For instance, CH_4 hydrate can be stored at atmospheric pressure below the melting point of ice (273 K), even though this temperature is well outside the zone of thermodynamic stability of the hydrate and allows dissociation;[3] the effect has been termed self-preservation.[4] The existence of anomalous CH_4 hydrate stability in the temperature range from 240 K to 273 K[5] is interesting not only from a scientific viewpoint, but there are also practical applications for the storage and transport of CH_4 and H_2 in the form of solid hydrate.[6] Takeya et al. measured the dissociation of structure I CH_4 hydrate using powder X-ray diffraction (PXRD) and concluded that the dissociation is controlled by the rate of gas diffusion through ice formed by the dissociation of the CH_4 hydrate.[7] Above 230 K, the reduction in diffusion rate owing to ice sheet formation, transformed from ice particles around dissociating hydrate, was suggested by Shimada et al.[8] On the other hand, Kuhs et al. reported formation of ice Ic with stacking faults (but not hexagonal ice, Ih) resulting from CH_4 hydrate dissociation at temperatures below 240 K,[9] and they suggested that transformation from ice Ic to ice Ih upon annealing hinders gas diffusion. These studies, based on crystal structure transformation, have clarified that the dissociation of CH_4 hydrate is controlled by the rate of gas diffusion through ice. One remaining puzzle is the fact that $CH_4 + C_2H_6$, a mixed gas hydrate of structure II, does not show preservation behavior comparable to CH_4 hydrate, whereas its dissociation pressure is lower than that of CH_4 hydrate at the same temperature.[5] Additionally, anomalously stable N_2, O_2, CO, and Ar hydrates have also been suggested.[10] Therefore, further studies are required for developing a comprehensive understanding of the dissociation mechanism of hydrates below 273 K. The experimental results in this study provide not only kinetic data using temperature-dependent PXRD, but also give new insight into the fundamentals of hydrate dissociation and the nature of guest-molecule adsorption on ice arising from the interaction energy between guests and H_2O molecules.

In Figure 1, the PXRD profiles for the CF_4 hydrate dissociation process are shown on going from structure I hydrate to ice as the temperature was increased from 163 to 243 K in steps of 5 K with a 2θ-scan time of 2.5 min. Several diffraction peaks assigned to ice appear at 163 K, and the peak intensities increase with temperature whereas the CF_4 hydrate diffraction peak intensities decrease. This indicates that the dissociated CF_4 hydrate transformed into ice. The

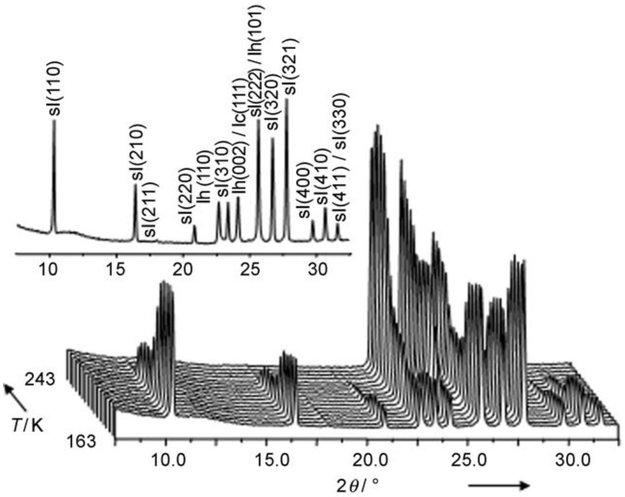

Figure 1. Temperature-dependent PXRD profiles during the transformation of CF_4 hydrate into ice. The initial temperature (163 K) was raised in 5 K steps up to 243 K. The PXRD profile at 183 K (insert) is used to designate the Miller index of each diffraction peak from the hydrate (sI), hexagonal ice (Ih), and cubic ice (Ic).

---

[*] Dr. S. Takeya,[+] Dr. J. A. Ripmeester
Steacie Institute for Molecular Sciences
National Research Council of Canada
100 Sussex Dr., Ottawa, ON, K1A0R6 (Canada)
Fax: (+1) 613-998-7833
E-mail: john.ripmeester@nrc-cnrc.gc.ca

[+] Permanent address: Research Institute of Instrumentation Frontier
National Institute of Advanced Industrial Science and Technology (AIST)
Central 5, Higashi 1-1-1, Tsukuba 305-8565 (Japan)

[**] We thank Drs. M. Sergey, H. Lu, K. Udachin, and D. D. Klug of NRC for their discussions and assistance on sample synthesis. S.T. also thanks Drs. R. Ohmura of Keio University and J. Nagao of AIST for their discussions.

relative volume ratios for various clathrate hydrates were measured by PXRD and were analyzed as a function of temperature (See Figure 2). Most of the hydrates began to dissociate between 180–200 K, even though their stability conditions are quite different (see Table 1). For C_2H_6, CH_2F_2, CHF_3, Xe, and H_2S hydrates (structure I), and C_3H_8 hydrate (structure II), the dissociation proceeded a single step up to around 220 K, whereas the rate of dissociation for CH_4, CH_3F, CF_4, and CO_2 hydrates (structure I) and O_2, N_2, Ar, and Kr hydrates (structure II) decreased in the temperature range between 180 K and 220 K. The dissociation rate then increased at temperatures higher than 220 K and decreased again above around 230 K. Below 273 K, these hydrates were self-preserved, even though the amounts of remaining hydrate were less than 30 %. These results, summarized in Table 1, show that there is a correlation between the self-preservation effect and the decomposition pressure, except in the case of CH_3F hydrate. It suggests that the hydrates with higher decomposition pressures tend to show self-preservation phenomena.

The 180–220 K temperature range is quite consistent with the ice transformation temperature, by which ice Ic transforms into ice Ih. Kuhs et al.[9] reported that the relative peak intensity ratios of the Ih(100) and Ih(002) reflections, which overlap with those of Ic(111), changed with temperature in this region because of formation of ice Ic and its transformation into ice Ih (see Figure 3). In the present work, ice Ic formation was observed for all hydrate samples as the hydrate dissociated. An early macroscopic study showed frost-like ice formation on the dissociating CH_4 hydrate surface; both H_2O and CH_4 molecules are likely to evaporate into the surrounding space, but H_2O molecules may condense again as frost on the hydrate surface because the surface temperature may be slightly lower than the controlled sample temperature owing to the endothermic hydrate dissociation reaction.[8] These results indicate that the dissociating hydrates were covered by a frost-like ice layer, not a dense solid ice layer as induced by a solid–solid transformation, and which is composed of ice Ic in the temperature range between 180 K and 220 K resulting from water condensation. It should also be noted that the PXRD profiles show a background increase (see Figure 3). It is known that the existence of stacking faults in ice Ic broaden the Ic(111) and Ic(222) reflections.[11] If the sample is a very fine powder (particles less than few μm in size), this also broadens the peak half-widths, but no other ice Ih peak (not shown in this 2θ region), showed such peak broadening. On the other hand, formation of a third ice phase, amorphous ice, which coexists metastably with ice Ic at least up to

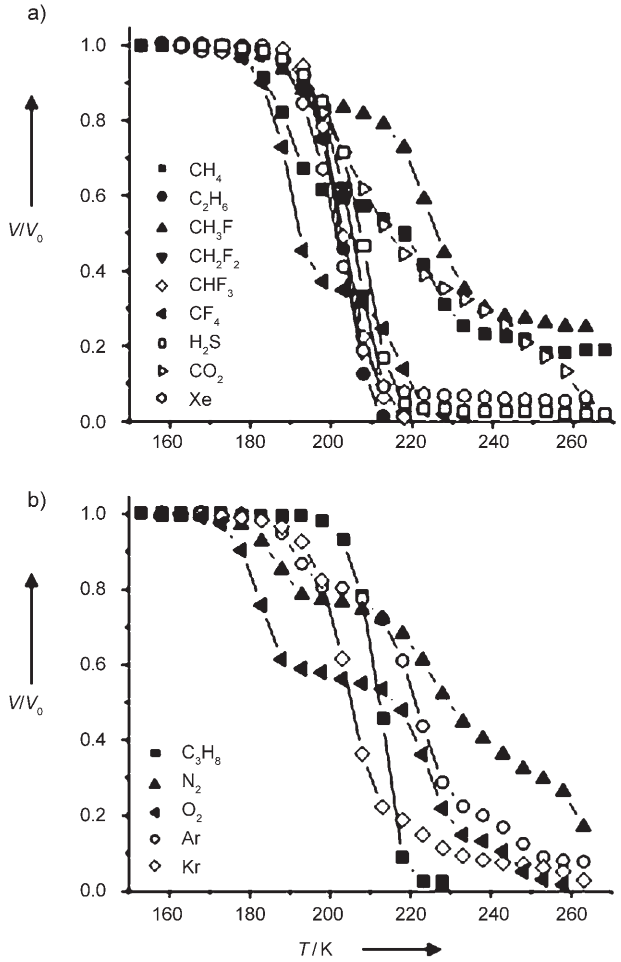

Figure 2. The volume ratio V/V_0 of hydrates as a function of temperature. V_0 is the initial volume, and the solid lines indicate trends. a) Structure I hydrate, b) Structure II hydrate.

Table 1: Properties of hydrates and guest molecules, and crystal data.[a]

Guest	Self-preservation[b]	P_d [MPa] at 273 K[c]	Structure	Lattice constant [Å] at 173 K	V_0[d]	T_m/T_b[e] [K]	V [Å^3]/Max. length [Å]
H_2S	●	0.1 [1]	sI	11.8757(3)	0.94	188/213	25.2/3.8
CH_3F	○	0.2 [20]	sI	11.8834(3)	0.83	131/195	33.5/4.7
CH_2F_2	●	0.2 [21]	sI	11.8981(6)	0.80	137/221	38.9/5.2
Xe	●	0.2 [22]	sI	11.8797(3)	0.61	161/165	42.2/2.2
C_3H_8	●	0.2 [1]	sII	17.1750(4)	0.93	85/231	62.4/6.7
CHF_3	●	0.3 [23]	sI	11.9211(7)	0.96	118/191	42.9/5.2
C_2H_6	●	0.5 [1]	sI	11.9554(8)	0.79	90/185	45.6/5.6
CO_2	○	1.2 [1]	sI	11.8794(7)	0.77	195 (Sublimation)	33.3/5.4
Kr	○	1.5 [22]	sII	17.1280(4)	0.89	116/120	34.5/2.0
CH_4	○	2.5 [1]	sI	11.8938(3)	0.93	91/112	28.6/4.3
CF_4	△	4.2 [24]	sI	11.9751(9)	0.64	89/145	49.4/5.3
Ar	○	10.5 [25]	sII	17.1131(4)	0.95	84/ 87	27.8/1.9
O_2	○	11.9 [25]	sII	17.1138(11)	0.40	55/ 90	20.6/3.9
N_2	○	15.9 [25]	sII	17.1665(5)	0.62	63/ 77	21.7/3.9

[a] The data sets are ordered according to dissociation pressure (P_d) at 273 K. Taken from references [1,20–25]. Volume and maximum length of guest molecules were calculated using the Winmoster program.[26] [b] The self-preservers are marked with an open circle (○) and non-self-preservers are marked with a solid circle (●). CF_4 hydrate is marked with an open triangle (△) as it showed preservation phenomena around 200 K. [c] P_d is the dissociation pressure of each hydrate at 273 K. [d] V_o is the initial volume of hydrate in the synthetic sample. [e] T_m and T_b indicate the melting and boiling points of the guest molecule, respectively.

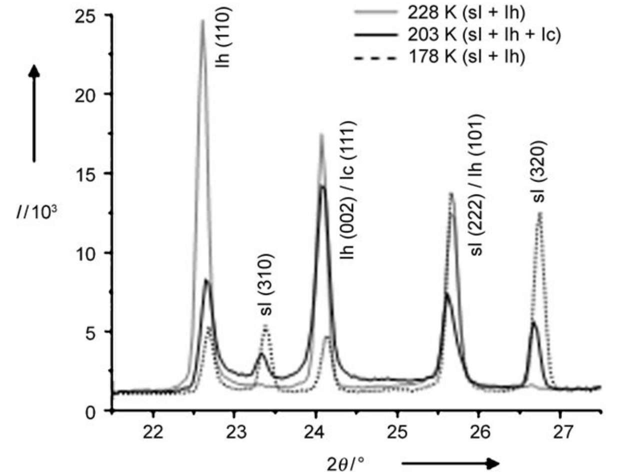

Figure 3. An enlarged portion of the PXRD profiles in Figure 1 for CF_4 hydrate at three different temperatures. The profile for 203 K has an increase in the background for 2θ between 22–26°. See text for details.

188 K, has also been reported.[12] Therefore, the ice formed in this temperature region is not necessarily ice Ic. Especially during the hydrate dissociation process, the guest molecule may well be trapped in the newly formed ice phase and thus support the formation of amorphous ice coexisting with ice Ic.

Where do guest molecules leaving the dissociating hydrate go? According to earlier studies, CH_4, N_2, Ar, Kr, CF_4, and CO molecules, all of which form hydrates that show self-preservation phenomena, interact only weakly with ice ASW.[13] For hydrofluorocarbon molecules (CH_4, CH_3F, CH_2F_2, and CHF_3), the length of the hydrogen bond between the fluorine carbon and the H_2O molecule (C–H···O) decreases and the C–H···O interaction energy increases with the number of fluorine (F) atoms in the molecules, according to theoretical calculations.[14] The CHF_3 molecule most likely orders the ice surface because of C–H···O interaction between H_2O molecules on the ice Ih(001) surface,[15] whereas for CH_4 and CF_4 the interactions with H_2O molecules are weak. Therefore, the experimental result for CH_3F hydrate suggests that relatively weak interactions (weaker than those of CH_2F_2 and CH_3F in this series) cause the self-preservation phenomenon because the interaction energy with H_2O molecules should reflect the thermal adsorption of molecules on ice surfaces. In fact, H_2S and Xe hydrate do not show self-preservation, and it has been suggested that H_2S adsorbs on ice surfaces more strongly than the above molecules and that Xe penetrates easily into ice Ih.[16] The higher decomposition pressures shown in Table 1 should reflect the weaker interaction strengths of the guest with H_2O molecules in general. Therefore, these results suggest that the weaker interactions cause self-preservation. The existence of self-preservation in a quenched high-pressure phase of structure H hydrate, which is stable between 460–770 MPa, was reported for the temperature range 170–230 K.[17] This finding is consistent with the experimental results observed for Ar hydrate herein even though the decomposition step above 230 K observed here was not observed previously. Therefore, the nature of guest molecules, not the thermodynamic stability or the crystal structure, determines whether self-preservation phenomena should be expected. In turn, self-preservation is shown to depend on the interaction strength between guest molecules and H_2O molecules as reflected by the dissociation pressures at 273 K.

We have shown that the observation of self-preservation phenomena depends on the type of guest molecule; CH_4, CH_3F, CF_4, and CO_2 hydrates (structure I) and O_2, N_2, Ar, and Kr hydrate (structure II) show self-preservation phenomena, and we conclude that interaction of guest molecules with H_2O molecules in ice play a crucial role in observing this phenomenon, even though there is still one exception. For the $CH_4+C_2H_6$ mixed gas hydrate,[5b] we believe that C_2H_6, used in forming the mixed gas hydrate, may hinder the occurrence of self-preservation phenomena because of the interaction of C_2H_6 with H_2O molecules in ice. However, we expect that mixed gas hydrates encaging molecules with weak interaction with H_2O molecules, such as H_2 and NO, should again show self-preservation phenomena, even though H_2 can probably diffuse out of the cages of the hydrate without decomposing the lattice, at least initially.[18]

Experimental Section

Gas hydrate samples were synthesized from fine ice powder using a method reported previously.[3]

PXRD measurements were carried out in θ/θ step scan mode using $Cu_{K\alpha}$ radiation ($\lambda = 1.5406$ Å) with a step width of 0.041° in the 2θ range of 7.5–32.5° for a 2.0-min total scan time (40 kV, 40 mA; BRUKER axs model D8 Advance). Powdered hydrate samples were mounted on a 0.20-mm thick copper PXRD sample holder under a N_2 atmosphere and kept below 100 K. Temperature-dependent PXRD measurements from 153 K up to 273 K were made every 5 K under a dry N_2 atmosphere to prevent vapor condensation on the sample surface by using a low-temperature chamber (Anton Paar model TTK 450). The temperature was kept at a constant value with maximum 0.1 K temperature deviations during each PXRD measurement. Immediately after each measurement, the temperature of the sample was raised 5 K within 30 s. The use of rather thin samples allowed us to control the sample temperature at specific values without any significant waiting time before each measurement. Identification of crystal structure and determination of the volume ratio of hydrate and ice and unit cell parameter were done by a Rietveld method using RIETAN-2000 program.[19]

Received: August 14, 2007
Revised: November 7, 2007

Keywords: adsorption · clathrates · host–guest systems · hydrates · inclusion compounds

---

[1] G. A. Jeffrey in *Comprehensive Supramoloecular Chemistry, Vol. 6* (Eds.: J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vogtle), Pergamon/Elsevier, Oxford, **1996**.

[2] a) A. Hallbrucker, *Angew. Chem.* **1994**, *106*, 677; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 691; b) C. A. Tulk, Y. Ba, D. D. Klug, G. McLaurin, J. A. Ripmeester, *J. Chem. Phys.* **1999**, *110*, 6475; c) H. Nakayama, D. D. Klug, C. I. Ratcliffe, J. A. Ripmeester, *Chem. Eur. J.* **2003**, *9*, 2969.

[3] Y. P. Handa, *J. Chem. Thermodyn.* **1986**, *18*, 891.

[4] V. S. Yakushev, V. A. Istomin, *Physics and Chemistry of Ice*, Hokkaido University Press, Sapporo, **1992**, p. 136.

[5] a) L. A. Stern, S. Circone, S. H. Kirby, W. B. Durham, *J. Phys. Chem. B* **2001**, *105*, 1756; b) L. A. Stern, S. Circone, S. H. Kirby, W. B. Durham, *Can. J. Phys.* **2003**, *81*, 271; c) S. Circone, L. A. Stern, S. H. Kirby, W. B. Durham, B. C. Chakoumakos, C. J. Rawn, A. J. Rondinone, Y. Ishii, *J. Phys. Chem. B* **2003**, *107*, 5529.

[6] a) J. Gudmundson, A. Borrehaug, *Proc. 2nd Int. Conf. on Natural Gas Hydrates* (Ed.: J. P. Monfort), Toulouse, **1996**, p. 415; b) L. J. Florusse, C. J. Peters, J. Schoonman, K. C. Hester, C. A. Koh, S. F. Dec, K. N. Marsh, E. D. Sloan, *Science* **2004**, *306*, 469; c) H. Lee, J. W. Lee, D. Y. Kim, J. Park, Y. T. Seo, H. Zeng, I. L. Moudrakovski, C. I. Ratcliffe, J. A. Ripmeester, *Nature* **2005**, *434*, 743.

[7] a) S. Takeya, W. Shimada, Y. Kamata, T. Ebinuma, T. Uchida, J. Nagao, H. Narita, *J. Phys. Chem. A* **2001**, *105*, 9756; b) S. Takeya, T. Ebinuma, T. Uchida, J. Nagao, H. Narita, *J. Cryst. Growth* **2002**, *237–239*, 379; c) S. Takeya, T. Uchida, J. Nagao, R. Ohmura, W. Shimada, Y. Kamata, T. Ebinuma, H. Narita, *Chem. Eng. Sci.* **2005**, *60*, 1383.

[8] W. Shimada, S. Takeya, Y. Kamata, T. Uchida, J. Nagao, T. Ebinuma, H. Narita, *J. Phys. Chem. B* **2005**, *109*, 5802.

[9] W. F. Kuhs, G. Genov, D. K. Satykova, T. Hansen, *Phys. Chem. Chem. Phys.* **2004**, *6*, 4917.

[10] A. Hallbrucker, E. Mayer, *J. Chem. Soc. Faraday Trans.* **1990**, *86*, 3785.

[11] W. F. Kuhs, D. V. Bliss, J. L. Finney, *J. Phys. Coll. (Paris)* **1987**, *48*, 631.

[12] P. Jenniskens, D. F. Blake, *Science* **1994**, *265*, 753.

[13] C. Manca, C. Martin, P. Roubin, *J. Phys. Chem. B* **2003**, 107, 8929.

[14] I. Alkorta, S. Maluendes, *J. Phys. Chem.* **1995**, *99*, 6457.

[15] A. P. Graham, A. Menzel, J. P. Toennies, *J. Phys. Chem. B* **1999**, *111*, 1169.

[16] a) J. P. Devlin, V. Buch, *J. Phys. Chem. B* **1997**, *101*, 6095; b) S. Mitlin, A. S. Lemak, B. H. Torrie, K. T. Leung, *J. Phys. Chem. B* **2003**, *107*, 9958.

[17] A. G. Ogienko, A. V. Kurnosov, A. Y. Manakov, E. G. Larionov, A. I. Ancharov, M. A. Sheromov, A. N. Nesterov, *J. Phys. Chem. B* **2006**, *110*, 2840.

[18] S. Alavi, J. A. Ripmeester, *Angew. Chem.* **2007**, *119*, 6214; *Angew. Chem. Int. Ed.* **2007**, *46*, 6102.

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

[20] M. Villard, *C. R. Chim.* **1890**, *111*, 183.

[21] S. Imai, K. Okutani, R. Ohmura, Y. Mori, *J. Chem. Eng. Data* **2005**, *50*, 1783.

[22] D. W. Davidson, *Water: A Comprehensive Treatise. Vol. 2.* (Ed.: F. Franks), Plenum, New York, **1973**, chap. 3.

[23] T. Sugahara, K. Ohgaki, *J. Chem. Eng. Jpn.* **2000**, *33*, 174.

[24] S. K. Garg, S. R. Gough, D. W. Davidson, *J. Chem. Phys.* **1975**, *63*, 1646.

[25] S. L. Miller, *Proc. Natl. Acad. Sci. USA* **1961**, *47*, 1798.

[26] a) Winmostar web site: http://winmostar.com/; b) T. Nagao, *Hakodate Kogyo Koto Senmon Gakko Kiyo* **1993**, *27*, 111 (in Japanese).