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Phase Equilibrium for Structure II Hydrates Formed with Methylfluoride Coexisting with Cyclopentane, Fluorocyclopentane, Cyclopentene, or Tetrahydropyran

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This paper reports the pressure−temperature conditions for the vapor + liquid + liquid + hydrate four-phase equilibrium in the systems of methylfluoride and water plus each of the following substances: cyclopentane, fluorocyclopentane, cyclopentene, and tetrahydropyran. The pressure ranges of the present measurements in the four systems are (0.138 to 2.998) MPa at temperatures from (287.9 to 305.9) K in the cyclopentane system, (0.122 to 2.560) MPa at temperatures from (290.1 to 307.0) K in the fluorocyclopentane system, (0.106 to 1.928 MPa) at temperatures from (283.6 to 300.8) K in the cyclopentene system, and (0.116 to 1.877) MPa at temperatures from (284.4 to 301.0) K in the tetrahydropyran system. These equilibrium pressures are lower by at least 0.6 MPa than those in the binary methylfluoride + water system, suggesting the formation of double hydrates with methylfluoride plus cyclopentane, fluorocyclopentane, cyclopentene, or tetrahydropyran. The crystallographic structure of the hydrates is identified to be structure II based on the powder X-ray diffraction measurements.

Introduction

Clathrate hydrates are molecular crystalline solids composed of hydrogen-bonded water molecules forming cages with guest molecules enclosed in the cages. Depending on the size and shape of the guest molecules, the configuration of the water-molecule cages changes, thereby yielding various hydrates with different crystallographic structures such as structures, I, II, and H.[1] As various substances, including hydrocarbons, noble gases, and diatomic gases, etc., may form hydrates, various novel technologies utilizing hydrates have been proposed and investigated. Hydrates may be used as media for the storage and transportation of natural gas[2] and hydrogen.[3] Carbon dioxide[4] and hydrogen sulfide[5] in flue gases and biogases may be removed through hydrate formation. An efficient refrigeration/heat-pump system may be established using hydrate formation and dissociation.[6] Among such hydrate-based technologies, this paper is concerned with the hydrate-based refrigeration system. Hydrates are generally stable at high pressures and low temperatures. This limited thermodynamic stability is often a major obstacle to developing the hydrate-based technologies. More specifically, increasing the hydrate equilibrium temperature is the key to realizing the hydrate-based heat pump/refrigeration system.[6] The following studies involving the increase in the hydrate equilibrium temperature for the development of the hydrate-based refrigeration system have been reported. Imai et al.[7] tested the addition of cyclopentane to the water + difluoromethane system and succeeded in an equilibrium temperature increase by 6 K. The maximum equilibrium temperature in the cyclopentane + difluoromethane double hydrate system is reported to be 299.75 K at 1.544 MPa. Takeya & Ohmura[8] then tested the addition of cyclopentane to the water + krypton system, noting that the highest equilibrium temperature is practically limited by the liquefaction of difluoromethane, a relatively low vapor pressure guest substance, but this limitation can be overcome by using a guest substance that is in the super critical state, such as krypton. They have reported that the equilibrium temperature exceeded 304 K at the pressure of 4 MPa. Imai et al.[9] then reported the phase equilibrium data for the hydrates formed with fluorocyclopentane + krypton and fluorocyclopentane + difluoromethane. They reported an equilibrium temperature exceeding 308 K at 5 MPa in the water + fluorocyclopentane + krypton system.

Following the above-mentioned previous attempts,[7–9] in the present study, we evaluated methylfluoride as the gaseous guest instead of difluoromethane and krypton. Methylfluoride[10] has a higher vapor pressure than difluoromethane.[11] Thus, a higher maximum hydrate equilibrium temperature may be obtained by using methylfluoride compared to the use of difluoromethane, as the maximum hydrate equilibrium temperature is limited by the liquefaction of the gaseous guest. The phase equilibrium conditions of the simple methylfluoride hydrate[12] are much lower than that for simple krypton hydrate,[13] and hence, the hydrate phase equilibrium temperature high enough for the hydrate-based refrigeration application may be obtained at a lower pressure compared to the system with krypton. As the second guest substance used together with methylfluoride to form a double hydrate, cyclopentane, fluorocyclopentane, cyclopentene, and tetrahydropyran were tested to increase the equilibrium temperatures. Each of these four substances is known to form a structure II hydrate under atmospheric pressure.[14–16] Thus, we expected that the equilibrium temperature of the double hydrates formed with methylfluoride and cyclopentane, fluorocyclopentane, cyclopentene, or tetrahydropyran would be higher than that of a simple methylfluoride

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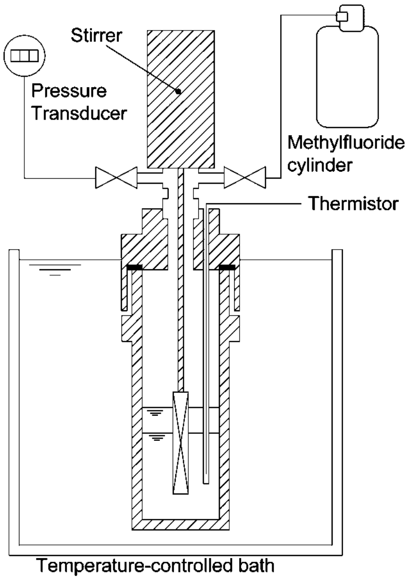

Figure 1. Schematic of the experimental apparatus.

hydrate. The crystallographic structures of the double hydrates were identified using a powder X-ray diffraction (PXRD) method.

Experimental Section

Materials. The fluid samples used in the experiments were deionized and distilled liquid water, methylfluoride of 99.9 % (mass basis) certified purity (Japan Fine Products Corp., Iga, Japan); cyclopentane of 99 % (mass basis) certified purity (Aldrich Chemical, Milwaukee, WI); fluorocyclopentane of 99 % (mass basis) certified purity (SynQuest Laboratories, Inc., Alachuam FL); cyclopentene of 98 % (mass basis) certified purity (Tokyo Chemical Industry, Tokyo); and tetrahydropyran of 99 % (mass basis) certified purity (Aldrich Chemical, Milwaukee, WI). The distilled water was laboratory made. The other fluid samples were used as received by the manufacturers.

Apparatus and Procedure. Figure 1 shows the experimental apparatus used to measure the pressure−temperature conditions for the four phases, i.e., the methylfluoride-rich vapor phase (V), the cyclopentane (or fluorocyclopentane, cyclopentene, or tetrahydropyran) -rich liquid phase (L_g), the water-rich liquid phase (L_w), and hydrate phase (H). The main part of the apparatus was a stainless-steel cylinder with the inner dimensions of 40 mm diameter and 110 mm height. A magnetic stirrer was installed in the vessel through its lid to agitate the fluids and hydrate crystals inside the vessel at 300 rpm. The vessel was immersed in a temperature-controlled bath to maintain the temperature inside the vessel, T, at the prescribed value of ± 0.1 K. A thermistor thermometer was inserted in the vessel to measure T. The pressure in the vessel, p, was measured by a strain-gauge pressure transducer (model PHB-5MP, KYOWA Electric Co., Ltd., Tokyo) when $p > 2.1$ MPa. For measuring p less than 2.1 MPa, another strain gauge pressure transducer (model PH-20KB, KYOWA Electric Co., Ltd.) was used. The estimated uncertainty of the temperature measurements is ± 0.1 K. The uncertainty of the pressure measurements is ± 0.012 MPa for $p > 2.1$ MPa and ± 0.004 MPa for $p < 2.1$ MPa.

The equilibrium conditions were measured using the batch, isochoric procedure, described by Danesh et al.[17] Each run was initiated by charging the vessel with 30 g of liquid water and 15 g of cyclopentane, fluorocyclopentane, cyclopentene, or tetrahydropyran. The vessel containing the liquids was then immersed in the temperature-controlled bath. The methylfluoride gas was supplied from a high-pressure cylinder through a pressure-regulating valve into the evacuated vessel until the pressure inside the vessel (p) had increased to the prescribed level between (0.1 and 3.0) MPa. After T and p had stabilized, the valve in the line connecting the vessel and the high-pressure cylinder was closed. T was then decreased to form the hydrate. If hydrate formation in the vessel was detected by a decrease in p and an increase in T, the temperature of the bath was maintained constant for six hours, thereby keeping T constant. We then incrementally increased T in steps of 0.1 K. At every temperature step, T was kept constant for (6 to 10) h to achieve a steady, equilibrium state in the vessel. In this way, we obtained a $p-T$ diagram for each experimental run, from which we determined a four-phase equilibrium point. If T was increased in the presence of a hydrate, the hydrate partially dissociated, thereby substantially increasing p. After the complete dissociation of the hydrate, only a lower increase in pressure is observed due to the change in the phase equilibria of the fluids in the vessel. Consequently, the point at which the slope of the $p-T$ data plots sharply changes was considered to be the point at which all the hydrate crystals dissociate and, hence, was the four-phase equilibrium point. This operation was repeated at several different initial pressures to obtain the four-phase equilibrium data over the temperature range.

Hydrate crystal samples for the PXRD measurements were prepared with liquid water, methylfluoride, and a liquid guest substance (cyclopentane, fluorocyclopentane, cyclopentene, or tetrahydropyran) using the experimental apparatus described in our previous studies.[8,12] The pressure and temperature were set at $p = 1$ MPa and $T = 287$ K, outside the conditions for the structure I simple methylfluoride hydrate formation to avoid the possible formation of the structure I simple methylfluoride hydrate, which may occur at $p > 1.1$ MPa at this temperature.[12] The line connecting the test cell and the high-pressure methylfluoride cylinder was opened during the hydrate formation in the test cell to keep p constant by continuously supplying methylfluoride gas to compensate for the pressure reduction in the test cell due to hydrate formation, so that a sufficient amount of hydrate crystals would be stored in the cell. p and T were maintained constant for over 20 h with continuous agitation in the vessel at 400 rpm after nucleation of the hydrate. The vessel was subsequently removed from 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 below ≈170 K and then disassembled the vessel to collect the hydrate crystals. The prepared samples were stored in a container kept at a temperature of ≈100 K and then later subjected to the PXRD measurements.

For the PXRD measurements, the hydrate samples were finely powdered in a nitrogen atmosphere at a temperature below 100 K. The fine-powdered hydrate samples were top-loaded on a specimen holder made of Cu. The PXRD measurements were done using Cu Kα radiation by a parallel beam optics (40 kV, 40 mA; Rigaku model Ultima III). The XRD measurements were performed in the $\theta/2\theta$ step scan mode with a step width of 0.02° at 93 K. Determination of the unit cell parameter was done by a full-pattern fitting method using the RIETAN-2000 program.[18]

Results and Discussion

The $p-T$ data of the $V + L_g + L_w + H$ four-phase equilibrium in the systems each containing the cyclopentane, fluorocyclopentane, cyclopentene, and tetrahydropyran are listed

Table 1. Methylfluoride-Rich Vapor + Water-Rich Liquid + Cyclopentane-Rich Liquid + Hydrate Four-Phase Equilibrium *p*, *T* Conditions in the Methylfluoride + Cyclopentane + Water System

T/K	p/MPa
287.9	0.138
290.0	0.189
293.7	0.336
297.0	0.557
299.1	0.787
302.0	1.233
303.0	1.515
305.0	2.349
305.9	2.988

Table 2. Methylfluoride-Rich Vapor + Water-Rich Liquid + Fluorocyclopentane-Rich Liquid + Hydrate Four-Phase Equilibrium *p*, *T* Conditions in the Methylfluoride + Fluorocyclopentane + Water System

T/K	p/MPa
290.1	0.122
290.9	0.136
292.0	0.161
293.4	0.206
294.9	0.266
297.7	0.409
300.6	0.647
303.1	0.996
305.4	1.683
306.2	2.051
307.0	2.560

Table 3. Methylfluoride-Rich Vapor + Water-Rich Liquid + Cyclopentene-Rich Liquid + Hydrate Four-Phase Equilibrium *p*, *T* Conditions in the Methylfluoride + Cyclopentene + Water System

T/K	p/MPa
283.6	0.106
288.1	0.227
293.5	0.528
296.8	0.895
299.5	1.418
300.8	1.928

Table 4. Methylfluoride-Rich Vapor + Water-Rich Liquid + Tetrahydropyran-Rich Liquid + Hydrate Four-Phase Equilibrium *p*, *T* Conditions in the Methylfluoride + Tetrahydropyran + Water System

T/K	p/MPa
284.4	0.116
288.9	0.239
294.0	0.531
297.2	0.892
300.0	1.483
301.0	1.877

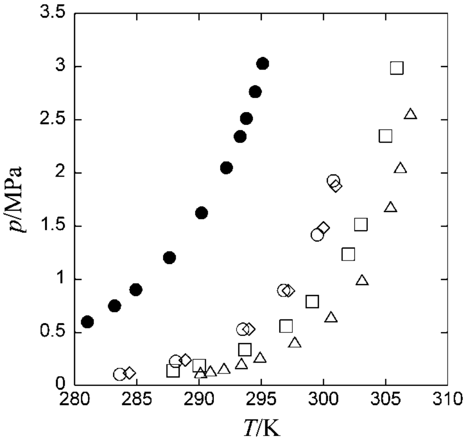

Figure 2. Equilibrium $p-T$ conditions for four phases involving clathrate hydrate formed with methylfluoride and each of the following guest substances: □, cyclopentane; △, fluorocyclopentane; ○, cyclopentene; ◇, tetrahydropyran (present study). The three-phase equilibrium $p-T$ conditions in the methylfluoride + water system are also indicated: ●, ref 12.

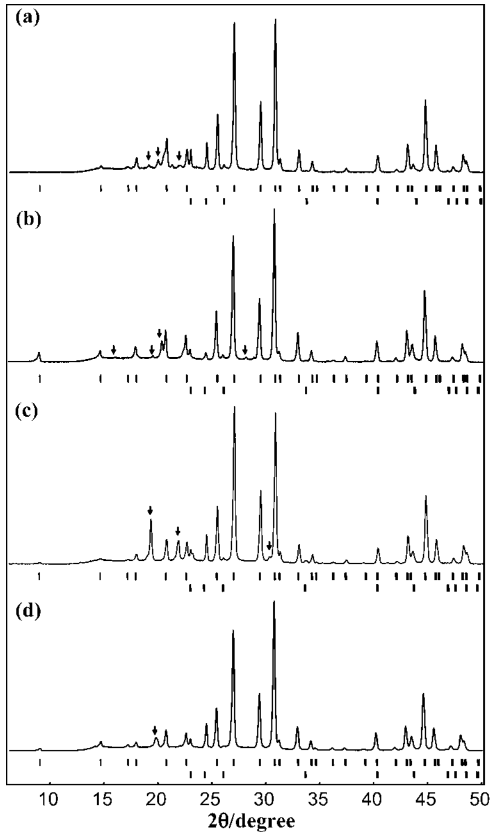

Figure 3. PXRD profiles obtained from hydrate samples prepared in the systems of water and methylfluoride plus each of the following substances: (a) cyclopentane; (b) fluorocyclopentane; (c) cyclopentene; (d) tetrahydropyran. The crystal samples were prepared at $p = 1$ MPa and $T = 287$ K. The diffraction measurements were performed at 93 K. The crystallographic structure of the hydrates was identified to be structure II. In the lower part, the upper stick patterns correspond to the refinement result of the structure II hydrate, and the lower stick patterns correspond to those of hexagonal ice that was transformed from interstitial water. The arrows indicate diffraction peaks of unknown crystals that would be formed from second guest substances.

in Tables 1 to 4. These data are plotted in Figure 2 together with the $p-T$ data of the V + L_w + H three-phase equilibrium conditions in the methylfluoride + water system.[12] The four-phase equilibrium pressures measured in the present study are lower by approximately 0.6 MPa at 283 K than the three phase equilibrium pressures for the simple methylfluoride hydrate system. This reduction in the equilibrium pressures increases with the increasing temperature and is greater than 2.5 MPa at 295 K. This change in the phase equilibria due to the addition of cyclopentane, fluorocyclopentane, cyclopentene, or tetrahydropyran to the methylfluoride + water system suggests the formation of double hydrates each with methylfluoride and cyclopentane, fluorocyclopentane, cyclopentene, or tetrahydropyran, instead of a structure I simple methylfluoride hydrate.

Considering the molecular size and shape of methylfluoride and cyclopentane, fluorocyclopentane, cyclopentene, or tetrahydropyran, the double hydrate is estimated to be a structure II hydrate with methylfluoride molecules mainly enclosed in 5^{12} cages and with molecules of the second guests in $5^{12}6^4$ cages.[19,20] The crystallographic structure of these hydrates was identified on the basis of the PXRD measurements. Figure 3

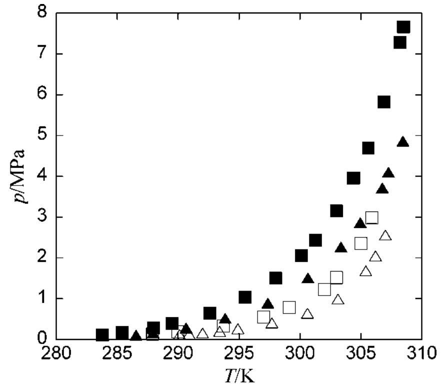

Figure 4. Comparison of the four-phase equilibrium conditions for the hydrates formed with methylfluoride and cyclopentane or fluorocyclopentane to those for the hydrates formed with krypton and cyclopentane or fluorocyclopentane: □, methylfluoride and cyclopentane; △, methylfluoride and fluorocyclopentane; ■, krypton and cyclopentane; ▲, krypton and fluorocyclopentane.

depicts the PXRD profiles obtained with the hydrate-crystal samples each prepared in the four systems. From these profiles, the crystallographic structures of the hydrates are all identified to be structure II. These profiles indicate that the lattice constants of each hydrate are 1.7213 nm for the cyclopentane + methylfluoride hydrate, 1.7237 nm for the fluorocyclopentane + methylfluoride hydrate, 1.7248 nm for the cyclopentene + methylfluoride hydrate, and 1.7255 nm for the tetrahydropyran + methylfluoride hydrate. These slight differences in the lattice constants would be caused by the different guest molecules.

Among the four systems tested in the present study, the highest equilibrium temperature (or the lowest equilibrium pressure) was possible with fluorocyclopentane, whereas the lowest was with cyclopentene. The equilibrium temperature in the fluorocyclopentane system exceeded 305 K at 2 MPa. The highest equilibrium temperature we measured in the fluorocyclopentane system was 307.0 K at 2.560 MPa. Also, in the cyclopentane system, the equilibrium temperature exceeding 305 K was available at 3 MPa. These temperatures are comparable to or higher than the typical ambient temperature in the summer season of most urban areas around the world. Thus, the mixture of methylfluoride gas + liquid cyclopentane or liquid fluorocyclopentane + liquid water may be used as the working medium of a hydrate-based residential air-conditioning refrigeration system. Figure 4 compares the four-phase equilibrium conditions in the systems with methylfluroide + cyclopentane or fluorocyclopentane to those in the systems with krypton + cyclopentane or fluorocyclopentane, which are reported to be used as the working medium of refrigeration systems.[9] This comparison indicates that the low-pressure/high-temperature phase equilibrium conditions are possible using the methylfluoride systems.

Literature Cited

(1) Sloan, E. D., Jr. *Clathrate Hydrates of Natural Gases*, 2nd ed.; Marcel Dekker Inc.: NY, 1998.

(2) Mori, Y. H. Recent advances in hydrate-based technologies for natural gas storage - a review. *J. Chem. Ind. Eng. (China)* **2003**, 1–17, 54-Suppl.

(3) Mao, W. L.; Mao, H. Hydrogen storage in molecular compounds. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 708–710.

(4) Seo, Y.-T.; Moudravski, I. L.; Ripmeester, J. A.; Lee, J.-W.; Lee, H. Efficient recovery of CO_2 from flue gas by clathrate hydrate formation in porous silica gels. *Environ. Sci. Technol.* **2005**, *39*, 2315–2319.

(5) Kamata, Y.; Yamakoshi, Y.; Ebinuma, T.; Oyama, H.; Shimada, W.; Narita, H. Hydrogen sulfide separation using tetra-n-butyl ammonium bromide semi-clathrate (TBAB) hydrate. *Energy Fuels* **2005**, *19*, 1717–1722.

(6) Ogawa, T.; Itoh, T.; Watanabe, K.; Tahara, K.; Hiraoka, R.; Ochiai, J.; Ohmura, R.; Mori, Y. H. Development of a novel hydrate-based refrigeration system: a preliminary overview. *Appl. Thermal Eng.* **2006**, *26*, 2157–2167.

(7) Imai, S.; Okutani, K.; Ohmura, R.; Mori, Y. H. Phase equilibrium for clathrate hydrates formed with difluoromethane + either cyclopentane or tetra-*n*-butylammonium bromide. *J. Chem. Eng. Data* **2005**, *50*, 1783–1786.

(8) Takeya, S.; Ohmura, R. Phase equilibrium for structure II hydrates formed with krypton coexisting with cyclopentane, cyclopentene or tetrahydropyran. *J. Chem. Eng. Data* **2006**, *51*, 1880–1883.

(9) Imai, S.; Miyake, K.; Ohmura, R.; Mori, Y. H. Phase equilibrium for clathrate hydrates formed with difluoromethane or krypton, each coexisting with fluorocyclopentane. *J. Chem. Eng. Data* **2006**, *51*, 2222–2224.

(10) Biswas, S. N.; Ten Seldam, C. A.; Bominaar, S.A.R.C.; Trappeniers, N. J. Liquid-vapour coexistence curve of methyl fluoride in the critical region. *Fluid Phase Equilib.* **1989**, *49*, 1–7.

(11) Sato, H., Higashi, Y., Okada, M., Takaishi, Y., Kagawa, N., Fukushima, M., Eds. *HFCs and HCFCs, ver. 1.0. (JAR Thermodynamic Tables)*; Japanese Association of Refrigerants: Tokyo, 1994; *Vol. 1.*

(12) Takeya, S.; Ohmura, R. Phase equilibrium for structure I and structure H hydrates formed with methylfluoride and methylcyclohexane. *J. Chem. Eng. Data* **2007**, *52*, 635–638.

(13) Holder, G. D.; Corbin, G.; Papadopoulos, K. D. Thermodynamic and molecular properties of gas hydrates from mixtures containing methane, argon, and krypton. *Ind. Eng. Chem. Fundam.* **1980**, *19*, 282–286.

(14) Palmer, H. A. Characterization of hydrocarbon-type hydrates. Ph.D. Thesis, University of Oklahoma, Norman, OK, 1950.

(15) Brouwer, D. H.; Brouwer, E. B.; Maclaurin, G.; Lee, M.; Parks, D.; Ripmeester, J. A. Some new halogen-containing hydrate-formers for structure I and II clathrate hydrates. *Supramol. Chem.* **1997**, *8*, 361–367.

(16) Udachin, K. A.; Ratcliffe, C. I.; Ripmeester, J. A. Single crystal diffraction studies of structure I, II, and H hydrates: Structure, cage occupancy and composition. *J. Supramol. Chem.* **2002**, *2*, 405–408.

(17) Danesh, A.; Tohidi, B.; Burgass, R. W.; Todd, A. C. Hydrate equilibrium data of methyl cyclopentane with methane or nitrogen. *Chem. Eng. Res. Des.* **1994**, *72*, 197–200.

(18) Izumi, F.; Ikeda, T. A. Rietveld-analysis propram RIETAN-98 and its application to zeolites. *Mater. Sci. Forum* **2000**, *321–323*, 198–203.

(19) Sloan, E. D., Jr. *Clathrate Hydrates of Natural Gases*, 2nd ed.; Marcel Decker: NY, 1998.

(20) Davidson, D. W. Clathrate hydrates. In *Water: A Comprehensive Treatise*; Franks, F., Ed.; Plenum Press: NY, 1973; Vol. 2.

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