Title	Structure-H Methane + 1,1,2,2,3,3,4-Heptafluorocyclopentane Mixed Hydrate at Pressures up to 373 Mpa
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Note	

Structure-H Methane+1,1,2,2,3,3,4-Heptafluorocyclopentane Mixed Hydrate at Pressures up to 373 MPa

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Abstract.

Thermodynamic stability boundary of structure-H hydrates with large guest species and methane (CH_4) at extremely high pressures has been almost unclear. In the present study, the four-phase equilibrium relations in the structure-H CH_4+1,1,2,2,3,3,4-heptafluorocyclopentane (1,1,2,2,3,3,4-HFCP) mixed hydrate system were investigated in a temperature range of (281.05 to 330.12) K and a pressure range up to 373 MPa. The difference between equilibrium pressures in the structure-H CH_4+1,1,2,2,3,3,4-HFCP mixed hydrate system and the structure-I simple CH_4 hydrate system gets larger with increase in temperature. The structure-H CH_4+1,1,2,2,3,3,4-HFCP mixed hydrate survives even at 330 K and 373 MPa without any structural phase transition. The maximum temperature where the structure-H CH_4+1,1,2,2,3,3,4-HFCP mixed hydrate is thermodynamically stable is likely to be beyond that of the structure-H simple CH_4 hydrate.

Keywords: gas hydrate; phase equilibria; X-ray diffraction; Raman spectroscopy

1. INTRODUCTION

Gas hydrate is a crystalline inclusion compound, which consists of water molecules and some guest species. Hydrate cages are formed with the hydrogen-bonded water molecules, and guest species are encaged in the vacant cages. There are five types of cages which are pentagonal dodecahedron (5^{12}, S-cage), dodecahedron ($4^3 5^6 6^3$, S'-cage), tetrakaidecahedron ($5^{12}6^2$, M-cage), hexakaidecahedron ($5^{12}6^4$, L-cage), and icosahedron ($5^{12}6^8$, U-cage). Each hydrate unit cell is composed of some cages. Structure-I (s-I) hydrate consists of two S-cages and six M-cages with 46 water molecules, structure-II (s-II) hydrate consists of sixteen S-cages and eight L-cages with 136 water molecules, and structure-H (s-H) hydrate consists of three S-cages, two S'-cages, and one U-cage with 34 water molecules. In general, simple gas hydrate belongs to either s-I or s-II hydrate, except at extremely high pressures.[1–3] In a part of s-II and s-H hydrates, small and large guest species occupy small and large cages, compartmentally. If the large guest species (LGS) does not form hydrates without small guest species, the small guest species is called as help gas.

Recently, s-H hydrates have attracted much attention as a new medium for the natural gas transport system.[4] The equilibrium pressure of an s-H hydrate formed by the addition of a small amount of LGSs is smaller than that of a simple gas hydrate (s-I or s-II, dependent on help gases). And also, larger amount of help gas can be stored because s-H hydrates have the largest storage potential in small cage(s) among s-I, s-II, and s-H by stabilizing large cage with LGSs.[4] The thermodynamic properties and storage abilities of s-H hydrates depend on the chemical and physical properties of LGSs,[5–7] for example, the molecular volume, the molar mass, the shape of LGSs, and so on.

One of the characteristic phenomena in an s-H hydrate system is the existence of the structural phase transition point, where s-H mixed hydrate is collapsed and instead simple gas hydrate, which contains only a help gas without LGSs, is formed. For example, in the case of the utilization of methane (CH_4) as help gas, phase equilibrium curve in the s-H mixed hydrate systems comes close to that of the simple CH_4 hydrate system as pressures and temperatures rise. Finally, the curve in the s-H mixed hydrate systems crosses that of the simple CH_4 hydrate system at the structural phase transition point. For example, methane CH_4+*cis*-4-methylcyclohexanol,[6] xenon+1,1-dimethylcyclohexane (1,1-DMCH),[7] carbon dioxide+2,2-dimethylbutane,[8] methylfluoride+methylcyclohexane[9] mixed hydrate systems exhibit such behavior. In other s-H mixed hydrate systems where such structural phase transition has not been reported, in addition, it has been considered that the s-H mixed hydrate is collapsed and changed to simple CH_4 hydrate at pressures higher than tens of MPa. Because the slope ($\mathrm{d}p/\mathrm{d}T$) of phase equilibrium curve in the typical s-H mixed hydrate is larger than that of simple gas hydrate containing only the once-help gas.

There are some important studies on the phase equilibria for the simple CH_4 hydrate system. Dyadin *et al.*[1] have reported that the simple CH_4 hydrate has the structural phase transition point at 620 MPa and 320 K on the three-phase (hydrate + aqueous + gas) equilibrium curve. They have claimed that phase equilibrium curve after the phase transition intersects the melting curve of ice-VI at 1.62–1.65 GPa and 331 K while the new crystal lattice was not identified definitely. Loveday *et al.*[2] have reported that the simple CH_4 hydrate above 620 MPa is very similar to s-H hydrate based on the X-ray and neutron diffraction analyses. And also, Kumazaki *et al.*[3] have reported the Raman spectra in a single crystal of the s-H CH_4 hydrate formed under three-phase equilibrium condition (1.0 GPa, 323 K).

In order to elucidate the characteristics of s-H hydrates, it is very important to investigate the phase equilibrium relations in s-H CH_4+LGS mixed hydrate systems at high pressures than ever, especially like several hundred MPa. In the present study, CH_4 and 1,1,2,2,3,3,4-heptafluorocyclopentane (1,1,2,2,3,3,4-HFCP) are adopted as a help gas and an LGS, respectively. Firstly, we identified the structure of CH_4+1,1,2,2,3,3,4-HFCP mixed hydrate because it has not been reported whether 1,1,2,2,3,3,4-HFCP forms hydrates. Thermodynamic stability of the CH_4+1,1,2,2,3,3,4-HFCP mixed hydrate was investigated at pressures up to 373 MPa.

2. EXPERIMENTAL SECTION

2.1 Materials

CH_4 (mole fraction purity, more than 0.9999) was purchased from Liquid Gas Co., Ltd. 1,1,2,2,3,3,4-HFCP (mole fraction purity, more than 0.98) was obtained from Zeon Co., Ltd. The distilled water (mole fraction purity, more than 0.9999) was obtained from Wako Pure Chemicals Industries, Ltd. All of them were used without further purification.

2.2 Experimental apparatus

The detail of the apparatus is the same as reported previously.[5,10] At a pressure up to 10 MPa, the high-pressure cell (inner volume and maximum working pressure are 150 cm^3 and 10 MPa) with sapphire windows for visual observation was used for the phase equilibrium measurement. The high-pressure optical cell (inner volume and maximum working pressure are 0.2 cm^3 and 400 MPa) was used for the phase equilibrium measurement at pressures above 10 MPa and the Raman analysis. Equilibrium pressure was measured by three types of pressure gauges according to the working pressures. At pressures up to 10 MPa and from (10 to 100) MPa, two pressure gauges (VALCOM VPRT) were used with an estimated maximum uncertainty of 0.02 MPa and

0.2 MPa, respectively. Above 100 MPa, a pressure transducer (NMB STD-5000K) and digital peak holder (NMB CSD-819) was used with the estimated maximum uncertainty of 2 MPa. Equilibrium temperature was measured with a thermistor probe (TAKARA D-641). The probe was calibrated with a Pt resistance thermometer defined by ITS-90. Programming thermocontroller (EYELA NCB-3100) adjusted the cell temperature. The maximum uncertainty of equilibrium temperature was 0.02 K.

2.3 Experimental procedures

Sufficient amount of liquid 1,1,2,2,3,3,4-HFCP was introduced into the high-pressure cell. After removal of the dissolved air, and then CH_4 was introduced into the cell up to a desired pressure. After that, the content was pressurized by supplying distilled water with use of a high-pressure pump. The system pressure after the pressurization did not exceed the equilibrium pressure of the simple CH_4 hydrate at the temperature. The content was cooled and agitated by a mixing-bar moved by permanent magnet (below 10 MPa) or a ruby ball in the cell (above 10 MPa). The phase behavior was observed straightforwardly with a charge-coupled device (CCD) camera through the sapphire window. After the formation of the mixed hydrates, the temperature was kept constant to establish the four-phase equilibrium condition. To determine the four-phase equilibrium pressure precisely, the s-H hydrate was formed or dissociated by the pressure control[5]. When the pressure change fell within the maximum uncertainties of pressure gauges, the system was regarded to be in the equilibrium state. Usually, it takes a couple of days to establish the equilibrium in the present study. Especially in the high temperature region, it takes more than four days for completing the equilibrium. When the four-phase equilibrium condition was established, pressure and temperature were recorded as an equilibrium datum set.

After established the four-phase equilibrium condition, hydrate samples were taken from the cell at 263 K and kept at 77 K. Samples were ground and set on the stage flatly. PXRD pattern was measured at 173 K using a diffractometer (Rigaku, Ultima IV) with a Rigaku D/teX ultra high-speed position sensitive detector and CuKα X-ray (40 kV, 50 mA). The measurements were performed in the stepscan mode with scan rate 10 deg・min^{-1} and step size of 0.02°. PXRD pattern indexing and cell refinement were obtained with use of the Chekcell,[11] PowderX,[12] and the initial lattice parameters[13] for the refinement.

After the single crystals of the CH_4+1,1,2,2,3,3,4-HFCP mixed hydrate were formed under four-phase coexistence conditions, the temperature was kept constant for more than a couple of days to establish the four-phase equilibrium conditions. The hydrate single crystal was analyzed by use of a laser Raman microprobe spectrometer with multichannel CCD detector (Jobin-Yvon, Ramanor T64000). The argon ion laser beam (514.5 nm, 100 mW) condensed to 2 μm in spot diameter was irradiated from the object lens to the hydrate single crystal through the upper sapphire window. The CCD detector was maintained at 140 K by liquid nitrogen for heat-noise reduction. The spectral resolution was approximately 0.7 cm^{-1}. The Raman shift was calibrated with the neon emission lines in the air.

3. RESULTS AND DISCUSSION

The PXRD pattern of the CH_4+1,1,2,2,3,3,4-HFCP mixed hydrate prepared at 3.31 MPa and 282.44 K is shown in Figure 1. The typical pattern derived from s-H hydrate (hexagonal, *P*6/*mmm*) was detected in the CH_4+1,1,2,2,3,3,4-HFCP mixed hydrate. The lattice constants are a = 1.221±0.002 nm, c = 1.002±0.001 nm at 173 K.

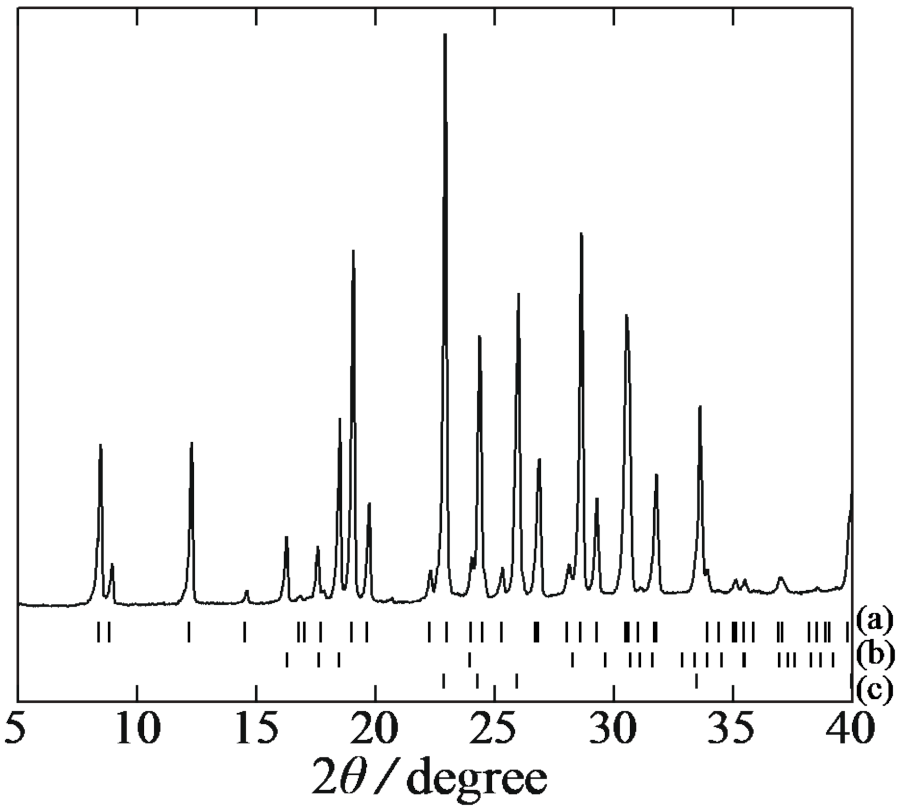

Figure 1. PXRD pattern of CH_4+1,1,2,2,3,3,4-HFCP mixed hydrate prepared at 3.31 MPa and 282.44 K (recorded at 173 K). The vertical bars represent the contributions from (a) s-H hydrate (b) solid 1,1,2,2,3,3,4-HFCP (c) ice-Ih.

Four-phase equilibrium relations of $H+L_1+L_3+G$ (open circles) and $S_3+L_1+L_3+G$ (open squares) in the CH_4+1,1,2,2,3,3,4-HFCP+water ternary system are shown in Figure 2 (The data are summarized in Table S1 of the Supporting Information). The symbols of H, S_3, L_1, L_3, and G represent the hydrate, solid 1,1,2,2,3,3,4-HFCP, aqueous, 1,1,2,2,3,3,4-HFCP-rich liquid, and gas phases. Dotted curve indicates the three-phase equilibrium relation of $H+L_1+G$ in the simple CH_4 hydrate system.[1,5,14,15]

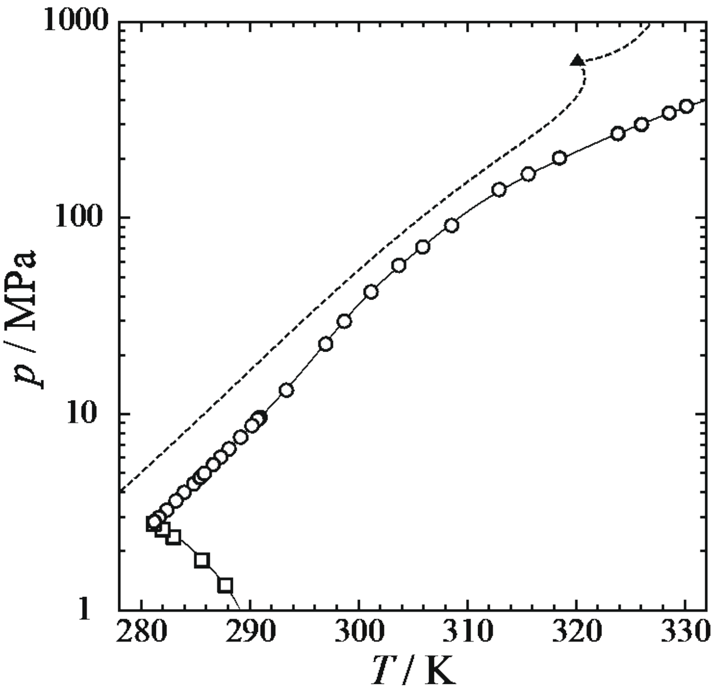

Figure 2. Four-phase ($H+L_1+L_3+G$ and $S_3+L_1+L_3+G$) equilibrium relations in the CH_4+1,1,2,2,3,3,4-HFCP+water ternary system. The symbols of H, S_3, L_1, L_3, and G represent the hydrate, solid 1,1,2,2,3,3,4-HFCP, aqueous, 1,1,2,2,3,3,4-HFCP-rich liquid, and gas phases. Open circles and open squares stand for the four-phase equilibrium relations of $H+L_1+L_3+G$ and $S_3+L_1+L_3+G$ in the CH_4+1,1,2,2,3,3,4-HFCP+water ternary system. Dotted curve and solid triangle stand for the three-phase equilibrium relation of $H+L_1+G$ in the simple CH_4 hydrate system[1,5,14,15] and the structural phase transition point from s-I to s-H of CH_4 hydrate.[1]

In the whole pressure and temperature range of the present study, the four-phase equilibrium curve of ($H+L_1+L_3+G$) is laid at the lower-pressure side than three-phase equilibrium curve of ($H+L_1+G$) in simple CH_4 hydrate system. Until now, it had been believed that the s-H mixed hydrate is collapsed at the intersection between the four-phase equilibrium curve of s-H hydrates and the three-phase equilibrium curve of simple gas hydrates containing only the once-help gas in s-H hydrate system. In fact, such phase behavior has been reported in some s-H hydrates helped by CH_4[6] and xenon.[7] Surprisingly, the four-phase equilibrium curve of ($H+L_1+L_3+G$) in the CH_4+1,1,2,2,3,3,4-HFCP mixed hydrate system does not intersect with the three-phase equilibrium curve of ($H+L_1+G$) in the simple CH_4 hydrate system up to 373 MPa and 330.12 K. Rather, the difference between both equilibrium curves gets larger with increase in temperature and pressure. The four-phase equilibrium curve of ($H+L_1+L_3+G$) exhibits no structural phase transition up to 373 MPa and 330.31 K. In addition, there is no significant difference in Raman shifts of the intramolecular vibration modes of the CH_4 and 1,1,2,2,3,3,4-HFCP molecules, as shown in Figure 3. On the other hand, the structure of simple CH_4 hydrate changes from s-I to s-H at 620 MPa and 320 K on the three-phase equilibrium curve of ($H+L_1+G$).[1–3] In the s-H simple CH_4 hydrate system, multiple CH_4 molecules surely occupy U-cage.[2,3,16] Directly comparing the stability boundary of the s-H CH_4+1,1,2,2,3,3,4-HFCP mixed hydrate with that of the s-H simple CH_4 hydrate, it is suggested that the contribution of LGSs to the stability of s-H hydrates is crucially significant.

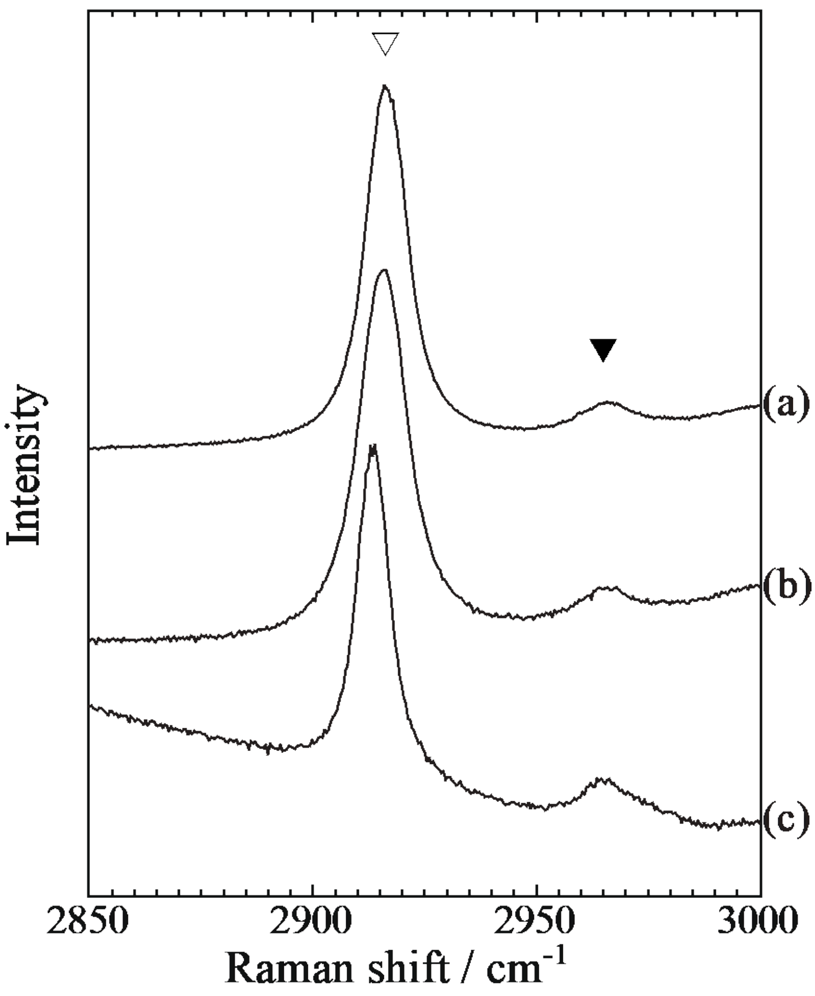

Figure 3. Raman spectra of the intramolecular vibrations of the enclathrated CH_4 (open triangle) and 1,1,2,2,3,3,4-HFCP (solid triangle) molecules in the CH_4+1,1,2,2,3,3,4-HFCP mixed hydrates at (a) 374 MPa, 330.31 K (b) 256 MPa, 322.50 K (c) 3.80 MPa, 283.28 K. There is no significant change except for the weak pressure and temperature dependences.

Among the LGSs forming s-H hydrates, 1,1-DMCH has been considered to be the most suitable for the s-H hydrate generation from the viewpoint of the pressure reduction.[17,18] The equilibrium pressure of the CH_4+1,1,2,2,3,3,4-HFCP mixed hydrate is slightly higher than that of CH_4+1,1-DMCH mixed hydrate at pressures up to 10 MPa. Therefore, 1,1,2,2,3,3,4-HFCP would also be one of suitable LGSs for the s-H hydrate generation. In addition, the four-phase (S_3+L_1+L_3+G) equilibrium curve in the present system, having negative slope (d*p*/d*T*), intersects with the four-phase (H+L_1+L_3+G) equilibrium curve at 2.79 MPa and 281.05 K.

4. CONCLUSIONS

1,1,2,2,3,3,4-HFCP generates an s-H hydrate in the presence of CH_4. Thermodynamic stability of the s-H CH_4+1,1,2,2,3,3,4-HFCP mixed hydrate was investigated at pressures up to 373 MPa. The most important finding is that the s-H CH_4+1,1,2,2,3,3,4-HFCP mixed hydrate remains thermodynamically stable even at 373 MPa and 330 K without any structural phase transition, although it had been believed that s-H hydrates with help gases would be collapsed and transformed to the simple hydrates enclathrating only help gases. Moreover, the stability boundary of the s-H CH_4+1,1,2,2,3,3,4-HFCP mixed hydrate is located beside that of the s-H CH_4+1,1-DMCH mixed hydrate. 1,1,2,2,3,3,4-HFCP would be one of the most suitable LGSs for the equilibrium pressure reduction derived from s-H hydrate formation.

Supporting Information

Four-phase equilibrium relations of H+L_1+L_3+G and S_3+L_1+L_3+G in the CH_4+1,1,2,2,3,3,4-HFCP+water ternary system are summarized in Table S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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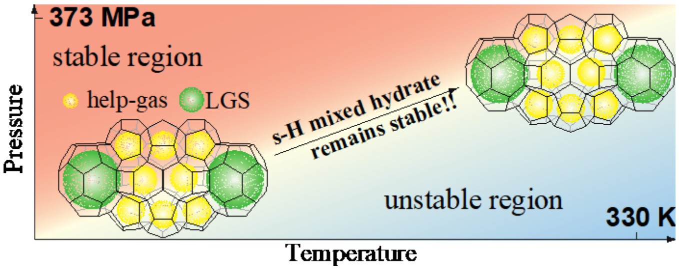
373 MPa
stable region
help-gas
LGS
s-H mixed hydrate remains stable!!
unstable region
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