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Isothermal Phase Equilibria and Cage Occupancies for CH_4 + CHF_3 Mixed-Gas Hydrate System

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Abstract: Isothermal phase equilibria for the CH_4 + CHF_3 mixed-gas hydrate system were investigated under three-phase equilibrium states at 291.1 K by using gas chromatography. In addition, the single-crystals of mixed-gas hydrate were analyzed by means of Raman spectroscopy. One of the most important findings in the present study is that there is no hydrate-structural transition, as the composition of mixed gas was varied at 291.1 K in the CH_4 + CHF_3 mixed-gas hydrate system.

INTRODUCTION

Gas hydrates are crystalline inclusion-compounds and consist of water molecules and some guest species (*ex.* hydrocarbons, noble gases). The hydrogen-bonded water molecules construct hydrate cages and guest species are encaged in the vacant spaces. Generally, three types of unit cells are well-known and called structure-I (s-I), -II (s-II), and -H (s-H). The unit cell of s-I consists of two small cages (S-cage, pentagonal dodecahedron (5^{12})) and six large cages (M-cage, tetrakaidekahedron ($5^{12}6^{2}$)). That is, the ratio of small cages to large cages is 1:3. The unit cell of s-II consists of sixteen small cages (S-cage) and eight large cages (L-cage, hexakaidekahedron ($5^{12}6^{4}$)) that are larger than M-cage. The ratio of small cages to large cages is 2:1.

Subramanian, Kini, Dec, and Sloan [1] have found that the CH_4 + C_2H_6 mixed-gas hydrate forms the s-II in a certain composition region, nevertheless each guest molecule separately generates an s-I hydrate. Makino, Tongu, Sugahara, and Ohgaki [2] also have reported that the CH_4 + cyclopropane (hereafter, c-C_3H_6) mixed-gas hydrate system shows hydrate-structural transition from the s-I to the s-II. Hydrate structure has large effects on contents of guest species and thermodynamic stabilities, so it is very important to elucidate the mechanism of the structural transition. However, there are not a lot of data of phase equilibria and spectroscopic measurements for the mixed-gas hydrates. It is necessary to accumulate fundamental information of mixed-gas hydrates.

It is said that the structural transition occurs, which depends on compositions of mixed guest-species, when two kinds of guest species have suitable diameters for the S-cages and the M- or the L-cages, respectively [3]. However, Sugahara, Makino, and Ohgaki [4] have reported that the CH_4 + C_2H_4 mixed-gas hydrate system does not show the structural transition at 293.2 K. There is not so much of a difference between molecular diameter of C_2H_6 and that of C_2H_4.

The molecular diameter of CHF_3 is very close to that of C_2H_6 or C_2H_4. Mooijer-van den Heuvel, Sawirjo, and Peter [5] reported that the structural phase-transition in the CH_4 + CHF_3 mixed-gas hydrate system does not occur when the mixed-gas hydrate coexists with the gas and water phases, while the s-II hydrate is generated in the certain condition with the coexistence of liquid (guest species) and water phases.

In the present study, isothermal phase equilibria for the CH_4 + CHF_3 mixed-gas hydrate system were measured under three-phase (gas + water + hydrate phases) equilibrium state at 291.1 K. In addition, the single-crystals of mixed-gas hydrate were analyzed by use of Raman spectroscopy to investigate directly which hydrate structure is stable under the present conditions.

EXPERIMENTAL

Materials

CH_4 (research grade of purity x = 0.9999) and CHF_3 (research grade of purity x = 0.99999) were purchased from Takachiho Trading Co., Ltd. The distilled water was obtained from Yashima Pure Chemicals Co., Ltd. All of them were used without further purification.

Apparatus and Procedure

Experimental apparatus used in the present study is the same as the one reported in the previous work [4]. The details are not mentioned here. Equilibrium temperatures were measured with an uncertainty of 0.02 K using a thermistor probe (Takara D-632). The probe was calibrated with a Pt resistance thermometer defined by ITS-90. The system pressure was measured by a pressure gage (Valcom VPRT) calibrated by RUSKA quartz Bourdon tube gage (Direct Reading Pressure Gage, series 6000) with an estimated maximum uncertainty of 0.02 MPa.

Raman Spectroscopic Analysis

Mixtures of CH_4 and CHF_3 were prepared at known compositions. The mixture was introduced into an evacuated high-pressure optical cell. The contents were pressurized up to a desired pressure by supplying distilled water succes-

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sively. The contents were cooled and agitated by an enclosed ruby ball to generate the CH_4 + CHF_3 mixed-gas hydrate. Temperature was controlled by circulating thermostated water through a jacket of the cell. The ruby ball was vibrated by low-frequency vibration from outside.

After the CH_4 + CHF_3 mixed-gas hydrate was generated, the temperature was changed gradually to prepare the single-crystals under three-phase coexisting state. A three-phase equilibrium state with the existence of single crystal was established to keep the temperature constant for more than one day. They were analyzed by *in situ* Raman spectroscopy by use of a laser Raman microprobe spectrometer with a multichannel CCD detector. Ar ion laser beam (wavelength: 514.5 nm, generation power: 100 mW) condensed to 2 μm in spot diameter was irradiated onto them from the object lens. The spectral resolution was about 1 cm^{-1}. The CCD detector was maintained at 140 K by liquid nitrogen for heat-noise reduction. Integration time was varied from (10 to 300) s, depending on the intensities of Raman scattering. Equilibrium compositions of gas and hydrate phases were determined by direct comparison of equilibrium Raman-peak area ratios of unknown samples with that of reference mixed-gas samples. The reference samples were prepared by mass on a precision balance (uncertainty of 0.1 mg, Max. 3 kg, Cho balance).

Phase Equilibrium Measurements

The mixture of guest species was introduced into another evacuated high-pressure cell (the inside volume is ca. 150 cm^3). Distilled water was also introduced into the cell to pressurize the contents. In order to generate the mixed-gas hydrates, the contents were agitated using a mixing bar that is moved up-and-down by magnetic attraction from outside of the cell. After generation of the mixed-gas hydrates, the temperature was kept constant to establish a three-phase equilibrium. Phase behaviors were observed straightforwardly through a sapphire window attached to the cell.

Small amount of sample was taken out from the gas phase to analyze equilibrium compositions. In order to confirm the validity of equilibrium compositions obtained from Raman spectroscopic analysis, the mixed-gas hydrates under several three-phase equilibrium conditions were quenched after the free water was removed. The quenched mixed-gas hydrates were melted at room temperature and atmospheric pressure. Equilibrium compositions were analyzed by using TCD-Gas Chromatography (hereafter TCD-GC, Shimadzu GC-7AG). A deviation among the samples was less than 0.01 in the mole fraction of CH_4.

RESULTS AND DISCUSSION

Raman Spectroscopic Analysis

Intramolecular C-F symmetric stretching and C-F symmetric deformation vibration modes of CHF_3 molecules, intramolecular C-H symmetric stretching vibration modes of the CHF_3 and CH_4 molecules were noticed in the present study. Raman intensities of these vibration modes are strong enough to analyze the properties of mixed-gas hydrate sufficiently.

Raman spectrum of the C-F symmetric stretching vibration of the CHF_3 molecules enclathrated in the pure CHF_3 hydrate is shown in Fig. (**1**) ($z_1 = 0.00$). Symbol z_1 stands for the equilibrium composition (on a water free basis) of CH_4 in the hydrate phase. One broad peak was detected at 1128 cm^{-1} in the spectrum. The pure CHF_3 hydrate constructs the s-I hydrate under experimental conditions of the present study [6]. This Raman peak corresponds to the CHF_3 molecule enclathrated in the M-cage. The peak has a broad tail in higher wave-number region, because there is another weak peak originated from intramolecular degenerate stretching vibration mode of CHF_3 molecule.

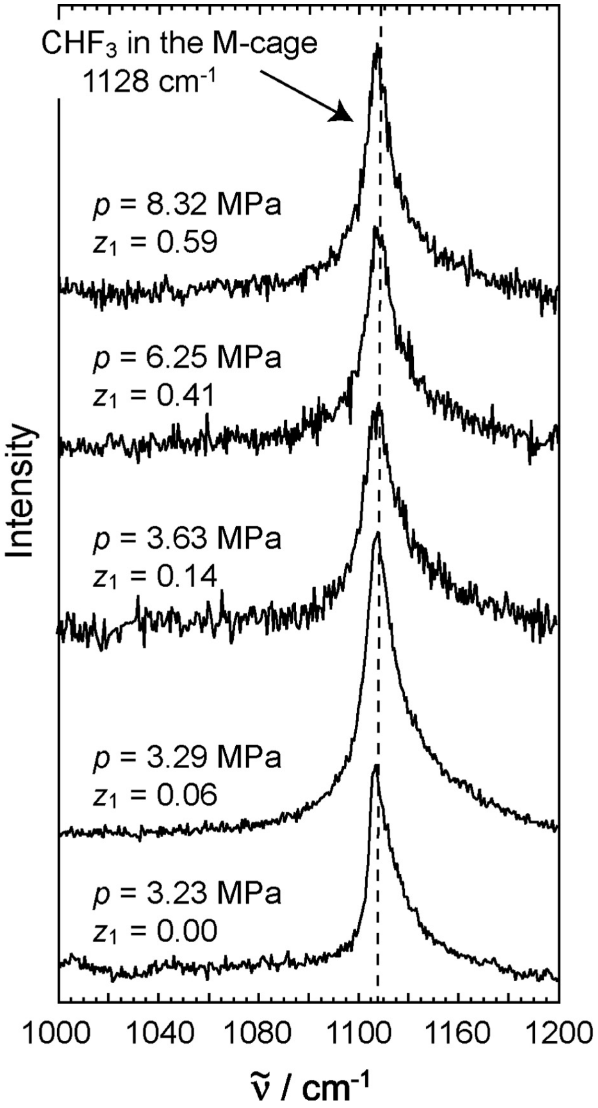

Fig. (1). Raman spectra of the intramolecular C-F symmetric stretching vibration mode of the enclathrated CHF_3 molecule in the pure CHF_3 hydrate or the CH_4 (1) + CHF_3 (2) mixed-gas hydrate under three-phase equilibrium (291.1 K). The symbols p and z stand for the equilibrium pressure and equilibrium composition in hydrate phase.

Raman spectra of the C-F symmetric stretching vibration of CHF_3 molecule enclathrated in the CH_4 + CHF_3 mixed-gas hydrate are also shown in Fig. (**1**). Raman peaks were detected at the same shift as the pure CHF_3 hydrate. This fact means that the mixed-gas hydrate constructs the s-I hydrate and the CHF_3 molecule is encaged in only the M-cage. Similar results were obtained from Raman spectra of the C-F symmetric deformation vibration of the CHF_3 molecules enclathrated in the CH_4 + CHF_3 mixed-gas hydrates shown in Fig. (**2**). The sharp single-peak was detected at 696 cm^{-1} in the whole composition range.

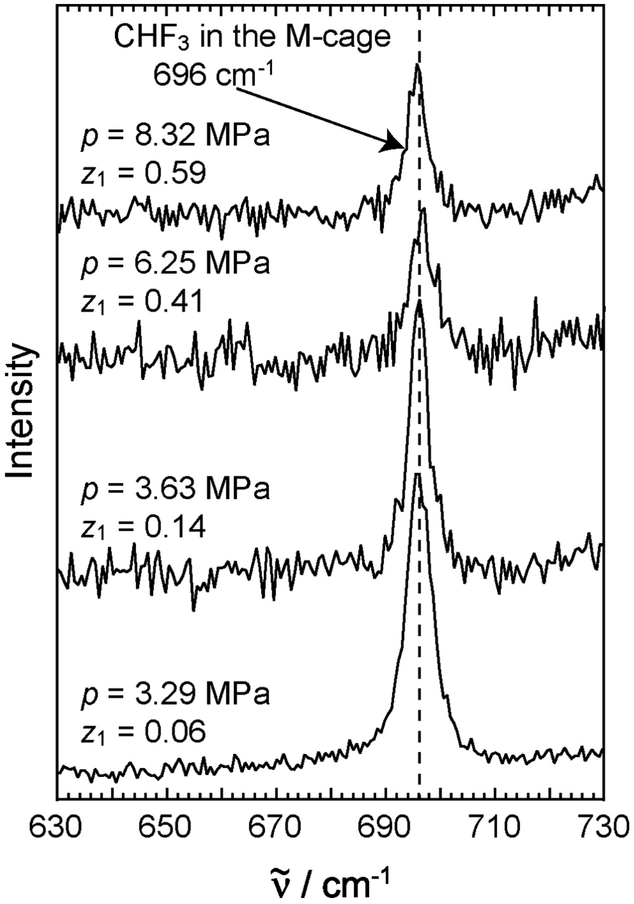

Fig. (2). Raman spectra of the intramolecular C-F symmetric deformation vibration mode of the enclathrated CHF_3 molecule in the CH_4 (1) + CHF_3 (2) mixed-gas hydrate under three-phase equilibrium (291.1 K). The symbols p and z stand for the equilibrium pressure and equilibrium composition in hydrate phase.

Fig. (**3**) shows Raman spectra of the C-H symmetric stretching vibration mode of both guest species enclathrated in the mixed-gas hydrate. Raman peaks detected at 2904 cm^{-1} and 2914 cm^{-1} are derived from the vibration of CH_4 molecule encaged in the M- and S-cages, respectively. The other peak at 3042 cm^{-1} corresponds to the CHF_3 molecule encaged in the M-cage. The CH_4 molecule can occupy both cages, while the CHF_3 molecule cannot occupy the S-cage under the conditions of the present study. Intensities of the Raman peaks of CHF_3 molecule become weaker with the equilibrium composition of CH_4 increasing. While, the intensities of the CH_4 molecules become stronger.

There are no significant differences (beyond Raman spectral resolution) between the positions of Raman peaks in the whole composition range (Figs. (**1**), (**2**), and (**3**)). These results suggest that there is no hydrate-structural transition depending on the composition of guest species and the CH_4+ CHF_3 mixed-gas hydrate constructs only the s-I hydrate at 291.1 K. The present experimental results elucidate directly the generation of s-I hydrate in the whole composition range by Raman spectroscopy.

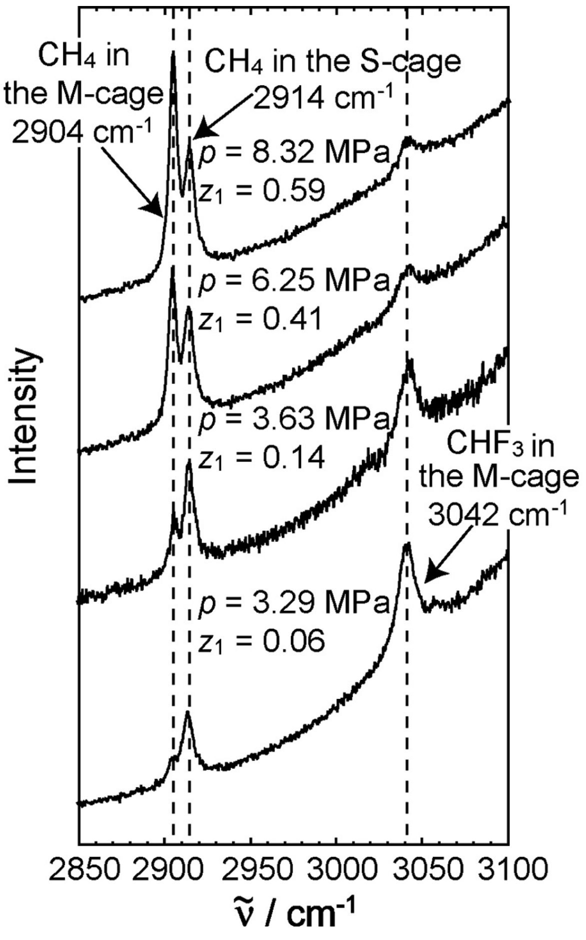

Fig. (3). Raman spectra of the intramolecular C-H symmetric stretching vibration mode of the enclathrated CH_4 and CHF_3 molecules in the CH_4 (1) + CHF_3 (2) mixed-gas hydrate under three-phase equilibrium (291.1 K). The symbols p and z stand for the equilibrium pressure and equilibrium composition in hydrate phase.

Isothermal Phase Equilibria

Fig. (**4**) shows isothermal phase equilibria for the CH_4 + CHF_3 mixed-gas hydrate system at 291.1 K. Open and solid circles correspond to phase equilibrium points of gas phase obtained by means of TCD-GC and Raman spectroscopy, respectively. Phase equilibrium points of hydrate phase measured by using TCD-GC and Raman spectroscopy are shown by open and solid squares. Three-phase equilibrium relations are summarized in Tables **1** and **2**. Symbol y_1 stands for the equilibrium composition (on a water free basis) of CH_4 in gas phase. The equilibrium compositions of gas and hydrate phases are obtained by means of TCD-GC. The Raman peak areas of the C-H symmetric stretching vibration of CH_4 molecule and the C-F symmetric stretching vibration of CHF_3 molecule are used to evaluate the equilibrium compositions of hydrate and gas phases. There are no significant differences between pressure-composition relations obtained from Raman spectroscopic analysis and those of TCD-GC in both gas and hydrate phases.

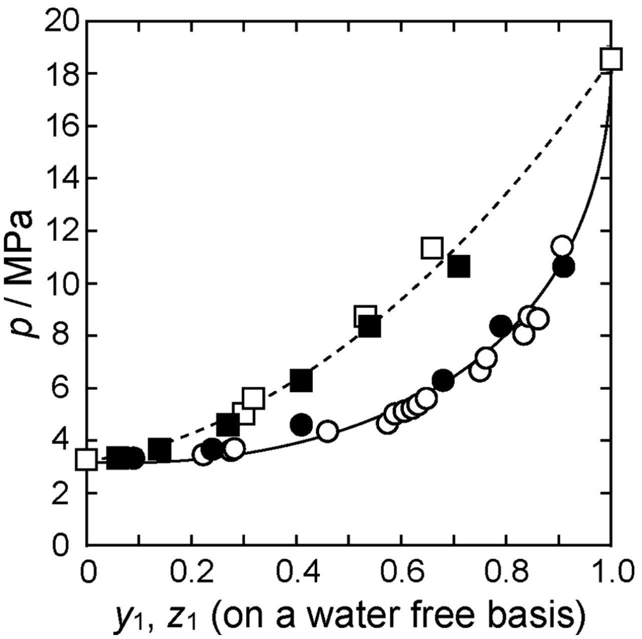

Fig. (4). Isothermal phase equilibria for the CH_4 (1) + CHF_3 (2) mixed gas hydrate system under three-phase equilibrium at 291.1 K. The symbols y and z stand for the equilibrium compositions in gas and hydrate phases. Phase equilibrium data of ○, gas phase obtained by TCD-GC; ● gas phase obtained by Raman spectroscopy; □, hydrate phase obtained by TCD-GC; and ■, hydrate phase obtained by Raman spectroscopy.

Table 1. Isothermal Phase Equilibria for the CH_4 (1) + CHF_3 (2) Mixed Gas Hydrate System Under Three-Phase Equilibrium at 291.1 K (Measured by Means of TCD-GC). The Symbols of p and y Stand for the Equilibrium Pressure and the Equilibrium Composition in the Gas Phase

p / MPa	y_1
3.23	0.000
3.42	0.223
3.58	0.276
3.65	0.282
4.31	0.460
4.62	0.574
5.08	0.606
5.19	0.621
5.33	0.632
6.62	0.750
7.11	0.762
8.02	0.834
8.60	0.861
18.5	1.00

Table 2. Isothermal Phase Equilibria for the CH_4 (1) + CHF_3 (2) Mixed Gas Hydrate System Under Three-Phase Equilibrium States at 291.1 K (Measured by Means of TCD-GC and Raman Spectroscopy). p Corresponds to the Equilibrium Pressure. The Symbols of y and z Stand for the Equilibrium Composition in the Gas and Hydrate Phases, Respectively

p / MPa	y_1	z_1
TCD-GC		
3.23	0.000	0.000
4.97	0.588	0.300
5.57	0.648	0.318
8.69	0.844	0.532
11.3	0.907	0.660
18.5	1.00	1.00
Raman Spectroscopy		
3.29	0.09	0.06
3.63	0.24	0.14
4.56	0.41	0.27
6.25	0.68	0.41
8.32	0.79	0.59
10.6	0.91	0.73

The equilibrium pressures of mixed-gas hydrate exist between those of pure-gas hydrate. Each equilibrium curve does not show abrupt change as observed in the CH_4 + c-C_3H_6 mixed gas hydrate system [2]. The equilibrium curves change continuously in the whole composition range. This also suggests that there is no structural transition depending on the composition of guest species.

Cage Occupancies of Guest Molecules

Cage occupancies of CH_4 molecule were estimated from the Raman peak areas with three assumptions. One is that the CHF_3 molecule cannot occupy the S-cage and the CH_4 molecule can occupy both cages. This is obvious from the Raman spectra obtained in the present study. The second is that all M-cages in the mixed-gas hydrate are always occupied completely by each guest species. This is reasonable because some reports have reported that almost all large cages are occupied by guest species [7,8]. The other is that the Raman cross-section area for CH_4 regardless of M- and S-cages is assumed to be always equal in the present study.

Following equations (1), (2), and (3) are used to estimate the cage occupancies.

$$\theta^{M}_{CH4} + \theta^{M}_{CHF3} = 1 \qquad (1)$$

$$\frac{6\theta^{M}_{CH4}}{2\theta^{S}_{CH4}} = \frac{A_{CH4\ in\ M\text{-}cage}}{A_{CH4\ in\ S\text{-}cage}} \qquad (2)$$

$$z = \frac{2\theta^{S}{}_{CH4} + 6\theta^{M}{}_{CH4}}{2\theta^{S}{}_{CH4} + 6\theta^{M}{}_{CH4} + 6\theta^{M}{}_{CHF3}} \tag{3}$$

The symbols of θ and A stand for the cage occupancies and the Raman peak area, respectively. Superscripts of M and S stand for the hydrate cages, the M- and S-cages. Subscripts of CH_4 and CHF_3 mean the cage occupancies of the CH_4 and CHF_3 molecules, respectively.

Composition dependency of estimated cage occupancies is shown in Fig. (**5**). Open and solid circles stand for estimated cage occupancies of CH_4 for the S- and M-cages, respectively. The cage occupancies of CH_4 molecules increase continuously with z increasing. This also suggests that the CH_4 + CHF_3 mixed-gas hydrates do not construct the s-II hydrates in the whole composition range.

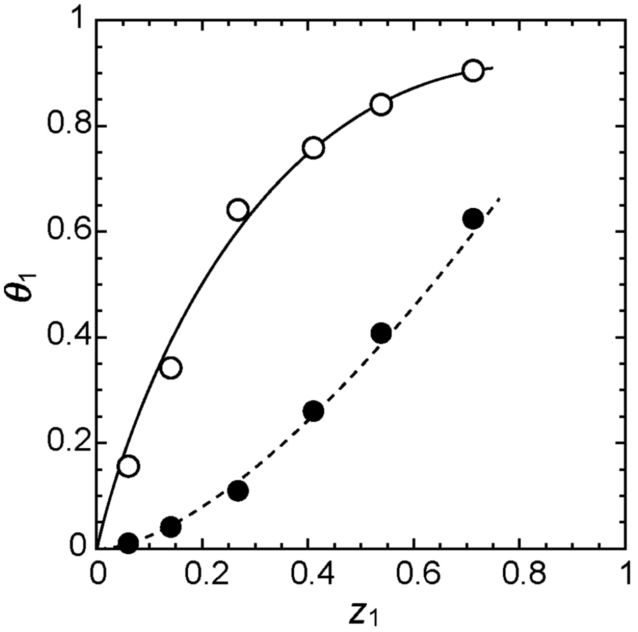

Fig. (5). Composition dependency of the cage occupancies of CH_4 (1) molecule enclathrated in the S- and M-cages. θ and z stand for the cage occupancy and the equilibrium composition in hydrate phase. ○, cage occupancy of CH_4 molecule for the S-cage; ●, cage occupancy of CH_4 molecule for the M-cage.

The cage occupancy of CH_4 molecule for the S-cage is always larger than that of the M-cage at any equilibrium states in the CH_4 + CHF_3 mixed-gas hydrate system at 291.1 K.

CONCLUSIONS

Isothermal phase equilibria for the CH_4 + CHF_3 mixed gas hydrate system were investigated under three-phase equilibrium at 291.1 K. In addition, the single crystals of mixed-gas hydrate were analyzed under three-phase equilibrium by means of Raman spectroscopy.

The isothermal phase equilibrium curves do not show discontinuous change at 291.1 K. The Raman peaks in all vibration modes are detected at the same positions in every Raman spectrum. The cage occupancies of CH_4 molecule for the S- and M-cages change continuously, depending on the equilibrium composition. These results mean that the CH_4 + CHF_3 mixed-gas hydrate constructs the s-I hydrate in the whole composition range at 291.1 K.

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REFERENCES

[1] S. Subramanian, R. A. Kini, S. F. Dec, and E. D. Sloan Jr., "Evidence of structure II hydrate formation from methane + ethane mixtures", *Chem. Eng. Sci.*, vol. 55, pp. 1981-1999, June 2000.

[2] T. Makino, M. Tongu, T. Sugahara, and K. Ohgaki, "Hydrate structural transition depending on the composition of methane + cyclopropane mixed gas hydrate", *Fluid Phase Equilibria*, vol. 233, pp. 129-133, June 2005.

[3] J. A. Ripmeester, "Hydrate research - from correlations to a knowledge - based discipline", *Annals N Y Acad Sci.*, vol. 912, pp. 1-16, June 2000.

[4] T. Sugahara, T. Makino, and K. Ohgaki, "Isothermal phase equilibria for the methane + ethylene mixed gas hydrate system", *Fluid Phase Equilibria*, vol. 206, pp. 117-126, April 2003.

[5] M. M. Mooijer-van den Heuvel, N. M. Sawirjo, and C. J. Peters, "Influence of fluoroalkanes on the phase behaviour of methane gas hydrate systems", *Fluid Phase Equilibria*, vol. 241, pp. 124-137, March 2006.

[6] E. Berecz, and M. Balla-Achs, *Gas Hydrates: Studies in Inorganic Chemistry*, Amsterdam: Elsevier, 1983.

[7] K. A. Udachin, C. I. Ratcliffe, and J. A. Ripmeester, "Single crystals diffraction studies of structure I, II and h hydrates: structure, cage occupancy and composition", *J. Supramol. Chem.*, vol. 2, pp. 405-408, August-October 2002.

[8] A. K. Sum, R. C. Burruss, and E. D. Sloan Jr., "Measurement of clathrate hydrate via raman spectroscopy", *J. Phys. Chem. B*, vol. 101, pp. 7371-7377, September 1997.

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