Thermodynamic Stability of H_2 + Tetrahydrofuran Mixed Gas Hydrate in Nonstoichiometric Aqueous Solutions

Shunsuke Hashimoto, Takeshi Sugahara, Hiroshi Sato, and Kazunari Ohgaki*

Division of Chemical Engineering, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan

Phase equilibria (pressure−temperature relations) of the H_2 + tetrahydrofuran mixed gas hydrate system have been measured for various concentrations of tetrahydrofuran aqueous solutions. The three-phase equilibrium lines obtained in the present study are shifted to the low-temperature or high-pressure side from that of the stoichiometric THF solution. Each three-phase equilibrium line of H_2 + tetrahydrofuran hydrate converges at the three-phase equilibrium line of the pure tetrahydrofuran hydrate. At the cross point on the lines, the tetrahydrofuran concentration of mother aqueous solution agrees with each other. The Raman spectra of H_2 and tetrahydrofuran for the H_2 + tetrahydrofuran mixed gas hydrate do not change with the variation of tetrahydrofuran mole fraction from 0.010 to 0.130 in the aqueous solution.

Introduction

The storage and transportation of H_2 are one of the most important techniques for developing a new society sustained by H_2 energies. Recently, gas hydrates have become the object of much attention as a medium for H_2 storage and transportation. It is well-known that the pure H_2 hydrate is generated only in extremely high-pressure regions.[1,2] In order to depress the equilibrium pressure of H_2-containing hydrate, the addition of other guest species is regarded as the most likely method. Tetrahydrofuran (THF) is one of the additives that is able to decrease the equilibrium pressure of pure gas hydrates. For example, a large depression of equilibrium pressure has been observed in the N_2 + THF mixed gas hydrate, and the depression degree depends on the THF concentration of mother aqueous solutions.[3]

Florusse et al.[4] have first reported that H_2 can be entrapped by hydrate cages with the existence of THF at low pressures. They have also revealed that H_2 + THF mixed gas hydrate has a structure-II hydrate crystal structure by X-ray diffraction measurement. In addition, Lee et al.[5] have investigated the binary-mixed gas hydrate containing H_2 + THF at various THF concentrations by use of nuclear magnetic resonance (NMR). They have claimed that the H_2 molecule can occupy the L-cage (hexakaidecahedron, $5^{12}6^4$) as well as the S-cage (dodecahedron, 5^{12}) at THF mole fractions lower than 0.020 and that THF occupies the L-cage completely and H_2 is entrapped by only the S-cage in the THF mole fraction region higher than 0.020. Recently, Strobel et al.[6] have reported that the cage occupancy of H_2 is independent of the THF concentration in the mole fraction range lower than 0.056 based on gas release data and that H_2 does not occupy the L-cage. The results about the L-cage occupancy of H_2 of Strobel et al.[6] are inconsistent with those of Lee et al.[5] In order to reveal the storage capacity of H_2, it is necessary to investigate the cage occupancy of H_2 by spectroscopic method other than NMR. Furthermore, the variation of the THF concentration results in the change of the phase

equilibrium relation for mixed hydrate containing THF. For example, it is well-known that phase equilibrium lines for the N_2 + THF mixed gas hydrate in non-stoichiometric THF concentration are shifted to a high-pressure or low-temperature condition as compared with those of stoichiometric concentration.[3] Considering this tendency in the N_2 + THF mixed gas hydrate system, the thermodynamic stability boundary of H_2 + THF mixed gas hydrate in non-stoichiometric THF concentration would be also shifted to a high-pressure or low-temperature condition. Therefore, it is necessary to determine both the phase behavior and cage occupancy of H_2 in the H_2 + THF mixed gas hydrate system simultaneously for H_2 storage using gas hydrates.

In the present study, phase equilibria for the H_2 + THF + water ternary mixture at various THF concentrations have been measured in order to investigate the effect of THF concentration. In addition, the cage occupancies of H_2 and THF in the mixed gas hydrate under three-phase equilibrium states have been measured by use of in situ Raman spectroscopy.

Experimental Section

Materials. Research grade H_2 (mole fraction purity 0.999999) was obtained from the Neriki Gas Co., Ltd. The maximum impurity was 0.2 ppm of nitrogen. Research grade THF (mole fraction purity 0.997) was obtained from Yashima Pure Chemicals Co., Ltd. The distilled water was obtained from the Yashima Pure Chemicals Co., Ltd. All of them were used without further purifications.

Apparatus. The experimental apparatus for the phase equilibrium measurements is the same as the previous one[7] except for the introducing line for the aqueous solution. The inner volume and maximum working pressure of the high-pressure cell were 150 cm³ and 10 MPa, respectively. The cell had a set of windows for visually observing the phase behavior. All parts of the high-pressure cell were immersed in a temperature-controlled water bath. The contents were agitated using an up-and-down mixing bar driven by an exterior permanent magnetic ring.

* Corresponding author. Phone: +81-6-6850-6290. Fax: +81-6-6850-6290. E-mail: ohgaki@cheng.es.osaka-u.ac.jp.

Table 1. Phase Equilibrium Data for H_2 + THF + Water Mixed System in the Presence of Gas Hydrate at THF Mole Fraction of 0.010, 0.024, and 0.130[a]

T/K	p/MPa	T/K	p/MPa
x = 0.010		x = 0.130	
273.86	4.86	276.23	0.09
274.08	5.43	276.30	0.42
274.36	6.02	276.42	0.70
274.42	6.36	276.53	1.01
274.68	6.83	276.74	1.55
274.94	7.36	276.91	2.01
275.11	7.86	277.25	2.61
275.29	8.33	277.54	3.24
275.56	8.88	277.87	4.31
275.69	9.38	278.26	5.37
275.91	9.73	278.79	6.74
276.26	11.0	279.15	7.64
277.36	13.8	279.55	8.56
x = 0.024		279.81	9.60
275.86	0.11	280.28	11.2
276.03	0.38	280.41	12.5
276.13	0.70		
276.21	0.90		
276.45	1.48		
276.68	2.09		
276.90	2.59		
277.13	3.34		
277.63	4.92		
278.50	7.15		
279.08	8.94		

[a] x represents the composition of THF aqueous solution.

The high-pressure optical cell for the Raman spectroscopic analysis had a pair of quartz (highly pure) windows on both the upper and lower sides. This high-pressure optical cell is the same as previous one[8] except for the window material. The thermostated water was circulated constantly in the exterior jacket of the high-pressure optical cell. A ruby ball was enclosed into the high-pressure optical cell. The contents were agitated by the ruby ball, which is rolled around by the vibration of vibrator from outside.

The system temperature was measured within an uncertainty of 0.02 K using a thermistor probe (Takara D-632), which was inserted into a hole in the cell wall. The probe was calibrated with a Pt resistance thermometer. The system pressure was measured by a pressure gauge (Valcom VPRT) calibrated by RUSKA quartz Bourdon tube gauge with an estimated maximum uncertainty of 0.01 MPa.

Procedures. The THF aqueous solution prepared at a desired mole fraction of 0.010, 0.024, or 0.130 was introduced into the evacuated high-pressure cell. The content was pressurized up to the desired pressure by supplying H_2. In the present study, we have adopted the method similar to the "T-cycle method[9]" for the three-phase equilibrium measurement. At first, the system temperature was decreased and kept constant at the point of pressure depression, which was caused by the H_2 + THF mixed gas hydrate formation (the formation can be confirmed through the window of the cell). We cannot directly measure the equilibrium composition of aqueous phase under the coexistence of the gas hydrate phase. Therefore, the content was heated very gradually and step by step (0.1 K each) until there was a negligibly small amount of gas hydrate left in order to minimize change of THF concentration in the aqueous solution. The interval time was taken adequately (at least 1 day) for establishing equilibrium state at each temperature step. When the last particle of hydrates disappeared on gradually heating, we adopted this point as the equilibrium point. In order to eliminate a hysterisis effect, we have used the annealing method (0.05 K one cycle per day) in addition to the "T-cycle method[9]". We
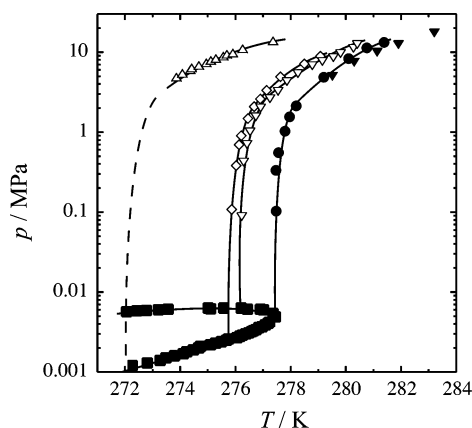
Figure 1. Three-phase equilibrium curves of the H_2 + THF mixed gas hydrate; ■, pure THF hydrate;[11] ▼, x = 0.056;[4] ●, x = 0.056;[15] △, x = 0.010; ◇, x = 0.024; ▽, x = 0.130. The solid lines are fitting lines for experimental data, and the broken line is an extrapolated line on the assumption that the three-phase equilibrium line for the THF mole fraction of 0.010 has a similar behavior as the other lines.

never fail to repeat several times the T-cycle and annealing methods. In addition, we also repeated the same equilibrium measurements using the fresh THF solution at the same THF mole fraction.

The single crystal of gas hydrate prepared from the H_2 + THF + water mixtures was analyzed through a quartz window by in situ Raman spectroscopy using a laser Raman microprobe spectrophotometer with multichannel CCD detector. The argon ion laser beam (wavelength, 514.5 nm; power, 100 mW) from the object lens was irradiated to the sample through the upper quartz window. The backscatter of the opposite direction was taken in with the same lens. The spectral resolution was about 1 cm^{-1}.

Results and Discussion

Phase equilibria for the H_2 + THF mixed gas hydrate systems at various THF concentrations are summarized in Table 1 and shown in Figure 1. The mole fractions of THF (x) in the aqueous solutions are 0.010, 0.024, and 0.130. Figure 1 contains the three-phase equilibrium diagram for the H_2 + THF mixed gas hydrate[4,15] at x = 0.056, which is the stoichiometric concentration of the pure THF hydrate.[10,11] The three-phase equilibrium lines of H_2 + THF mixed gas hydrate, which were obtained from the THF aqueous solution of x = 0.024 and 0.130, converge at each equilibrium point of pure THF hydrate prepared from the same mole fraction solution, (275.73 K, 2.6 kPa) and (276.21 K, 6.3 kPa),[11] respectively. Each equilibrium line vertically rises up in the pressure up to about 3 MPa, which may be attributed to the hydrogen content in the hydrate. Each three-phase equilibrium pressure increases continuously with the temperature increase. The quadruple point of gas, aqueous solution, ice, and hydrate phases for the THF + water mixed system is located at x = 0.0106, 272.06 K, and 1.1 kPa.[11] The three-phase equilibrium line of H_2 + THF mixed gas hydrate of x = 0.010 would converge at the vicinity of the above quadruple point as well as those of x = 0.024, 0.056, and 0.130.

In the present study, the Raman spectra of single crystals for H_2 + THF mixed gas hydrate were measured under the three-phase equilibrium state. Figure 2 shows a single crystal of H_2 + THF mixed gas hydrate at x = 0.010. The Raman spectra obtained in the present study are shown in Figures 3 and 4. As shown in Figure 3, the Raman peaks of (919 and 1033) cm^{-1} in the hydrate phase are derived from the enclathrated THF molecule.[12,13] In addition, the Raman peaks corresponding to
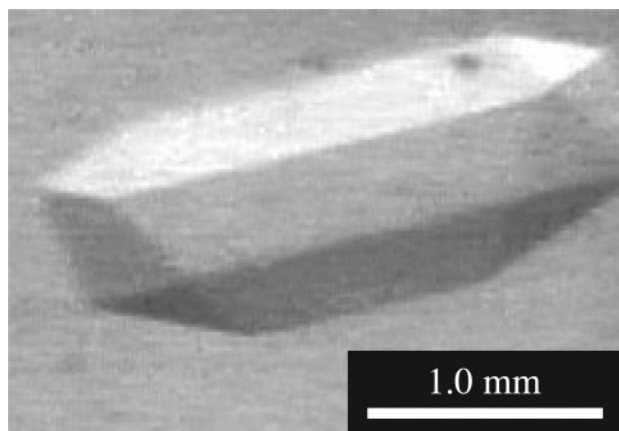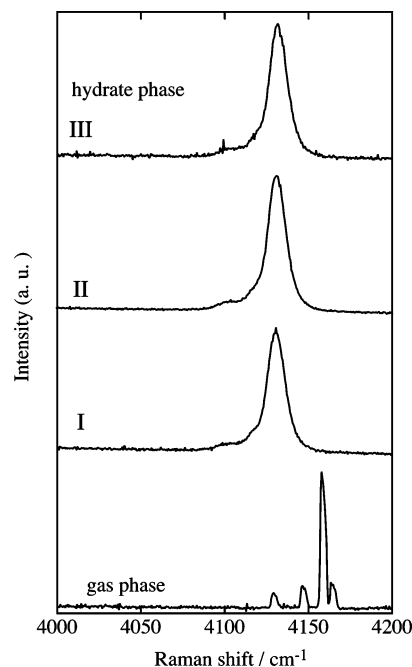
Figure 2. Photo of a hydrate single crystal for the H_2 + THF mixed gas hydrate at $x = 0.010$.
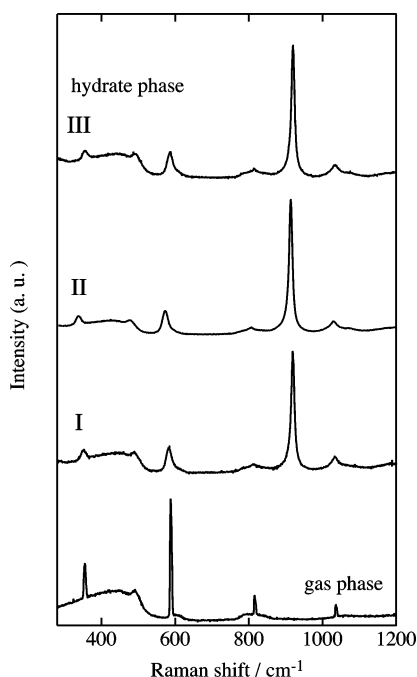
Figure 3. Raman spectra of the intramolecular vibration for THF in the gas and hydrate phases at various THF mole fractions. Contains the spectra corresponding to the rotation of H_2. In the hydrate phase, I: $x = 0.010$, 276.26 K, 11.0 MPa; II: $x = 0.056$, 280.80 K, 11.3 MPa;[15] III: $x = 0.130$, 280.28 K, 11.2 MPa. The broad signals that appear in lower than 520 cm^{-1} and at (600, 810, and 1060) cm^{-1} correspond to the quartz windows of high-pressure optical cell.

the rotation modes of the H_2 molecule[14] are detected at (354, 588, 817, and 1036) cm^{-1} in the gas phase, while they are detected at (351, 583, and 814) cm^{-1} in the hydrate phase. In the hydrate phase, the peak of H_2 rotation around 1036 cm^{-1} overlaps with that of THF. As shown in Figure 4, the peaks corresponding to the H−H stretching vibration of H_2 are detected at (4129, 4146, 4159, and 4165) cm^{-1} in the gas phase, while a broad and single peak is detected at 4131 cm^{-1} in the hydrate phase. The position and shape of all peaks derived from H_2 obtained in the present study agree well with those of H_2 + THF mixed gas hydrate at the stoichiometric THF concentration.[15] There is no remarkable change of Raman spectrum with the variations of THF concentration. Therefore, the cage occupancies of H_2 + THF mixed gas hydrate are independent of THF concentrations in the aqueous solutions under the present experimental condition. That is, the THF molecule occupies the L-cage completely while the H_2 selectively occupies the S-cage

Figure 4. Raman spectra of the intramolecular vibration for H_2 in the gas and hydrate phases at various THF mole fractions. In the hydrate phase, I: $x = 0.010$, 276.26 K, 11.0 MPa; II: $x = 0.056$, 280.80 K, 11.3 MPa;[15] III: $x = 0.130$, 280.28 K, 11.2 MPa.

of structure-II hydrate. The results obtained in the present study are consistent with those of Strobel et al.[6] on the point that the H_2 molecule cannot occupy the L-cage for the H_2 + THF mixed gas hydrate.

Conclusion

Phase equilibria for the H_2 + THF + water mixed system at the various mole fractions of THF from 0.010 to 0.130 were measured. The three-phase (hydrate + aqueous solution + gas) equilibrium lines of the H_2 + THF mixed gas hydrate converge at the equilibrium point of pure THF hydrate prepared from the same THF aqueous solution. From Raman spectroscopy for the single crystal of H_2 + THF mixed gas hydrate, it is concluded that the S- and L-cages are selectively occupied by H_2 and THF in the THF mole fraction range from 0.010 to 0.130, respectively.

Literature Cited

(1) Dyadin, Y. A.; Larionov, E. G.; Aladko, E. Y.; Manakov, A. Y.; Zhurko, F. V.; Mikina, T. V.; Komarov, V. Y.; Grachev, E. V. Clathrate formation in water−noble gas (hydrogen) systems at high pressures. *J. Struct. Chem.* **1999**, *40*, 790−795.

(2) Mao, W. L.; Mao, H.; Goncharov, A. F.; Struzhkin, V. V.; Guo, Q.; Hu, J.; Shu, J.; Hemley, R. J.; Somayazulu, M.; Zhao, Y. Hydrogen clusters in clathrate hydrate. *Science* **2002**, *297*, 2247−2249.

(3) Seo, Y.-T.; Kang, S.-P.; Lee, H. Experimental determination and thermodynamic modeling of methane and nitrogen hydrates in the presence of THF, propylene oxide, 1,4-dioxane and acetone. *Fluid Phase Equilib.* **2001**, *189*, 99−110.

(4) Florusse, L. J.; Peters, C. J.; Schoonman, J.; Hester, K. C.; Koh, C. A.; Dec, S. F.; Marsh, K. N.; Sloan, E. D. Stable low-pressure hydrogen clusters stored in a binary clathrate hydrate. *Science* **2004**, *306*, 469−471.

(5) Lee, H.; Lee, J.-W.; Kim, D. Y.; Park, J.; Seo, Y.-T.; Zeng, H.; Moudrakovski, I. L.; Ratcliffe, C. I.; Ripmeester, J. A. Tuning clathrate hydrates for hydrogen storage. *Nature* **2005**, *434*, 743−746.

(6) Strobel, T. A.; Taylor, C. J.; Hester, K. C.; Dec, S. F.; Koh, C. A.; Miller, K. T.; Sloan, E. D., Jr. Molecular hydrogen storage in binary THF-H$_2$ clathrate hydrates. *J. Phys. Chem. B* **2006**, *110*, 17121−17125.

(7) Sugahara, T.; Murayama, S.; Hashimoto, S.; Ohgaki, K. Phase equilibria for H$_2$ + CO$_2$ + H$_2$O system containing gas hydrates. *Fluid Phase Equilib.* **2005**, *233*, 190−193.

(8) Nakano, S.; Moritoki, M.; Ohgaki, K. High-pressure phase equilibrium and Raman microprobe spectroscopic studies on the CO$_2$ hydrate system. *J. Chem. Eng. Data* **1998**, *43*, 807−810.

(9) Ohgaki, K.; Makihara, Y.; Takano, K. Formation of CO$_2$ hydrate in pure and sea waters. *J. Chem. Eng. Jpn.* **1993**, *26*, 558−564.

(10) Gough, S. R.; Davidson, D. W. Composition of tetrahydrofuran hydrate and the effect of pressure on the decomposition. *Can. J. Chem.* **1971**, *49*, 2691−2699.

(11) Makino, T.; Sugahara, T.; Ohgaki, K. Stability boundaries of tetrahydrofuran + water system. *J. Chem. Eng. Data* **2005**, *50*, 2058−2060.

(12) Manakov, A. Y.; Goryainov, S. V.; Kurnosov, A. V.; Likhacheva, A. Y.; Dyadin, Y. A.; Larionov, E. G. Clathrate nature of the high-pressure tetrahydrofuran hydrate phase and some new data on the phase diagram of the tetrahydrofuran−water system at pressures up to 3 GPa. *J. Phys. Chem. B* **2003**, *107*, 7861−7866.

(13) Tulk, C. A.; Klug, D. D.; Ripmeester, J. A. Raman spectroscopic studies of THF clathrate hydrate. *J. Phys. Chem. A* **1998**, *102*, 8734−8739.

(14) Fink, U.; Wiggins, T. A.; Rank, D. H. Frequency and intensity measurements on the quadrupole spectrum of molecular hydrogen. *J. Mol. Spectrosc.* **1965**, *18*, 384−395.

(15) Hashimoto, S.; Murayama, S.; Sugahara, T.; Sato, H.; Ohgaki, K. Thermodynamic and Raman spectroscopic studies on H$_2$ + tetrahydrofuran + water and H$_2$ + tetra-*n*-butyl ammonium bromide + water mixtures containing gas hydrates. *Chem. Eng. Sci.* **2006**, *61*, 7884−7888.