Thermodynamic Stability of Mixed Gas Hydrates Containing Hydrogen

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Abstract. Phase equilibrium curves of H₂ + tetrahydrofuran and H₂ + tetra-n-butyl ammonium bromide mixed gas hydrates were measured. Each three-phase equilibrium curve converges at three-phase equilibrium point of pure tetrahydrofuran and tetra-n-butyl ammonium bromide hydrates, respectively. It is directly confirmed by use of Raman spectroscopy that H₂ is enclathrated in the hydrate cages by adding a small amount of tetrahydrofuran or tetra-n-butyl ammonium bromide. In both mixed gas hydrates, H₂ is selectively enclathrated in the small cage despite the concentrations of aqueous solution.

1. Introduction

H₂ has become the object of attention as a clean and promising energy resource. Recently, H₂ hydrate has been considered as a medium of H₂ storage and transportation. However, the pure H₂ hydrate is generated only in extremely high-pressure region of 100-360 MPa [1]. Mao et al. [2] and Mao and Mao [3] reveal that H₂ + H₂O mixtures generate the structure-II (s-II) hydrate at high pressure of 200 MPa and low temperature of ca. 80 K, where the hydrate cages are multiply occupied by two H₂ molecules in the S-cage and four in the L-cage. Much milder conditions are desired to utilize H₂ hydrate as a medium of H₂ storage and transportation.

Tetrahydrofuran (hereafter, THF), well known as a common solvent, generates s-II hydrate [4] below atmospheric pressures. THF can be enclathrated in the L-cage while it cannot occupy the S-cage [5]. THF has been widely used as an additive that would reduce the equilibrium pressure of other gas hydrates. Furthermore, the effect of THF was the highest among several additives [6, 7]. Florusse et al. [8] have reported the first results that the clusters of H₂ can be stabilized and stored at low pressures in the s-II THF hydrate. According to Florusse et al. [8], Lee et al. [9], and Strobel et al. [10], one or two H₂ molecules are enclathrated in the S-cage and one THF molecule in the L-cage. Lee et al. [9] have claimed that the H₂ molecule can occupy the L-cage as well as the S-cage at low THF mole fraction region. On the other hand, Strobel et al. [10] have reported that the cage occupancy of H₂ is independent of the THF concentration and H₂ never occupies the L-cage in low mole fraction region. Therefore, the cage occupancy of H₂ for H₂ + THF mixed gas hydrate is still unclear. Shimada et al. [12] have reported that isobaric phase equilibrium (T-x) relations for the tetra-n-butyl ammonium bromide (hereafter, TBAB) hydrate have the maximum temperature point (285.15 K) at atmospheric pressure with 40.5 wt% (3.7 mol%) water solution (the structure of TBAB hydrate is considered to be less certain, therefore, described as Type A). TBAB hydrate is a semi-clathrate hydrate where TBAB
is incorporated with the water molecules to construct the hydrate cage. TBAB hydrate also has some empty S-cages [12], which is similar to THF hydrate. It has been reported that H₂ can be entrapped with hydrate cages of TBAB hydrate [13, 14]. In order to reveal the cage occupancy of H₂, it is necessary to investigate the composition effect on the thermodynamic stability and cage occupancy of H₂ for H₂-containing mixed gas hydrate.

In the present study, thermodynamic stabilities of H₂ + THF and H₂ + TBAB hydrates were measured. In addition, Raman spectra for each single crystal of H₂ + THF and H₂ + TBAB hydrates were measured under the three-phase coexisting conditions. Both measurements were performed for the several concentrations of THF or TBAB aqueous solutions.

2. Experimental Section

2.1. Materials
Research grade H₂ of mole fraction purity 99.9999 % was obtained from the Neriki Gas Co., Ltd. The maximum impurity was 0.2 ppm of nitrogen. Research grade THF of mole fraction purity 99.7 % was obtained from Merck, Ltd., Japan. Research grade TBAB of mole fraction purity 98.0 % (a major impurity is H₂O) was obtained from Wako Pure Chemical Industries, Ltd. The distilled water was obtained from the Wako Pure Chemical Industries, Ltd. All of them were used without further purifications.

2.2. Experimental apparatus and procedures
The experimental apparatus for the phase equilibrium measurements is the same as the previous one [15] except for the introducing line for the THF or TBAB aqueous solution under the conditions of three-phase (the aqueous solution, gas phase, and hydrate phase) coexisting. The inner volume and maximum working pressure of high-pressure cell were 150 cm³ and 10 MPa, respectively. The cell had a set of windows for visually observing the phase behavior in the high-pressure cell. All of them 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. 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 [16] except for the window material. The thermostated water was circulated constantly in the exterior jacket of high-pressure optical cell. A ruby ball was enclosed to agitate the contents by the vibration from outside. The system temperature was measured within a reproducibility 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 the pressure gauge (Valcom VPRT) calibrated by RUSKA quartz Bourdon tube gauge with an estimated maximum uncertainty of 0.01 MPa.

Either THF or TBAB aqueous solution prepared at a desired mole fraction (x) was introduced into the evacuated high-pressure cell. The contents were pressurized up to a desired pressure by supplying H₂ and then continuously agitated by a mixing bar. At first, the system temperature was decreased and kept constant at the point of pressure depression which is caused by 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 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 or TBAB concentration in the aqueous solution. When the last particle of hydrates disappeared on gradually heating, we adopted this point as the equilibrium point. The single crystal of gas hydrate prepared from the mixtures of H₂ + THF solution and H₂ + TBAB solution 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.
3. Results & Discussion
Phase equilibria of the H$_2$ + THF and H$_2$ + TBAB mixed gas hydrate systems for various concentrations of aqueous solutions are shown in Fig. 1. The stoichiometric concentration of the pure THF and TBAB hydrates is $x = 0.056$ and $x = 0.037$, respectively [11, 12]. The three-phase equilibrium curve of pure THF hydrate has a maximum temperature point at 277.45 K and 4.9 kPa [11]. The three-phase equilibrium curve of H$_2$ + THF hydrate, which is prepared from the THF stoichiometric aqueous solution, converges at the maximum temperature point. The equilibrium curve vertically rises up in the pressure range up to 3 MPa, which may be attributed to the hydrogen content in the hydrate. In the high-pressure region, the equilibrium curve agrees well with that of Florusse et al. [8]. The other three-phase equilibrium curves converge at each equilibrium point of pure THF hydrate prepared from the same mole fraction solution. They exhibit similar behavior to that of stoichiometric aqueous solution. Each three-phase equilibrium pressure increases continuously with the temperature increasing. The equilibrium temperature for the pure TBAB hydrate of stoichiometric mole fraction at atmospheric pressure is 285.15 K [12]. The three-phase equilibrium curves of H$_2$ + TBAB mixed gas hydrate are similar to those of H$_2$ + THF mixed gas hydrate, while the three-phase equilibrium curve of H$_2$ + TBAB mixed gas hydrate shifts to the higher temperature of about 8 K than that of H$_2$ + THF mixed gas hydrate.

In the present study, Raman spectroscopic measurements were carried out for each single crystal of H$_2$ + THF and H$_2$ + TBAB mixed hydrates at the various mole fractions of aqueous solution. The results are shown in Fig. 2. The experimental pressure range is from 11.0 to 14.0 MPa. The Raman spectra corresponding to the intramolecular vibration of H$_2$ and THF for various THF concentration in the aqueous solution are shown in Fig. 2(a) and (b). In the hydrate phase, the Raman peaks are detected at 919 and 1033 cm$^{-1}$, which correspond to the enclathrated THF molecules [17, 18]. On the other hand, the three peaks are detected at 883, 920, and 1036 cm$^{-1}$ in the aqueous phase. The THF molecule was hydrogen-bonded with H$_2$O. The peak of 883 cm$^{-1}$ corresponds to the C-O-C stretching vibration mode [8]. In the gas phase, four peaks corresponding to the rotation of H$_2$ molecules are observed at 354, 588, 816, and 1036 cm$^{-1}$, which are consistent with the reference data [19]. They are slightly shifted to 351, 584, and 814 cm$^{-1}$ in the hydrate phase. The peak detected around 1036 cm$^{-1}$

![Figure 1](image_url)
overlaps with that of THF. As shown in Fig. 2(b), four peaks corresponding to the H-H stretching vibration mode are detected at 4128, 4146, 4158, and 4165 cm$^{-1}$ in the gas phase, while a broad single peak is detected at 4139 and 4131 cm$^{-1}$ in the aqueous and hydrate phases, respectively. The Raman spectra in the present study are consistent with those of Florusse et al. [8]. On the other hand, our data are not consistent with the Raman spectra of H$_2$ in the S-cage measured by Mao et al. [2]. In the present experimental conditions, it is suggested that not a bimolecular cluster of H$_2$ but an H$_2$ molecule is entrapped by only the S-cage, and THF occupies the L-cage of s-II hydrate. In addition, the position and shape of all peaks derived from H$_2$ agree well with those of H$_2$ + THF mixed gas hydrate at the stoichiometric THF concentration. 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$_2$ occupies the S-cage of s-II hydrate. The results obtained in the present study are consistent with those of Strobel et al. [10] on the point that H$_2$ molecule cannot occupy the L-cage for the H$_2$ + THF mixed gas hydrate. Figure 2(c) shows the Raman spectra of H$_2$ for H$_2$ + TBAB mixed hydrate at the various mole fractions of TBAB. The experimental pressure range is from 12.0 to 14.0 MPa. In the H$_2$ + TBAB + water mixed system, four peaks corresponding to the H-H stretching vibration mode are observed at 4130, 4147, 4159, and 4166 cm$^{-1}$ in the gas phase. In the aqueous and hydrate phases, a broad single peak is detected at 4140

Figure 2. Raman spectra of the intramolecular vibration for THF (a) and H$_2$ (b) in the H$_2$ + THF mixed gas hydrates, and H$_2$ (c) in the H$_2$ + TBAB mixed gas hydrates at various mole fractions of aqueous solutions. Panel (a) contains the spectra corresponding to the rotation of H$_2$. The broad signals which 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.
and 4132 cm⁻¹, respectively. In addition, no peak is detected around 4100 cm⁻¹ from the pure TBAB hydrate. It is suggested that the H₂ molecules are entrapped in the empty S-cages of TBAB hydrate. In addition, there is no remarkable change of Raman spectrum with the variations of TBAB concentration, which is similar to the results of H₂ + THF mixed gas hydrate. That is, H₂ would occupy the S-cage of TBAB semi-clathrate hydrate.

4. Conclusion
Phase equilibria for the H₂ + THF + water and H₂ + TBAB + water ternary systems were measured at the various mole fractions of aqueous solution. Each three-phase equilibrium curve of H₂ + THF hydrate converges at the three-phase equilibrium point of pure THF hydrate. The three-phase equilibrium curves of H₂ + TBAB mixed gas hydrate are similar to those of H₂ + THF hydrate, while they lie at about 8 K higher temperature than those of H₂ + THF hydrate. The Raman spectra in the single crystal for these mixed systems reveal that the H₂ molecule occupies the S-cage separately. The cage occupancy of H₂ molecule in these mixed gas hydrates does not depend on the variation of mole fraction in aqueous solutions.

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References
[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. 1999 J. Struct. Chem. 40 790-95.
[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. 2002 Science 297 2247-49.
[3] Mao, W. L.; Mao, H. 2004 Proc. Nat. Acad. Sci. USA 101 708-10.
[4] Hawkins, R. E.; Davidson, D. W. 1966 J. Phys. Chem. 70 1889-94.
[5] Gough, S. R.; Davidson, D. W. 1971 Can. J. Chem. 49 2691-99.
[6] Kang, S. -P.; Lee, H.; Lee, C. -S.; Sung, W. -M. 2001 Fluid Phase Equilib. 185 101-09.
[7] Seo, Y. -T.; Kang, S. -P.; Lee, H. 2001 Fluid Phase Equilib. 189 99-110.
[8] Florusse, L. J.; Peters, C. J.; Schoonman, J.; Hester, K. C.; Koh, C. A.; Dec, S. F.; Marsh, K. N.; Sloan, E. D. 2004 Science 306 469-71.
[9] Lee, H.; Lee, J. -W.; Kim, D. Y.; Park, J.; Seo, Y. -T.; Zeng, H.; Moudrakovski, I. L.; Ratcliffe, C. I.; Ripmeester, J. A. 2005 Nature 434 743-46.
[10] Strobel, T. A.; Taylor, C. J.; Hester, K. C.; Dec, S. F.; Koh, C. A.; Miller, K. T.; Sloan, E. D., Jr. 2006 J. Phys. Chem. B 110 17121-25.
[11] Makino, T.; Sugahara, T.; Ohgaki, K. 2005 J. Chem. Eng. Data 50 2058-60.
[12] Shimada, W.; Ebinuma, T.; Oyama, H.; Kamata, Y.; Takeya, S.; Uchida, T.; Nagao, J.; Narita, H. 2003 Japanese J. Appl. Phys. 42 129-31.
[13] Hashimoto, S.; Murayama, S.; Sugahara, T.; Sato, H.; Ohgaki, K. 2006 Chem. Eng. Sci. 61 7884-88.
[14] Chapoy, A.; Anderson, R.; Tohidi, B. 2007 J. Am. Chem. Soc. 129 746-47.
[15] Sugahara, T.; Murayama, S.; Hashimoto, S.; Ohgaki, K. 2005 Fluid Phase Equilib. 233 190-93.
[16] Nakano, S.; Moritoki, M.; Ohgaki, K. 1998 J. Chem. Eng. Data 43 807-10.
[17] Tulk, C. A.; Klug, D. D.; Ripmeester, J. A. 1998 J. Phys. Chem. A 102 8734-39.
[18] Manakov, A. Y.; Goryainov, S. V.; Kurnosov, A. V.; Likhacheva, A. Y.; Dyadin, Y. A.; Larionov, E. G. 2003 J. Phys. Chem. B 107 7861-66.
[19] Fink, U.; Wiggins, T. A.; Rank, D. H. 1965 J. Mol. Spectrosc. 18 384-95.