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Thermodynamic and Raman spectroscopic studies on H_2 + tetrahydrofuran + water and H_2+ tetra-*n*-butyl ammonium bromide + water mixtures containing gas hydrates

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Abstract

Phase equilibrium curves of H_2+ tetrahydrofuran and H_2+ tetra-*n*-butyl ammonium bromide mixed gas hydrates were measured in a pressure range from 0.1 to 13.6 MPa. Each three-phase equilibrium curve converges at the maximum temperature point of pure tetrahydrofuran and tetra-*n*-butyl ammonium bromide hydrates, respectively. The difference of maximum temperatures is about 8 K, that is, the equilibrium curve of H_2+ tetra-*n*-butyl ammonium bromide mixed gas hydrate shifts to the high-temperature side from that of H_2+ tetrahydrofuran mixed gas hydrate. It is directly confirmed by use of Raman spectroscopy that H_2 is enclathrated in the hydrate cages by adding a small amount of tetrahydrofuran or tetra-*n*-butyl ammonium bromide. In both mixed hydrates, H_2 is enclathrated in only the small cage while tetrahydrofuran or tetra-*n*-butyl ammonium bromide occupies the large cages of each mixed hydrate.

Keywords: Gas hydrate; Phase equilibria; Gas storage; Stability; Solutions; Gases

1. Introduction

Gas hydrates are stabilized by guest species in the cavity of cages composed of the hydrogen-bonded water molecules. Three types of hydrate cages are well known, pentagonal dodecahedron (5^{12}, S-cage), tetrakaidecahedron ($5^{12}6^2$, M-cage) and hexakaidecahedron ($5^{12}6^4$, L-cage). Several types of hydrate unit-cells can be formed from a few types of hydrate cages depending on the size and physical properties of guest species. For example, the structure-I (s-I) hydrate lattice is composed of two S-cages and six M-cages, and the structure-II (s-II) hydrate lattice is 16 S-cages and eight L-cages.

H_2 has become the object of attention as a clean and promising energy resource. Recently, H_2 hydrate is being considered as a medium of H_2 storage and transportation. However, the pure H_2 hydrate is generated only in an extremely high-pressure region of 100–360 MPa (Dyadin et al., 1999). Mao et al. (2002) and Mao and Mao (2004) reveal that $H_2 + H_2O$ mixtures generate the s-II hydrate at a high pressure of 200 MPa and a low temperature of ca. 80 K, where the hydrate cages are occupied by two H_2 molecules in the S-cage and four in the L-cage. Much milder conditions are desired to utilize the H_2 hydrate as a medium of H_2 storage and transportation.

Tetrahydrofuran (THF), well known as a common solvent, generates s-II hydrate (Hawkins and Davidson, 1966) below atmospheric pressures. THF can be enclathrated in the L-cage while it cannot occupy the S-cage. The chemical formula of ideal THF hydrate is written as THF • $17H_2O$ (Gough and Davidson, 1971). THF has been widely used as an additive that would reduce the equilibrium pressure of other gas hydrates (for example, CH_4 and N_2 hydrates). Furthermore, the effect of THF was the highest among several additives (for example, acetone, 1, 4-dioxane) (Kang et al., 2001; Seo et al., 2001). Florusse et al. (2004) have reported the first results that clusters of H_2 can be stabilized and stored at low pressures in the s-II THF hydrate. According to Florusse et al. (2004) and Lee et al. (2005), two H_2 molecules are only enclathrated in the S-cage and one THF molecule in the L-cage. The phase behavior of H_2 + THF hydrate, however, is unclear in a low pressure

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region where the pure THF hydrate exists stably (Makino et al., 2005).

Shimada et al. (2003) have reported that isobaric phase equilibrium (T–x) relations for the tetra-*n*-butyl ammonium bromide (TBAB) hydrate have the maximum temperature point (285.15 K) at atmospheric pressure with 40.5 wt% (3.6 mol%) water solution. TBAB hydrate is a semi-clathrate hydrate where TBAB is incorporated with the H_2O molecules to construct the hydrate cage. TBAB hydrate also has some empty S-cages, which is similar to THF hydrate. Therefore, H_2 storage in TBAB hydrate has prospects of large advantage.

In the present study, thermodynamic stabilities of $H_2 + THF$ and $H_2 + TBAB$ hydrates were measured (for the $H_2 + THF$ hydrate, in the lower pressure region than the previous report, Florusse et al., 2004). In addition, Raman spectra for each single crystal of $H_2 + THF$ and $H_2 + TBAB$ hydrates were measured under the three-phase coexisting conditions.

2. Experimental section

2.1. Experimental apparatus

The experimental apparatus for the phase equilibrium measurements is the same as the previous one (Sugahara et al., 2005) except for the introducing line for the THF or TBAB aqueous solution. The inner volume and maximum working pressure of high-pressure cell were 150 cm^3 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. 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.

2.2. Experimental procedures

Either THF or TBAB aqueous solution prepared at a desired composition was introduced into the evacuated high-pressure cell. The contents were pressurized up to a desired pressure by supplying H_2 and then continuously agitated by a mixing bar. After the formation of gas hydrates, the system temperature was kept constant to establish the three-phase coexisting state of hydrate + aqueous solution + gas. The phase behavior was observed directly through the window. After establishing the equilibrium state of three-phase coexistence, the system pressure and temperature were measured.

The single crystal of gas hydrate prepared from the mixtures of $H_2 + THF$ solution and $H_2 + TBAB$ 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}.

2.3. Materials

Research grade H_2 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 Yashima Pure Chemicals Co., Ltd. Research grade TBAB of mole fraction purity 98.0% 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.

3. Results and discussion

3.1. Phase equilibrium measurements

Phase equilibria for the $H_2 + THF$ and $H_2 + TBAB$ mixed hydrate systems are summarized in Table 1 and shown in Fig. 1. The composition of THF and TBAB aqueous solutions

Table 1
Phase equilibrium data for the $H_2 + THF + water$ and $H_2 + TBAB + water$ mixed systems

	T (K)	p (MPa)
$H_2 + THF + water$ system	277.5	0.10
	277.5	0.33
	277.6	0.55
	277.8	1.03
	278.0	1.55
	278.2	2.13
	279.2	4.87
	280.1	8.30
	280.8	11.3
	281.4	13.3
$H_2 + TBAB + water$ system	285.4	0.13
	285.4	0.18
	285.5	0.70
	285.8	1.19
	285.9	2.19
	286.1	3.27
	286.2	5.30
	286.3	6.05
	286.5	7.10
	286.6	7.93
	286.7	8.66
	287.2	13.4
	287.3	13.6