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Hydrate structural transition depending on the composition of methane + cyclopropane mixed gas hydrate

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Abstract

The methane + cyclopropane mixed gas hydrate system has been investigated at 291.1 K by means of gas chromatography and Raman spectroscopy. Both of pure guest species generate the structure-I hydrate in the present conditions. Isothermal phase equilibria exhibit discontinuity around the equilibrium cyclopropane composition (water-free) in the gas phase of 0.20. The Raman shifts have changed bordering at the point. These results reveal that the methane + cyclopropane mixed gas hydrate generates the structure-II crystal in the methane rich region, while the structure-I crystal is generated in the cyclopropane rich region.

Keywords: Clathrate hydrate; Solid–fluid equilibria; Data; Structural transition; Methane; Cyclopropane

1. Introduction

Clathrate hydrates are one kind of inclusion compounds and their appearances are ice-like crystal. They are composed of some cages, which are constructed by the hydrogen-bonded H_2O molecules, and the enclathrated guest species, which stabilize the hydrate structures. There are well-known several types of hydrate structures; the structure-I, -II, and -H. Their unit lattices have a common cage, the S-cage of pentagonal dodecahedron (5^{12}). In addition, the structure-I and -II have other type of cage, the M-cage of tetrakaidecahedron ($5^{12}6^2$) and the L-cage of hexakaidecahdron ($5^{12}6^4$), respectively. The structure-I unit lattice has 2 S-cages and 6 M-cages with $46H_2O$ molecules and the structure-II has 16 S-cages and 8 L-cages with $136H_2O$ molecules. The structures of clathrate hydrates primarily depend on the shape and size of guest species.

Ballard and Sloan [1], Subramanian et al. [2,3], and Mooijer-van den Heuvel et al. [4] have reported that the hydrate structural transition occurs from the structure-I to -II and back to structure-I in a certain composition region of methane + ethane and methane + trifluoromethane mixed gas hydrates. Sugahara et al. [5] have reported that there is no hydrate structural transition for the methane + ethylene mixed gas hydrate at 293 K.

Suzuki et al. [6] have reported that the cyclopropane molecule generates the structure-I hydrate in the temperature region between 278.52 and 320.01 K, while Hafemann and Miller [7] have reported that the structure-II hydrate is generated in the temperature region between 257.13 and 274.6 K. In the conditions of present study, cyclopropane generates the structure-I hydrate as well as methane, ethane, and ethylene. In addition, the cyclopropane molecule has the largest van der Waals diameter (0.58 nm, which is almost same with the diameter of cavity of M-cage) among the above guest species. Thakore and Holder [8], however, have reported that the methane + cyclopropane mixed gas hydrate forms the structure-I in the whole composition region at 277.15 and 281.15 K on the thermodynamic studies. It is suggested that there is every possibility that the hydrate structural transition occurs in the methane + cyclopropane mixed gas hydrate system.

In the present study, isothermal phase equilibria for the methane + cyclopropane mixed gas hydrate system were investigated at 291.1 K by means of gas chromatography. In

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addition, the single crystals of mixed gas hydrate were analyzed by means of laser Raman spectroscopy.

2. Experimental

The experimental apparatus used in this work, both phase equilibrium measurement and Raman spectroscopic analysis are the same as the ones reported previously [5]. So, the details are not mentioned here. In both experiments, the system temperature and pressure were measured within an accuracy of ±0.02 K and ±0.01 MPa, respectively.

2.1. Phase equilibrium measurement

The mixtures of methane and cyclopropane were prepared at a desired composition by measuring the partial pressure of each guest species. After the mixture was introduced into the evacuated high-pressure cell, the contents were pressurized up to a desired pressure by supplying the distilled water successively. Then, methane + cyclopropane mixed gas hydrate was generated by agitating the contents continuously. A mixing bar was used for agitation and it was moved up and down by the permanent magnet outside. After the mixed gas hydrate formation, the system temperature was kept constant to establish the three-phase equilibrium state (hydrate phase + water phase + gas phase). The phase behavior was observed through the sapphire windows installed in the cell. After the system reached the three-phase equilibrium state, small amounts of gas and liquid phases were separately taken out in order to analyze the equilibrium composition by means of TCD gas chromatography (TCD-GC, Shimadzu GC-7AG).

2.2. Raman spectroscopic analysis

A mixture, which was prepared at a desired cyclopropane composition by measuring the partial pressure of each guest species, was introduced into the evacuated high-pressure optical cell. Then, the contents were pressurized up to a desired pressure by introducing the distilled water. After confirming the existence of interface between gas and liquid phases, the methane + cyclopropane mixed gas hydrate was generated by agitating the contents and cooling the system temperature. A ruby ball was enclosed in the cell to agitate the contents by low-frequency vibration from outside. The phase behavior was observed by a CCD camera through a sapphire window. After the generation of methane + cyclopropane mixed gas hydrate, the hydrate single crystals were prepared under the three-phase coexisting state (hydrate phase + water phase + gas phase) by controlling the system temperature. The single crystals were analyzed under the three-phase equilibrium state by in situ Raman spectroscopy by use of a laser Raman microprobe spectrometer with a multi-channel CCD detector. The Ar ion laser (wavelength: 514.5 nm, generating power: 100 mW), which was condensed to 2 μm in spot diameter, was irradiated from the object lens to the hydrate single crystal through the upper sapphire window. The spectral resolution was about 1 cm^{-1} and the CCD detector was maintained at 140 K by liquid-nitrogen for heat-noise reduction. The integration time was varied within the range of 30–300 s, depending on the intensity of Raman spectrum. The equilibrium compositions of gas and hydrate phases were estimated from the Raman peak area of C–H stretching vibration mode by direct comparison of known-composition samples.

2.3. Materials

Methane (research grade of purity 99.95 mol%) and cyclopropane (research grade of purity 99.5 mol%) 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.

3. Results and discussion

3.1. Isothermal phase equilibria

Isothermal phase equilibrium (p–x, y relation) data at 291.1 K, obtained from the TCD gas chromatography in the present study, are summarized in Table 1 and shown in Fig. 1. The symbols of x and y stand for the equilibrium composition of cyclopropane in the water and gas phases (water-free) under the three-phase equilibrium conditions, respectively. The equilibrium pressures of pure methane and cyclopropane hydrates are 18.7 and 13.2 MPa (the open square in Fig. 1; [6]) at 291.1 K, respectively. The most characteristic behavior for the methane + cyclopropane mixed gas hydrate system is the extremely large pressure reduction.

3.2. Raman spectroscopic analysis

Figs. 2 and 3 show the Raman spectra obtained from 10 different methane + cyclopropane mixed gas hydrates under three-phase equilibrium conditions at 291.1 K. The symbol

Table 1
Isothermal phase equilibria for the methane + cyclopropane mixed gas hydrate system at 291.1 K by means of TCD gas chromatography[a]

p (MPa)	x	y
Structure-I region		
18.7	0.000	0.000
Structure-II region		
9.28	0.146	0.012
3.95	0.280	0.066
3.02	0.409	0.133
2.51	0.481	0.194
Structure-I region		
1.47	0.764	0.347
1.26	0.802	0.478
1.00	0.861	0.603
0.95	0.888	0.664

[a] The mole fraction of cyclopropane in the hydrate phase (z) is not measured.