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Four-Phase Equilibrium Relations of Methane + Methylcyclohexanol Stereoisomer + Water Systems Containing Gas Hydrate

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Four-phase equilibrium relations (gas + water + methylcyclohexanol + gas hydrate phases) have been measured in methane + methylcyclohexanol + water systems. We have discovered five new guest species of the methane structure-H hydrate: 1-methylcyclohexanol; *cis*-2-methylcyclohexanol; *trans*-2-methylcyclohexanol; *cis*-4-methylcyclohexanol; *trans*-4-methylcyclohexanol. Decomposition pressures of these methane-structure-H hydrates increase in this order under isothermal conditions.

Introduction

Clathrate hydrate is a kind of inclusion compound. It consists of hydrogen-bonded water molecules and guest species (e.g., hydrocarbons, noble gases). Clathrate hydrates have received much attention as one of the effective media to transport and store methane.[1] Methane hydrate, which constructs the structure-I (s-I) form, requires high pressures and low temperatures. Therefore, to produce the methane-containing clathrate hydrate under a mild condition, the equilibrium pressure should be reduced.

We have focused our attention on the structure-H (s-H) hydrate because it has a lower isothermal equilibrium pressure than the s-I methane hydrate. s-H is one of the well-known hydrate structures. The unit cell has one icosahedron cage (U-cage, $5^{12}6^{8}$), two dodecahedron cages (S'-cage, $4^{3}5^{6}6^{3}$), and three pentagonal dodecahedron cages (S-cage, 5^{12}).[2] Two kinds of guest species are indispensable for the s-H hydrate generation except for extremely high-pressure conditions. One is a small guest species called "help gas" (e.g., methane, xenon), and the other is a large guest species (LGS) like dimethylcyclohexane.

Reportedly, pressure reduction from the s-I methane hydrate depends largely on the molecular size and shape of LGS.[3] 1,1-Dimethylcyclohexane (1,1-DMCH) is able to generate the s-H hydrate under the lowest equilibrium pressure conditions of all DMCH stereoisomers.[4] It is suggested that 1,1-disubstituted cyclohexanes have more appropriate molecular shapes and sizes for the U-cage than the other disubstituted cyclohexanes, whereas there are enclathration boundaries of the U-cage between *cis*- and *trans*-1,2-DMCHs[5] as well as *cis*- and *trans*-1,4-DMCHs.[6] In particular, the molecular size of *trans*-1,2-DMCH is very close to the enclathration boundary, so it can be encaged with a little expansion of the U-cage under the cooperative assistance of methane and *cis*-1,2-DMCH.[7] Thus, when the methyl group is substituted for other smaller functional groups, it is considered that *trans*-1,2- and *trans*-1,4-disubstituted cyclohexanes can generate the s-H hydrate with only the help of methane. To establish these inferences, disubstituted cyclohexane stereoisomers other than DMCH should be investigated.

In the present study, we have investigated the methane + methylcyclohexanol (MCHol) stereoisomer + water systems containing gas hydrates. MCHols are slightly smaller than DMCHs because the hydroxyl group is smaller than the methyl group. In addition, because of their higher solubility in water, it is suggested that the hydration rate of methane + MCHol hydrate is higher than any other methane + hydrocarbon s-H hydrate (such a phenomenon is reported in the methane + methylcyclohexanone s-H hydrate systems[8]). Therefore, they are also worthy of further consideration in light of natural gas storage and transportation.

Four-phase equilibrium relations (gas + water + MCHol + gas hydrate phases) have been measured in methane + methylcyclohexanol + water systems up to 10 MPa. Five MCHol stereoisomers were studied: 1-MCHol; *cis*-2-MCHol; *trans*-2-MCHol; *cis*-4-MCHol; *trans*-4-MCHol. In addition, in situ Raman spectroscopic analysis has been performed under four-phase equilibrium conditions to investigate the hydrate crystal structure in the methane + 1-MCHol + water system.

Experimental Methods

(a) Phase Equilibrium Measurement. The experimental apparatus is the same as the one used in our previous study.[5] Equilibrium temperature was measured by use of a thermistor probe (Takara D-641) calibrated by a Pt resistance thermometer (25 Ω) defined by ITS-90. Equilibrium pressure was recorded by a pressure gauge (Valcom VPRT) calibrated by a RUSKA quartz Bourdon tube gauge. The uncertainties of equilibrium temperature and equilibrium pressure were 0.02 K and 0.02 MPa, respectively.

First, water, MCHol, and methane were introduced into the evacuated high-pressure cell. Pressurization and depressurization were performed by controlling the molar amount of methane. Then, the contents were cooled and agitated to generate the gas hydrate. The cell was immersed in a thermostated bath to control the temperature. Thermostated water was circulated by a thermocontroller (Taitec CL-80R). A mixing bar, which was magnetically manipulated in a vertical fashion, was used to agitate the contents. After the gas hydrate was generated, the

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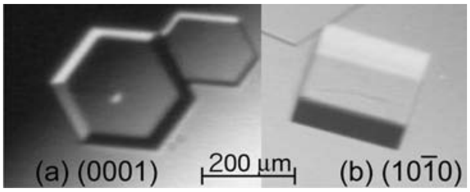

Figure 1. Single crystals of methane + 1-methylcyclohexanol mixed gas hydrate under four-phase equilibrium conditions: (a) (0001) face; (b) $(10\bar{1}0)$ face.

temperature was kept to establish the four-phase equilibrium state (gas + water + 1-MCHol + gas hydrate phases). To precisely determine the four-phase equilibrium relation, the gas hydrate was formed and dissociated by the pressure control method as reported in our previous study.[5] It always required more than two days to determine an equilibrium point.

(b) Raman Spectroscopic Analysis. The experimental apparatus in the present study is the same as the one reported previously.[9] Equilibrium pressure and temperature were measured by the same procedure mentioned in the previous section (Phase Equilibrium Measurement). The uncertainties were also the same.

Single crystals were prepared with the coexistence of gas, water, and liquid 1-MCHol phases by the same procedure in our previous study.[9] We spent more than two weeks to anneal the crystal and establish the four-phase equilibrium. The single crystal was analyzed by in situ Raman spectroscopy by use of a laser Raman microprobe spectrometer with a multichannel CCD detector. Ar ion laser (wavelength: 514.45 nm, generating power: 100 mW), which was condensed to 2 μm in a spot diameter, was irradiated from an object lens onto the samples through the upper sapphire window. Spectral resolution in the present study was 0.7 cm^{-1}. Raman peaks were calibrated with the Ne emission lines in the air. The CCD detector was maintained at 140 K by liquid N_2 for heat-noise reduction. The integration time was varied depending on Raman peak intensities.

(c) Materials. 1-MCHol (purity: > 96 %), *cis*-4-MCHol (purity: > 98.0 %), and *trans*-4-MCHol (purity: > 98.0 %) were purchased from Tokyo Chemical Industry Co., Ltd. *cis*-2-MCHol (purity: 99+ %) was obtained from Wako Pure Chemical Industries, Ltd. Aldrich supplied *trans*-2-MCHol (purity: 99 %). We could not obtain pure *cis*- and *trans*-3-methylcyclohexanols because only their mixture was sold. Methane (purity: 99.99 %) was purchased from Neriki GAS Co., Ltd. Distilled water was obtained from Wako Pure Chemical Industries, Ltd. All of them were used without further purification.

Results and Discussion

Figure 1 shows single crystals of the methane + 1-MCHol hydrate under four-phase equilibrium conditions. The crystal morphology shown in Figure 1 indicates that the crystal structure seems to be hexagonal. It is suggested that the crystal face of Figure 1(a) is the (0001) face of the hexagonal crystal and that of Figure 1(b) is the $(10\bar{1}0)$ one. Figures 2 and 3 are Raman spectra obtained from the methane + 1-MCHol hydrate system under the four-phase equilibrium conditions (297.8 K and 24.7 MPa). The symbol of ν stands for Raman shift. The Raman peaks detected around 720 cm^{-1} correspond to the C−C−C ring-breathing mode of 1-MCHol molecules.[10] The Raman peak of the hydrate phase has a higher Raman shift (Figures 2(a) and (b), 722 cm^{-1}) than that of the LGS phase (Figure 2(c), 720 cm^{-1}). A broad single peak at 2913 cm^{-1} in Figure 3 is a characteristic peak of the methane molecule enclathrated in the s-H hydrate,[9,11,12] and the other peaks are derived from intramolecular vibrations of 1-MCHol. These results indicate the following: the 1-MCHol molecule is enclathrated in the gas hydrate; the methane + 1-MCHol hydrate is in the s-H form. In addition, the Raman spectrum obtained from the (0001) face is different in the spectral shape from that of the $(10\bar{1}0)$ one as shown in Figures 2 and 3. Taking the literature[13] into the consideration, the reason why is that the 1-MCHol molecule cannot rotate isotropically in the U-cage.

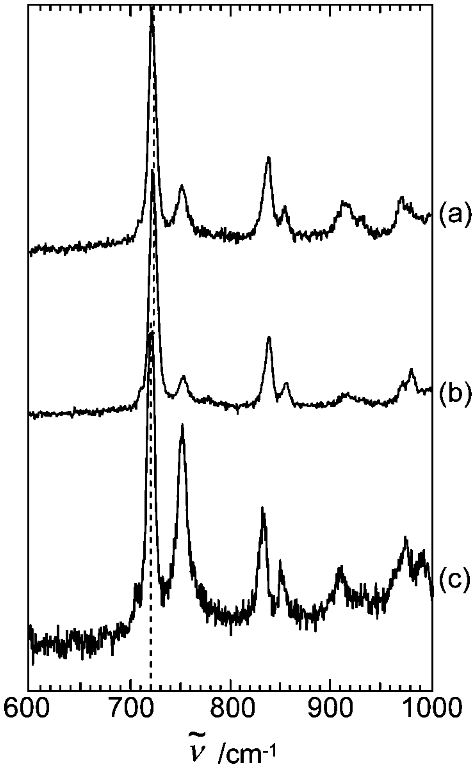

Figure 2. Raman spectra (Raman shift $\tilde{\nu}$) of 1-methylcyclohexanol (1-MCHol) molecules in the methane + 1-MCHol mixed gas hydrate system under the four-phase equilibrium condition (297.8 K and 24.7 MPa). (a) (0001) face of the hydrate single crystal; (b) $(10\bar{1}0)$ face of the hydrate single crystal; (c) 1-MCHol phase.

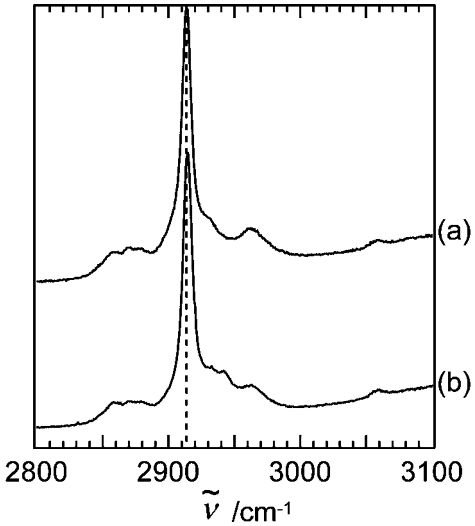

Figure 3. Raman spectra (Raman shift $\tilde{\nu}$) of enclathrated guest species in the methane + 1-MCHol mixed gas hydrate under the four-phase equilibrium condition (297.8 K and 24.7 MPa). (a) (0001) face of the hydrate single crystal; (b) $(10\bar{1}0)$ face of the hydrate single crystal.

Table 1. Four-Phase Equilibrium Relations (Temperature *T*, Pressure *p*) of the Methane + Methylcyclohexanol (MCHol) Stereoisomer + Water Systems Containing Gas Hydrate (Structure-H or -I)

T/K	*p*/MPa	*T*/K	*p*/MPa
methane + 1-MCHol system		methane + *cis*-4-MCHol system	
273.90	1.61	277.74	3.61
275.84	2.01	278.86	4.16
277.63	2.44	279.98	4.68
280.33	3.30	280.57	5.05
282.68	4.31	281.28	5.50
284.70	5.46	282.14	6.11
285.68	6.13	283.07	6.86
286.95	7.14	284.01	7.59
287.92	8.05	284.74	8.35
288.80	8.98	284.98	8.63
methane + *cis*-2-MCHol system		285.07	8.75
273.54	1.68	285.31	8.97
275.34	2.06	286.09	9.89
277.80	2.75	286.74	10.77
279.76	3.44	286.89	10.96
281.93	4.42	methane + *trans*-4-MCHol system	
283.40	5.26	273.89	2.65
284.69	6.12	274.38	2.79
285.86	7.05	274.89	2.97
286.78	7.89	275.19	3.07
288.28	9.52	275.68	3.24
methane + *trans*-2-MCHol system		276.18	3.44
274.13	2.38	276.69	3.61
274.61	2.51	277.28	3.88
275.07	2.65	277.56	4.02
275.60	2.80	277.66	4.08
276.10	2.98	277.77	4.10
276.60	3.15	277.84	4.15
276.98	3.30	277.93	4.20
277.46	3.48	278.02	4.25
277.95	3.66	278.29	4.36
278.45	3.87	278.59	4.51
278.89	4.11	278.75	4.60
279.35	4.30	278.94	4.70
279.53	4.40	279.12	4.81
279.83	4.56	279.16	4.85
280.15	4.71	279.33	4.95
280.43	4.85	279.63	5.09
280.62	4.98	279.82	5.19
281.09	5.25	280.03	5.33
281.88	5.74	280.26	5.45
283.08	6.64	280.46	5.59

Four-phase equilibrium relations of methane + MCHol stereoisomer + water systems containing gas hydrate are summarized in Table 1 and shown in Figure 4. The equilibrium pressure and temperature are presented by the symbols of *p* and *T*, respectively. Open squares, filled circles, open circles, filled triangles, and open triangles stand for the methane + 1-MCHol, + *cis*-2-MCHol, + *trans*-2-MCHol, + *cis*-4-MCHol, and + *trans*-4-MCHol systems, respectively. Each equilibrium pressure is lower than that of the s-I methane hydrate (solid line in Figure 4) under the isothermal conditions, thus five MCHols are enclathrated in gas hydrates. Molecular sizes of *cis*-2-, *trans*-2-, *cis*-4-, and *trans*-4-MCHols are similar to that of 1-MCHol. It is suggested that all five MCHol stereoisomers can generate the methane s-H hydrate. As mentioned above, *trans*-1,2-DMCH and *trans*-1,4-DMCH have slightly larger molecular sizes than the cavity size of the U-cage.[4,5] Our results reveal that molecular sizes of *trans*-1,2- and *trans*-1,4-DMCHs are reduced sufficiently by the substitution of the methyl group with a hydroxyl group so as to occupy the U-cage with the help of methane (summary is shown in Table 2).

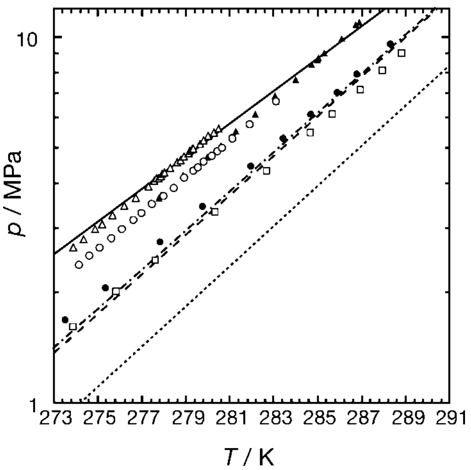

Figure 4. Four-phase equilibrium curves (temperature *T*−pressure *p* projection) of methane + methylcyclohexanol (MCHol) stereoisomer + water systems containing gas hydrate. □, methane + 1-MCHol system; ●, methane + *cis*-2-MCHol system; ○, methane + *trans*-2-MCHol system; ▲, methane + *cis*-4-MCHol system; △, methane + *trans*-4-MCHol system; dotted line, methane + 1,1-dimethylcyclohexnae (1,1-DMCH) system (ref 4); dashed line, methane + *cis*-1,2-DMCH system (ref 5); dashed-dotted line, methane + *cis*-1,4-DMCH system (ref 6); solid line, pure methane system (structure-I) (ref 5).

Table 2. Enclathration of Dimethylcyclohexnaes (DMCHs) and Methylcyclohexanols (MCHols) in the Methane Structure-H Hydrate

DMCHs	enclathration	MCHols	enclathration
1,1-DMCH	○	1-MCHol	○
cis-1,2-DMCH	○	*cis*-2-MCHol	○
trans-1,2-DMCH	×[a]	*trans*-2-MCHol	○
cis-1,4-DMCH	○	*cis*-4-MCHol	○
trans-1,4-DMCH	×	*trans*-4-MCHol	○

[a] Enclathration in the structure-H hydrate with the help of both methane and *cis*-1,2-DMCH (ref 7).

Four-phase equilibrium pressures of 1-MCHol, *cis*-2-MCHol, *trans*-2-MCHol, *cis*-4-MCHol, and *trans*-4-MCHol s-H hydrates increase in this order under the isothermal conditions. 1-MCHol has the most suitable molecular shape and size for the U-cage of the MCHol stereoisomers. Of the DMCH stereoisomers, 1,1-DMCH (dotted line in Figure 4) is the most appropriate for s-H hydrate generation with regard to equilibrium pressure, followed by *cis*-1,2-DMCH (dashed line in Figure 4) and *cis*-1,4-DMCH (dashed-dotted line in Figure 4).[4] These phase equilibria illustrate that the 1,1-disubstituted cyclohexane has the most suitable molecular size and shape of the disubstituted cyclohexane stereoisomers. The *cis*-1,2-disubstituted would be the second suitable stereoisomer with respect to equilibrium conditions.

Derivatives of pressure with respect to temperature (d*p*/d*T*) of MCHol s-H hydrate are slightly smaller than that of DMCH s-H hydrate. For example, the isothermal equilibrium pressure of 1-MCHol s-H hydrate goes below that of *cis*-1,2-DMCH s-H hydrate around 279 K. Furthermore, the isothermal equilibrium pressures of 1-MCHol and *cis*-2-MCHol s-H hydrates approach those of 1,1-DMCH and *cis*-1,2-DMCH s-H hydrates, respectively.

A temperature−pressure curve of the methane + *trans*-4-MCHol system intersects with that of the s-I methane hydrate around 278.7 K and 4.6 MPa and exhibits a discontinuity in gradient around 279.4 K and 5.0 MPa. The discontinuity indicates the occurrence of any phase transition; however, no phase transitions occur in the water, gas, and *trans*-4-MCHol phases around 279.4 K in the present study. It is suggested that the methane + *trans*-4-MCHol hydrate constructs the s-H hydrate up to 279.4 K and is transformed from the s-H hydrate into the s-I methane hydrate, even though equilibrium pressures of this system are slightly higher than that of the s-I methane hydrate (without LGS) between (278.7 and 279.4) K. It is speculated that the hydroxyl group of *trans*-4-MCHol inhibits the hydration of methane. Therefore, the solid phase transition is observed in the lower temperature and the higher pressure region relative to the equilibrium curve of the s-I methane hydrate. A similar behavior is reported in the methane + isoamylalcohol hydrate system.[14]

Conclusion

We have discovered that 1-MCHol, *cis*-2-MCHol, *trans*-2-MCHol, *cis*-4-MCHol, and *trans*-4-MCHol are able to generate s-H gas hydrates with the help of methane. The substitution of the functional group is one of the effective methods to find new LGSs and investigate the enclathration boundary of the U-cage.

The isothermal equilibrium pressures of the methane + 1-MCHol, methane + *cis*-2-MCHol, methane + *trans*-2-MCHol, methane + *cis*-4-MCHol, and methane + *trans*-4-MCHol s-H hydrate systems increase in this order. It is suggested that 1,1-disubstituted cyclohexane has the most suitable size and shape for the U-cage in each disubstituted cyclohexanes.

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