Phase Equilibrium for Structure-H Hydrates Formed with Methane and Methyl-Substituted Cyclic Ether

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Clathrate hydrate formation in a (methane + either 3-methyltetrahydropyran or 2-methyltetrahydrofuran + water) system is demonstrated. The first data of the quadruple (water + structure-H hydrate + either 3-methyltetrahydropyran or 2-methyltetrahydrofuran + methane) equilibrium pressure–temperature conditions are measured over temperatures from 273 to 286 K. In the 3-methyltetrahydropyran system, the equilibrium pressures are lower by 1.6–2 MPa than those of the structure-I methane hydrate formed in the methane + water system at given temperatures. In the 2-methyltetrahydrofuran system, equilibrium pressures at temperatures below 278 K are lower than those for the structure-I methane hydrate, and at temperatures above 278 K, they are higher. These phase equilibria suggest the formation of hydrates other than structure-I methane hydrates in the two systems. The crystallographic structures of the hydrates are determined to be structure H by means of X-ray diffraction as expected from considerations of sizes and shapes of the 3-methyltetrahydropyran and 2-methyltetrahydrofuran molecules.

1. INTRODUCTION

The idea of utilizing clathrate hydrates as a natural-gas-storage medium has aroused industrial interests in both gas-importing and gas-exporting countries. Recent advances in the past decade have been reviewed by Mori [1]. Hydrates formed in systems of water and natural gas are considered to be structure I or structure II, depending on the composition of the gas

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and the thermodynamic conditions in the systems. The crystallographic structure of the hydrates may be altered to structure H in the presence of an additional substance with 0.8 nm molecular size which fits into the $5^{12}6^8$ cages of structure-H hydrates.

Structure-H hydrates may offer the unique characteristic of low-pressure, high-density methane storage media, because a structure H hydrate forms with methane, which fits into five of the six cages in a unit cell of the hydrate crystal, and with a large molecule guest substance (LMGS) fitting into one of the six cages, under a considerably lower pressure than that required for the structure-I methane hydrate formation. This potential advantage of using structure-H hydrates for methane storage and transportation was first proposed by Khokhar et al. [2]. Their proposal has led to subsequent engineering-science studies on structure H hydrates as natural-gas storage media [3–8].

There is a selection in the chemical species of LMGSs to be used for practical application of structure-H hydrates for natural-gas storage and transportation technology. One important aspect is the phase-equilibrium pressure-temperature condition. Obviously, we can readily expect two merits with LMGSs that form structure-H hydrates under lower equilibrium pressures: (a) a higher hydrate formation rate under a thermodynamic condition set in a hydrate production process because of a larger driving force for hydrate formation and (b) once formed, the hydrate crystals may be stored under lower pressure. Both of these aspects impact the economics of hydrate-based natural-gas storage and transportation systems. Tsuji et al. [7] recently indicated another important aspect for selecting LMGSs to be used for practical application in addition to phase-equilibrium pressure–temperature conditions. They tested hydrate formation rates (measured as the rate of methane-gas supply into a high-pressure water-spray-type hydrate-formation chamber due to the hydrate formation inside) for five different LMGSs and concluded that a higher hydrate formation rate is available with an LMGS having a higher solubility with liquid water. Thus, a search for new LMGSs that have low-pressure phase-equilibrium properties as well as higher solubility in liquid water is required for a highly economical hydrate-based technology.

This paper reports the result of our efforts to find LMGSs having high solubility in liquid water, which may lead to more favorable selection of LMGSs to be used for the natural-gas storage and transportation applications. According to currently available literature, water-soluble LMGSs with which phase-equilibrium data in combination with methane are available include an ether, ketones, and an alcohol, as summarized in Table I. In the present study, we focus on methyl-substituted cyclic ethers as possible LMGSs that have solubilities in liquid water comparable to those

Table I. Phase-Equilibrium Properties of Large-Molecule Guest Substances Having High Solubility in Liquid Water

Substances	Solubility in water (mol%)	Equilibrium pressure at 275 K (MPa)
tert-butyl methyl ether	1.8[a]	1.91[c]
3,3-dimethyl-butanone	0.55[a]	1.40[d]
2-methyl cyclohexanone	0.48[a]	1.68[e]
3-methyl cyclohexanone	Not available	1.82[e]
4-methyl cyclohexanone	0.59[a]	1.94[e]
3,3-dimethyl-2-butanol	0.56[b]	1.85[d]

[a] Experimental data measured at $T = 273.15$ K under atmospheric pressure [9].
[b] Experimental data measured at $T = 273.15$ K under atmospheric pressure [10].
[c] Interpolated from the experimental data by Hütz and Englezos [11].
[d] Interpolated from the experimental data by Ohmrua et al. [5].
[e] Interpolated from the experimental data by Ohmrua et al. [6].

indicated in Table I. The tested methyl-substituted cyclic ethers are 3-methyltetrahydropyran and 2-methyltetrahydrofuran.

2. EXPERIMENTAL

2.1. Materials, Apparatus and Procedures for Phase-Equilibrium Measurements

Fluid samples used in the experiments are deionized and distilled liquid water; methane of 99.99 vol.% certified purity from Takachiho Chemical Industrial Co., LTD., Tokyo; 3-methyltetrahydropyran of 97 mass% certified purity from Aldrich Chemical, Milwaukee, Wisconsin; and 2-methyltetrahydrofuran of 99 mass% certified purity from Aldrich Chemical, Milwaukee, Wisconsin.

3-methyltetrahydropyran and 2-methyltetrahydrofuran may be viewed as methylcyclohexane and methylcyclopentane (both of which are known to be LMGSs for structure-H hydrates), respectively, with a methylene replaced by an ether group. Thus, 3-methyltetrahydropyran and 2-methyltetrahydrofuran are expected to be LMGSs, considering the shape and size of these molecules. The solubility of 3-methyltetrahydropyran in liquid water is 0.7 mol%, and that of 2-methyltetrahydrofuran in liquid water is 5.2 mol% at 273.15 K under atmospheric pressure [9], which are comparable to or higher than the solubility of the known LMGSs in liquid water, as indicated in Table I.

The experimental apparatus and procedure for measuring the equilibrium pressure–temperature conditions for the four phases, water-rich liquid

(L$_w$), hydrate (H), LMGS-rich liquid (L$_g$), and methane-rich vapor (V) are the same as those used in our previous studies [5, 6]. The test section is a stainless-steel cylindrical vessel equipped with a magnetic stirrer. The inner volume of the test vessel is 200 cm^3. The vessel is immersed in a temperature-controlled bath to maintain the temperature inside the vessel, T, at a prescribed level. Two thermocouples are inserted into the vessel to measure the gas and liquid temperatures. The pressure in the vessel, p, is measured with a strain-gauge pressure transducer (Model PH-100KB, Kyowa Electric Co. Ltd). The estimated uncertainties of temperature and pressure measurements are ± 0.1 K and ± 0.016 MPa. The batch, isochoric procedure described by Danesh et al. [12] is used to determine the four-phase equilibrium conditions. Each run is commenced by charging the vessel with the sample liquids, 35 cm^3 of water and 20 cm^3 of an LMGS. The vessel containing the liquids is then immersed into the temperature-controlled bath to set T at 287 K. We set p at a prescribed level from 1 MPa to 10 MPa by supplying methane gas from the high-pressure cylinder through the pressure-regulating valve into the evacuated vessel. Then, T is decreased to form a hydrate. If hydrate formation in the vessel is detected from the decrease in p and the increase in T, the temperature of the bath is kept constant for 6 hours, thereby keeping T constant. T is then increased incrementally by 0.1 K, holding each level of T for 6 hours to achieve a steady equilibrium state in the vessel. By this operation, we obtain a $p-T$ plot diagram for each experimental run, from which we determine a four-phase equilibrium $p-T$ point. If T is increased in the hydrate-forming region, hydrate crystals partially dissociate, thereby substantially increasing p. If T is increased in the region without hydrate, a smaller increase occurs in p, due to the change in the phase equilibria of the fluids in the vessel. Consequently, the point at which the slope of $p-T$ data plots changes sharply is considered to be the point at which all hydrate crystals dissociate and hence the point of the four-phase equilibrium. This operation is repeated at several different initial pressures to obtain the four-phase equilibrium data over a temperature range from 273 to 286 K.

2.2. X-ray Diffraction

Using the same experimental apparatus as described above, we prepare hydrate crystal samples in the two systems, each with either 3-methyltetrahydropyran or 2-methyltetrahydrofuran for the X-ray diffraction measurements, in order to determine the crystallographic structures of the hydrates. The thermodynamic conditions under which the samples are prepared are 274.0 K and 2.50 MPa in the 3-methyltetrahydropyran system and 274.0 K and 3.50 MPa in the 2-methyltetrahydrofuran system.

The thermodynamic condition in the 3-methyltetrahydropyran system is set outside structure-I methane hydrate formable conditions to avoid the possible formation of structure-I methane hydrate. However, the condition in the 2-methyltetrahydrofuran system is inevitably set in the range of structure-I methane-hydrate formation conditions because the phase-equilibrium conditions in the 2-methyltetrahydrofuran system are quite close to those in the methane + water system without any LMGSs. The procedures for charging the fluids and setting the p–T conditions are the same as those employed for the phase-equilibrium measurements described in the previous section. The line connecting the test cell and the high-pressure methane cylinder is opened during hydrate formation in the test cell to keep p constant by continuously supplying methane gas through a pressure-regulating valve to compensate for pressure reduction in the test cell due to hydrate formation and ensure that a sufficient amount of hydrate crystals will be stored in the cell. p and T are kept constant for 12 hours with continuous agitation in the test cell at 400 rpm after nucleation of the hydrate. The test cell is subsequently taken out of the temperature-controlled bath and then immediately immersed into a liquid nitrogen pool in a stainless-steel container. We allow 20 minutes for T to decrease below 170 K and then disassemble the test cell to remove the hydrate crystals inside. The prepared samples are stored in a container kept at a temperature of 170 K and subjected to X-ray-diffraction measurements.

The procedure for X-ray diffraction measurements outlined below is the same as described previously by Takeya et al. [13]. A portion of the stored sample is ground into fine powder at a temperature below 100 K, thereby preventing the hydrate crystals in the sample from dissociating. The fine powdered sample crystals are put in a quartz glass capillary cell (Hilgenberg; ϕ 2.0 mm, 0.01-mm thick) that is set at the top of the goniometer of the X-ray diffraction apparatus. The diffraction intensity measurement is conducted using CuKα X-ray (40 kV, 250 mA; Rigaku Model Rint-2000). The temperature of the sample is controlled within ± 1 K at 113 K under atmospheric pressure by continuously supplying a cold, dry nitrogen gas flow around the capillary sample cell. The capillary cell is rotated 360 degrees during the measurement to avoid possible effects of preferred orientations of the sample crystals.

3. RESULTS AND DISCUSSION

The (L_w + H + L_g + V) four-phase equilibrium data obtained in the (methane + 3-methyltetrahydropyran + water) system are tabulated in Table II, and the data for the similar system with 2-methyltetrahydrofuran are presented in Table III. Both data sets are depicted in Fig. 1 together

with literature data for $(L_w + H + V)$ equilibrium in the (methane + water) system [14]. The equilibrium pressures in the system with 3-methyltetrahyropyran are 1.6–2 MPa lower than those in the (methane + water) system, suggesting the formation of a structure-H hydrate with 3-methyltetrahydropyran as an LMGS. A similar comparison for the 2-methyltetrahydrofuran system indicates that the equilibrium pressure in the system with 2-methyltetrahydrofuran is 0.1 MPa lower at 274 K than that in the system without 2-methyltetrahydrofuran. The difference of these two pressures decreases with increasing temperature. The equilibrium data points obtained in the system with 2-methyltetrahydrofuran, indicating a nearly straight line in Fig. 1, intersect with the three-phase line for methane + water at ∼278 K, and extend with the same slope to the point of 285.2 K and 9.624 MPa, the highest temperature and pressure data obtained in the present study. The slope of the data-point line for the 2-methyltetrahydrofuran system differs from that for the methane + water system without 2-methyltetrahydrofuran. This phase equilibrium in the 2-methyltetrahydrofuran system suggests the formation of a hydrate different from the structure-I methane hydrate.

Table II. $(L_w + H + L_g + V)$ Four-Phase Equilibrium $p-T$ Conditions in a (Methane + 3-Methyltetrahydropyran + Water) System

T (K)	p (MPa)	T (K)	p (MPa)
273.5	1.223	279.8	2.631
275.3	1.515	281.2	3.121
277.5	1.966	282.2	3.496
278.7	2.291	282.9	3.817

Table III. $(L_w + H + L_g + V)$ Four-Phase Equilibrium $p-T$ Conditions in a (Methane + 2-Methyltetrahydrofuran + Water) System

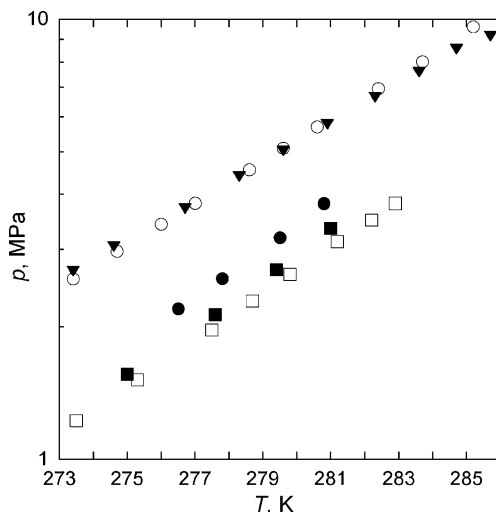| T (K)	p (MPa)	T (K)	p (MPa)
273.4	2.571	279.6	5.097
274.8	2.970	280.6	5.698
276.0	3.428	282.5	6.957
277.1	3.821	283.7	8.016
278.6	4.543	285.2	9.624

Fig. 1. Four-phase $(L_w + H + L_g + V)$ equilibrium $p-T$ conditions in methane and water plus each of the following substances: $\square$, 3-methyltetrahydropyran; $\bigcirc$, 2-methyltetrahydrofuran (present study). The following literature data are also indicated: $\blacktriangledown$, $L_w + H + V$ three-phase $p-T$ conditions in methane and water system [14] and $L_w + H + L_g + V$ four-phase equilibrium $p-T$ conditions in methane and water plus each of the following substances: $\blacksquare$, methylcyclohexane [6]; $\bullet$, methylcyclopentane [15].

Literature data of $L_w + H + L_g + V$ four-phase equilibrium conditions in the methane + water system with methylcyclohexane or methylcyclopentane as an LMGS are also indicated in Fig. 1. The effect of the substitution of a methylene in an LMGS molecule by an ether group on the resulting hydrate-phase equilibrium can be determined by comparing the equilibrium conditions in the 3-methyltetrahydropyran (2-methyltetrahydrofuran) system with those in the methylcyclohexane (methylcyclopentane) system. The comparisons indicate that the substitution of a methylene in methylcyclohexane by an ether group results in a small reduction in the equilibrium pressure (by 0.1 MPa), whereas a similar substitution in methylcyclopentane results in a significant increase in the equilibrium pressure (by 1.5 MPa).

The crystallographic structures of the hydrates formed in the systems, each with 3-methyltetrahydropyran or 2-methyltetrahydrofuran, are determined by X-ray diffraction measurements. Figure 2 depicts the X-ray diffraction profiles, measured at 113 K, obtained from the prepared hydrate samples. The profiles in Fig. 2 indicate that the crystallographic structure
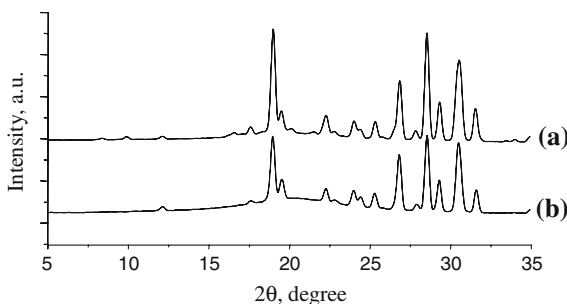
Fig. 2. X-ray diffraction profiles obtained with the hydrate samples prepared in (a) the 3-methyltetrahydropyran system at $p = 2.50$ MPa, $T = 274.0$ K and (b) the 2-methyltetrahydrofuran system at $p = 3.50$ MPa, $T = 274.0$ K. The diffraction measurements were performed at 113 K.

of both hydrates is structure H, as suggested by the phase-equilibrium data and the molecular-shape considerations.

4. CONCLUSIONS

Clathrate hydrate formation in the systems of methane and water plus either 3-methyltetrahydropyran or 2-methyltetrahydrofuran has been investigated by phase-equilibrium and X-ray-diffraction measurements. The phase equilibria are different from those in the methane + water system, indicating the formation of hydrates different from the structure-I methane hydrate. X-ray diffraction measurements are used to determine that the crystallographic structure of the hydrates formed in the two systems is structure H.

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