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Phase Equilibrium for Structure-H Hydrates at Temperatures below the Freezing Point of Water

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Four-phase (ice + structure-H hydrate + large-molecule guest substance liquid + methane-rich vapor) equilibrium pressure−temperature conditions were measured at temperatures from 252 K to 272 K in systems of water + methane + LMGS, where LMGS is a large-molecule guest substance for a structure-H hydrate. The tested LMGSs were 2,2-dimethylbutane (neohexane), methylcyclohexane, and *tert*-butyl methyl ether. The results obtained in the 2,2-dimethylbutane system agree with the corresponding data reported by Makogon et al., which were the only data set on the structure-H hydrate phase equilibrium at temperatures below the freezing point of water. Among the three systems studied, the lowest equilibrium pressure at a given temperature was observed in the 2,2-dimethylbutane system, and the highest, in the *tert*-butyl methyl ether system.

Introduction

The idea of storing and transporting natural gas in the state of clathrate hydrates, crystalline solid compounds consisting of hydrogen-bonded water molecules forming cages containing guest molecules (mostly hydrocarbons for the natural gas storage and transportation), has aroused the industrial interest of hydrate-related researchers and engineers as recently reviewed by Mori.[1] Hydrates formed with a natural gas are considered to be structure I or structure II, depending on the composition of the natural gas and the pressure−temperature conditions set for the hydrate formation. The crystallographic structure of the hydrates may be structure H if an LMGS is fed to the natural-gas hydrate-forming systems, where LMGS means a large-molecule guest substance for a structure-H hydrate. The storage and transportation of such hydrates at low temperatures, typically 250 K to 265 K, and under low pressures, favorably under atmospheric pressure, have been under consideration for practical application.[1] Because the pressures for dissociation of the hydrates at temperatures of 250 K to 265 K are considered to be higher than atmospheric pressure, we need to anticipate the self-preservation effect for hydrate storage under atmospheric pressure. The self-preservation effect is the apparent, long-term preservation of hydrate crystals under atmospheric pressure, which is lower than the equilibrium pressure for the hydrate. Whether or not we rely on the currently unclarified utility of the self-preservation effect, relevant phase-equilibrium data are essential for designing the process of hydrate-based natural gas storage and transportation. Concerning structure-I or structure-II hydrates, each of which is formed with natural gas components, there is enough phase-equilibrium experimental data at temperatures above and below the freezing point of water, and a predictive method with reasonable accuracy for industrial use has been established on the basis of the statistical-thermodynamics modeling as reviewed by Sloan.[2] For the structure-H hydrate, there are also phase-equilibrium data at temperatures above the freezing point of water,[2] but only three pressure−temperature data points at temperatures below the freezing point of water were reported by Makogon et al.[3] exclusively for the methane + 2,2-dimethyl butane (neohexane) + water system. This study aims to provide equilibrium data for four phases (ice + structure-H hydrate + liquid LMGS + methane) at temperatures below the freezing point of water. The measurements have been performed in the systems with methane, water, and each of the following three large-molecule guest substances for structure-H hydrate formation: neohexane, methylcylohaxane, and *tert*-butyl methyl ether. The measurements in the neohexane system have been performed to confirm the reliability of the present measurements by comparing the results obtained in the present study with the data obtained by Makogon et al.[3] Methylcyclohexane and *tert*-butyl methyl ether were selected because they are considered to be candidates for the practical application of structure-H hydrates to natural gas storage and transportation.[4,5]

Experimental Section

Materials. Fluid samples used in the experiments were deionized and distilled liquid water; methane of 99.99 vol % certified purity from Takachiho Chemical Industrial, Tokyo; neohexane (2,2-dimethyl-butane) of 99 mass % certified purity from Tokyo Kasei Kogyo; methylcyclohexane of 99 mass % certified purity from Tokyo Kasei Kogyo, Tokyo; and *tert*-butyl methyl ether of 99.7 mass % certified purity from Aldrich Chemical, Milwaukee, WI.

Apparatus. Figure 1 schematically illustrates the experimental system used to measure the temperature−pressure conditions for the four phases (ice (I), hydrate (H), an LMGS-rich liquid (L_g), and a methane-rich vapor phase (V)). The main part of the apparatus is the same as employed in our previous study[6] (a stainless steel vessel with a 200 cm^3 inner volume). This vessel is equipped with a magnetic stirrer through its lid to agitate the fluids and hydrate crystals inside the vessel. The vessel is immersed in a temperature-controlled bath to maintain the temper-

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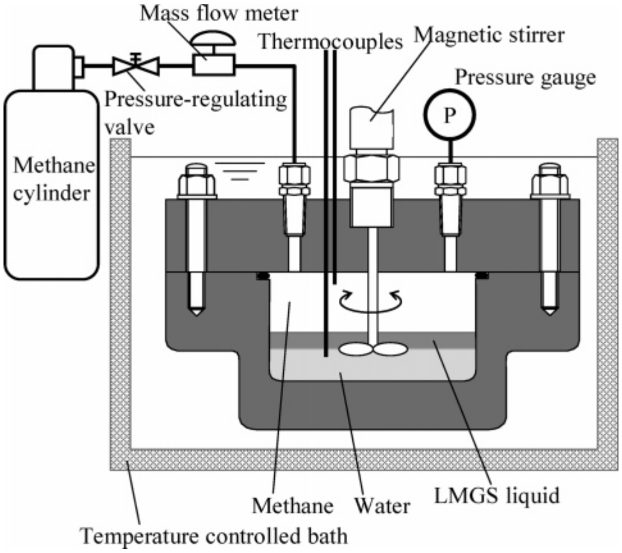

Figure 1. Schematic of the experimental apparatus.

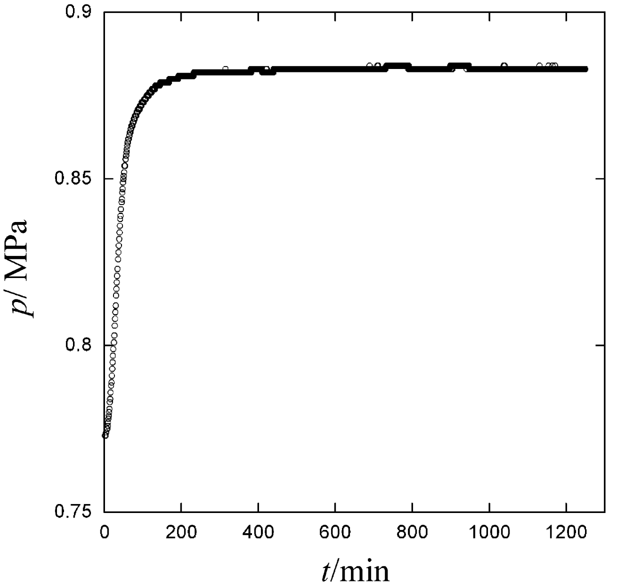

Figure 2. Typical data of the time variation of pressure obtained for determining phase equilibrium conditions in the methane + methylcyclohexane + water system. The data are recorded with a stepwise increase in temperaturefrom 261.0 K to 264.0 K. The stabilized pressure−temperature values were recorded as a four-phase equilibrium condition, and thus the four-phase equilibrium condition was determined to be $T = 264.0$ K and $p = 0.873$ MPa with the data that are plotted.

Table 1. I + H + Lg + V Four-Phase Equilibrium *p*−*T* Conditions in a Methane + Neohexane + Water System

T/K	p/MPa
254.4	0.509
255.9	0.548
257.85	0.597
258.85	0.623
260.85	0.678
263.35	0.751
267.35	0.882
269.65	0.966
271.35	1.025
272.85	1.095

ature 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-20KB, KYOWA Electric Co., Ltd.). The estimated uncertainties of temperature and pressure measurements are ±0.1 K and ±0.004 MPa. A mass flow meter (Oval Corp., model MASFLO-OVAL F-111S) is incorporated in the line connecting the test vessel and the high-pressure methane cylinder to measure the rate of methane gas supplied to the test vessel with an estimated uncertainty of ±1.0 cm^3/min.

Procedure. Each experimental run began by charging the vessel with 35 cm^3 of liquid water and 20 cm^3 of LMGS liquid. The vessel was then immersed in the temperature-controlled bath to set T at 273.5 K. The air in the vessel was replaced with methane by repeating the pressurization with methane and depressurization to atmospheric pressure. The pressure p was set at 2.1 MPa to form hydrate crystals in the vessel. The inside of the vessel was agitated during hydrate formation at $p = 2.1$ MPa and $T = 273.5$ K. The rate of methane flowing into the vessel was measured continuously with the mass flow meter. When the total amount of methane supplied to the vessel reached $4.2 \pm 0.5 \times 10^3$ cm^3, the valve in the line was shut. Because the molar ratio of water to methane in the resulting structure-H hydrate is considered to be approximately 8, based on the experimental determinations by means of gas consumption measurement during hydrate formation,[7] NMR measurement,[7] and single-crystal X-ray diffraction[8,9] as well as the statistical-thermodynamics prediction,[10] 70% to 80% of the liquid water in the vessel was considered to be converted into structure-H hydrate with this amount of methane. Thus, there were four phases—liquid water, liquid LMGS, methane, and hydrate—in the vessel at this stage of the hydrate reaction. T was subsequently decreased to ~250 K so that the liquid water inside the vessel was converted to ice. A small increase in T was observed during this cooling process, indicating the formation of ice from the liquid water in the vessel. The formation of ice was also indicated by the stopping of the magnetic stirrer. We kept T at 250 K for 10 h to ensure the complete conversion of liquid water to ice and then decreased p to nearly atmospheric pressure. T was then increased stepwise by 1 K to 3 K, holding each level of T for 20 to 30 h to achieve equilibrium in the vessel. Figure 2 depicts an example of a chronological change in p after a stepwise increase in T from 261.0 K to 264.0 K in the methylcyclohexane system. While T was held, stabilization in p was observed. These stabilized p and T values were recorded as the I + H + L_g + V four-phase equilibrium condition. The stepwise increase in T was repeated until T reached 272 K. In this procedure for four-phase equilibrium measurements, the test section is not agitated nor are the solids and fluids in the test section mechanically mixed. However, the stepwise increase in T should cause partial dissociation of the hydrate, resulting in the formation of ice, LMGS liquid, methane gas. The remaining hydrate phase and the three phases (ice + LMGS + methane) thus generated from the dissociating hydrate are considered to be in mutual contact. Thus, the four-phase equilibrium should eventually be achieved.

Results and Discussion

The reliability of the present measurements was examined by comparing our I + H + L_g + V four-phase equilibrium data obtained in the methane + neohexane + water system to the corresponding data in the literature. The data measured in the present study are given in Table 1. Figure 3 plots the data for the pressure below 0.7 MPa and the corresponding literature data reported by Makogon

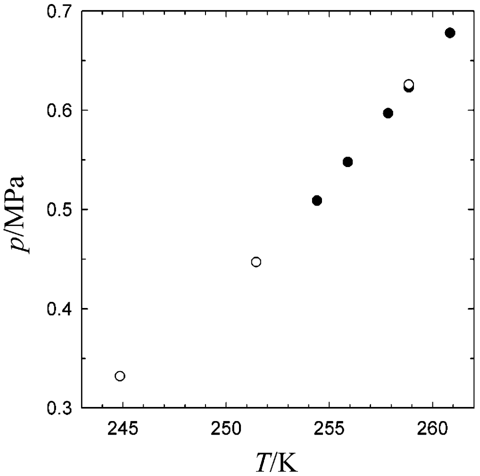

Figure 3. Comparison of I + H + Lg + V four-phase equilibrium $p-T$ data for the methane + neohexane + water system obtained in the present study with the corresponding values reported by Makogon et al.:[3] ●, present study; ○, Makogon et al.[3]

Table 2. I + H + Lg + V Four-Phase Equilibrium *p*−*T* Conditions in a Methane + Methylcyclohexane + Water System

T/K	p/MPa
251.5	0.519
253.15	0.559
255.7	0.619
258.1	0.686
261.0	0.774
264.0	0.873
267.0	0.984
269.05	1.063
271.0	1.145
272.6	1.213

Table 3. I + H + Lg + V Four-Phase Equilibrium *p*−*T* Conditions in a Methane + *tert*-Butyl Methyl Ether + Water System

T/K	p/MPa
252.85	0.652
256.35	0.731
259.84	0.836
263.25	0.947
266.65	1.070
269.85	1.203
270.85	1.252

et al.[3] for comparison and indicates that the data obtained in the present study are consistent with those by Makogon et al.[3] Specifically, the datum of $T = (258.85 \pm 0.1)$ K and $p = (0.632 \pm 0.004)$ MPa obtained in the present study coincides, within the estimated mutual uncertainties, with the corresponding datum of $T = (258.85 \pm 0.3)$ K and $p = (0.626 \pm 0.007)$ MPa reported by Makogon et al.[3] This comparison supports the reliability of the present measurements.

The I + H + L_g + V four-phase equilibrium data obtained in the systems with each of *tert*-butyl methyl ether and methylcyclohexane are given in Tables 2 and 3 and are plotted in Figure 4 together with the data in Table 1. Also plotted are the relevant literature data for liquid water (L_w) + H + L_g + V four-phase equilibrium at temperatures above 273 K,[6,11,12] and I + H + V[13] and L_w + H + V[14] three-phase equilibria in the methane + water system without any LMGS. The lowest equilibrium pressure at a given temperature was observed with neohexane, whereas the highest equilibrium pressure was observed with *tert*-butyl methyl ether. This trend in phase equilibrium is consistent with that at temperatures above the freezing point of water. Quantitatively, the equilibrium temperatures at a given pressure in the systems with methylcyclohexane and *tert*-butyl methyl ether are higher by approximately 3 K and 6 K than the corresponding equilibrium temperatures in the neohexane system. In comparison with the three-phase equilibrium conditions for structure-I methane hydrate, the four-phase equilibrium pressures for the three structure-H hydrates are lower by (0.9 to 1.1) MPa at 263 K.

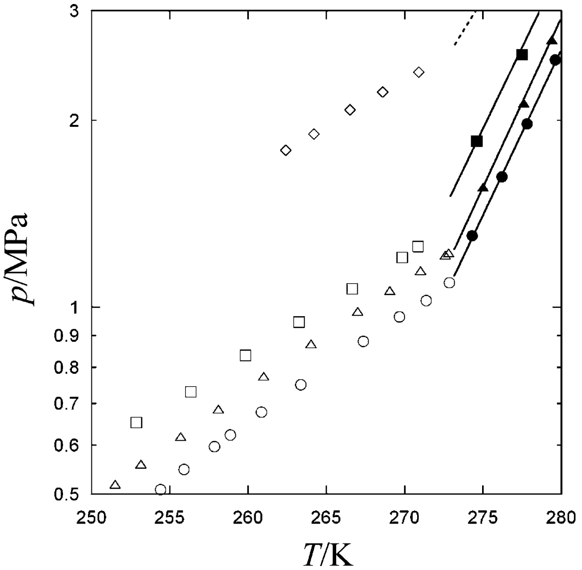

Figure 4. Equilibrium $p-T$ conditions for four phases involving the structure-H hydrate formed with methane and each of the following large-molecule guest substances: ○, neohexane; △, methylcyclohenxane: and □, *tert*-butyl methyl ether (present study). Closed symbols indicate L_w + H + L_g + V four-phase equilibrium $p-T$ conditions: ●, neohexane (Ohmura et al.[6]); ▲, methylcyclohexane (Ohmura et al.[11]); ■, *tert*-butyl methyl ether (Hütz and Englezos[12]). Solid lines are exponential functional fits to the data. Three-phase equilibrium $p-T$ conditions in methane + water system are also indicated: ◇, I + H + V (Deaton and Frost[13]); - - -, L_w + H + V (prediction given by CSMHYD[14]).

The equilibrium temperature at the corresponding equilibrium pressure of 1.1 MPa, or 1 MPa in gauge pressure, may be of industrial interest, particularly for Japanese engineers, with regard to the enforcement regulation due to the “High-Pressure Gas Safety Law” in Japan. This temperature is estimated to be 273 K for the neohexane system, 270 K for the methylcyclohexane system, and 267.5 K for the *tert*-butyl methyl ether on the basis of the data obtained in the present study.

Conclusions

The present study reports the four-phase (ice + structure-H hydrate + large-molecule guest substance liquid + methane-rich vapor) equilibrium temperature−pressure data in the systems of methane plus neohexane, *tert*-butyl methyl ether, or methylcyclohexane at temperatures from 252 K to 272 K. Among the three structure-H hydrates tested in the present study, the highest (lowest) equilibrium temperatures were observed with neohexane (*tert*-butyl methyl ether), as observed at temperatures above the freezing point of water. The results also indicate that the equilibrium pressures for the three structure-H hydrates tested in the present study are approximately 1 MPa lower than that for structure-I methane hydrate at a temperature of 263 K.

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