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Phase Equilibrium for Structure I and Structure H Hydrates Formed with Methylfluoride and Methylcyclohexane

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This paper reports the pressure−temperature conditions for the three-phase aqueous liquid + hydrate + vapor equilibrium in the structure I hydrate forming water + methylfluoride water system and for the four-phase aqueous liquid + hydrate + liquid hydrocarbon + vapor equilibrium in the water + methylcyclohexane + methylfluoride system. The pressure and temperature ranges of the present measurements are from (0.267 to 3.582) MPa and from (273.5 to 296.2) K in the water + methylfluoride system and from (0.185 to 2.703) MPa and from (273.7 to 294.2) K in the water + methylcyclohexane + methylfluoride system. The crystallographic structure of the hydrate formed in the water + methylcyclohexane + methylfluoride system at 279.7 K was determined to be structure H based on the X-ray diffraction measurement. The phase equilibrium data suggest the formation of structure I simple methylfluoride hydrate at temperatures above 289 K in the system with methylcyclohexane.

Introduction

Clathrate hydrates are crystalline solid compounds consisting of hydrogen-bonded water molecules forming cage structures with guest molecules enclosed in the cages. Depending on the size and shape of the guest molecules, water molecules form different cages that interconnect to yield various hydrates of different crystallographic structures such as structures I, II, and H.[1] The phase equilibrium conditions in the hydrate forming systems also depend on the chemical species of the guest substances. Novel technologies utilizing hydrates, such as natural gas and hydrogen storage,[2,3] separation/purification,[4] and heat pump/refrigeration systems,[5−8] etc., have been proposed. The high pressure or low temperature required to form hydrates is often a major obstacle to developing the hydrate-based technologies. Particularly, increasing the hydrate equilibrium temperature is the key for the development of the hydrate-based heat pump/refrigeration system, which is the direct background technology of this study. For increasing the hydrate equilibrium temperature, Imai et al.[5] tested the addition of cyclopentane to the water + difluoromethane system and succeeded in an equilibrium temperature increase by 6 K. The maximum equilibrium temperature available with the cyclopentane + difluoromethane double hydrate is reported to be 299.75 K at 1.544 MPa. Takeya and Ohmura[7] then tested the addition of cyclopentane to the water + krypton system, noting that the highest equilibrium temperature is practically limited by the liquefaction of difluoromethane. This is a relatively low vapor pressure guest substance, but this limitation can be overcome by using a guest substance that is in the super critical state, such as krypton. They have reported that the equilibrium temperature exceeded 304 K at the pressure of 4 MPa. Very recently, Imai et al.[8] reported the hydrate phase equilibrium data for the water + fluorocyclopentane + krypton and water + fluorocyclopentane + difluoromethane systems. They reported an equilibrium temperature exceeding 308 K at the pressure of approximately 5 MPa in the water + fluorocyclopentane + krypton system.

Following previous attempts,[5,7,8] we consider in the present study a different option to obtain a higher hydrate equilibrium temperature other than the use of supercritical guests. This option is simply the use of a guest substance having a relatively high vapor pressure. As an example of such high vapor pressure guest, we focused on methylfluoride (or monofluoromethane) that has a higher vapor pressure than difluoromethane; the vapor pressure of methylfluoride at 290 K is approximately 3 MPa,[9] much higher than the corresponding vapor pressure of difluoromethane (1.5 MPa).[10] Recently, Prager et al.[11] showed that the crystallographic structure of the simple methylfluoride hydrate is structure I based on neutron scattering measurements. As for the phase equilibrium conditions for methylfluoride hydrate, Villard[12] reported the temperature−pressure data at the end of the 19th century. However, the uncertainty of the phase-equilibrium measurements as well as the purity of the material was not specified by Villard.[12] Thus, we performed accurate measurements on the equilibrium pressure−temperature conditions for the simple methylfluoride hydrate formed in the water + methylfluoride system. We also experimentally demonstrated the formation of a structure H hydrate with methylfluoride and methylcyclohexane, which was previously mentioned by Ripmeester and Ratcliffe[13] but was not experimentally confirmed. In addition to the phase equilibrium measurement results, the determination of the crystallographic structure of the methylfluoride + methylcyclohexane double hydrate is also reported in this paper.

Experimental Section

Materials. Fluid samples used in the experiments were deionized and distilled liquid water; methylfluoride of 99.9 % (mass fraction basis) certified purity from Japan Fine Products Corp., Iga, Japan; and methylcyclohexane of 99 % (mass fraction basis) from Tokyo Chemical Industry, Tokyo. The

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Table 1. Aqueous Liquid + Hydrate + Methylfluoride-Rich Vapor Three-Phase Equilibrium $p-T$ Conditions in the Water + Methylfluoride System

T/K	p/MPa	T/K	p/MPa
273.5	0.267	290.2	1.625
276.6	0.371	292.2	2.049
278.6	0.468	293.3	2.343
281.0	0.598	293.8	2.514
283.2	0.749	294.5	2.765
284.9	0.902	295.1	3.029
287.6	1.204	296.2	3.582

Table 2. Aqueous Liquid + Hydrate + Methylcyclohexane-Rich Liquid + Methylfluoride-Rich Vapor Four-Phase Equilibrium p, T Conditions in the Water + Methylcyclohexane + Methylfluoride System

T/K	p/MPa	T/K	p/MPa
273.7	0.185	287.0	1.054
275.7	0.240	289.0	1.400
278.7	0.356	290.2	1.609
279.9	0.415	291.6	1.906
282.5	0.577	292.5	2.115
284.9	0.794	294.2	2.703

distilled water was laboratory-made. The other samples were used as supplied by the manufacturers.

Apparatus and Procedure. The experimental apparatus used to measure the pressure−temperature conditions for the three phases, aqueous liquid (L_w) + hydrate (H) + methylfluoride-rich vapor (V) and the four phases, aqueous liquid (L_w) + hydrate (H) + methylcyclohexane-rich liquid (L_g) + methylfluoride-rich vapor (V) are the same as those used in our previous studies.[7,14] The main part of the apparatus is a stainless steel cylinder with inner dimensions of 80 mm diameter and 40 mm height. A magnetic stirrer was installed in the vessel through its lid to agitate the fluids and hydrate crystals inside the vessel at 400 rpm. The vessel was immersed in a temperature-controlled bath to maintain the temperature inside the vessel (T) at a prescribed value to ± 0.1 K. Two platinum-wire resistance thermometers were inserted into the vessel to measure T. The pressure in the vessel, p, was measured with a strain-gauge pressure transducer (model PH 100 KB, Kyowa Electric Co., Ltd., Tokyo) when $p > 2.1$ MPa. For measuring p less than 2.1 MPa, another strain gauge pressure transducer (model PH-20KB, Kyowa Electric Co., Ltd.) was used. The estimated uncertainty of the temperature measurements are ± 0.1 K. The uncertainty of the pressure measurements was ± 0.016 MPa for $p > 2.1$ MPa and ± 0.004 MPa for $p < 2.1$ MPa.

The equilibrium conditions were measured with the batch, isochoric procedure described by Danesh et al.[15] Each run was initiated by charging the vessel with 50 g of liquid water or 35 g of liquid water and 20 g of methylcyclohexane. The vessel containing the liquid was then immersed in the temperature-controlled bath. The methylfluoride gas was supplied from a high-pressure cylinder through a pressure-regulating valve into the evacuated vessel until the pressure inside the vessel (p) was increased to the prescribed level between 0.18 and 3.6 MPa. After T and p stabilized, the valve in the line connecting the vessel and the high-pressure cylinder was closed. Subsequently, T was decreased to form the hydrate. If hydrate formation in the vessel was detected by a decrease in p and an increase in T, the temperature of the bath was kept constant for 6 h, thereby keeping T constant. We then incrementally increased T in steps of 0.1 K. At every temperature step, T was held constant for 6 h to achieve a steady, equilibrium state in the vessel. In this way, we obtained a $p-T$ diagram for each experimental run, from which we determined a four-phase equilibrium point. If T is increased in the presence of a hydrate, the hydrate partially dissociates, thereby substantially increasing p. After the complete dissociation of the hydrate, only a smaller increase in pressure is observed due to the change in the phase equilibria of the fluids in the vessel. Consequently, the point at which the slope of the $p-T$ data plots sharply changes is considered to be the point at which all hydrate crystals dissociate and hence as the point of the four-phase equilibrium. This operation was repeated at several different initial pressures to obtain the four-phase equilibrium data over the temperature range from (273.5 to 296.2) K for the water + methylfluoride system and from (273.7

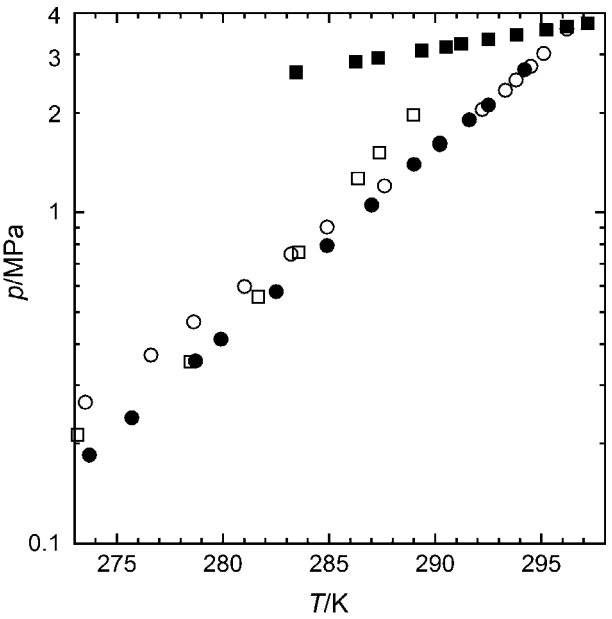

Figure 1. Equilibrium p, T conditions for aqueous liquid + hydrate + vapor three phases in the water + methylfluoride system: ○, present study; and aqueous liquid + hydrate + hydrocarbon liquid + vapor four phases in the water + methylcyclohexane + methylfluoride system; ●, present study. The three-phase equilibrium p, T conditions reported by Villard[12] are also indicated; □, ref 12. Closed squares indicate the saturated vapor pressure of methylfluoride; ■, ref 9.

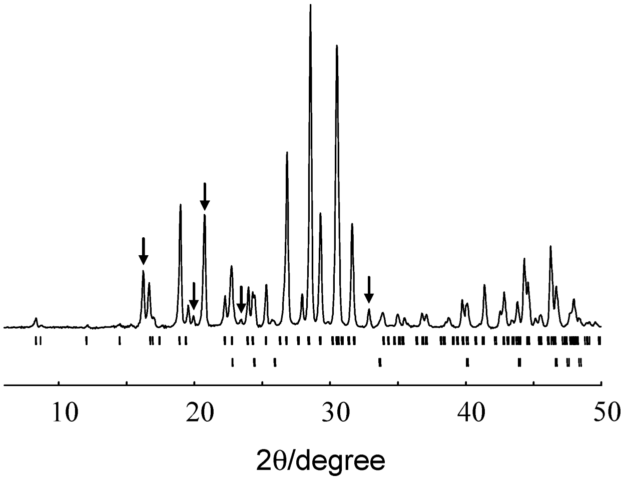

Figure 2. PXRD profiles obtained from hydrate sample prepared in the water + methylcyclohexane + methylfluoride systems. The crystal sample was prepared at p = 0.45 MPa and T = 279.7 K in the water + methylcyclohexane + methylfluoride system. The diffraction measurement was performed at 93 K. The crystallographic structure of the hydrate was determined to be structure H. In the lower part, the upper stick patterns correspond to the structure refinement results of the structure H hydrate, and the lower stick patterns correspond to those of hexagonal ice that was transformed from interstitial water. The arrows indicate the diffraction peaks of unknown crystals that would be formed from methylfluoride, methylcyclohexane, and water. Only the 2θ range from 6° to 50° is shown here.

to 294.2) K for the water + methylcyclohexane + methylfluoride system.

A hydrate crystal sample for the powder X-ray diffraction (PXRD) measurement was prepared with liquid water, methylfluoride and methylcyclohexane using the same experimental apparatus as used for the phase equilibrium measurements. The amounts of the liquid samples were the same as those for the phase equilibrium measurements. The pressure and temperature was set at $p = 0.45$ MPa and $T = 279.7$ K slightly outside the conditions for the simple methylfluoride hydrate formation. The line connecting the test cell and the high-pressure methylfluoride cylinder was opened during the hydrate formation in the test cell to keep p constant by continuously supplying methylfluoride gas to compensate for the pressure reduction in the test cell due to hydrate formation, so that a sufficient amount of hydrate crystals would be stored in the cell. p and T were kept constant for over 200 h along with continuous agitation in the vessel at 400 rpm after nucleation of the hydrate. The vessel was subsequently taken out of the temperature-controlled bath and then immediately immersed into a liquid nitrogen pool in a stainless steel container. We allowed 20 min for T to decrease below $\approx$ 170 K and then disassembled the vessel to remove the formed hydrate crystals. The sample thus prepared was stored in a container kept at a temperature of $\approx$ 120 K and then subjected to PXRD measurements.

For the PXRD measurements, the hydrate sample was finely powdered in a nitrogen atmosphere at a temperature below 100 K. The fine-powdered hydrate samples were top-loaded on a specimen holder made of Cu, and the measurement was done using the parallel beam method (40 kV, 40 mA; Rigaku model Ultima III). The PXRD measurement was performed in the $\theta/2\theta$ step scan mode with a step width of 0.02° in the 2θ renge of 6° to 100° using CuKα radiation. The diffraction measurement was performed at 93 K. Determination of the unit cell parameters was done by a Rietveld method using RIETAN-2000.[16] For the parameter determination, the line position and line profile standard sample LaB_6 (660a, NIST) was used as the external standard.

Results and Discussion

The $p-T$ data of the L_w + H + V three-phase equilibrium in the water + methylfluoride system and of the L_w + H + L_g + V four-phase equilibrium in water + methylcyclohexane + methylfluoride system are listed in Tables 1 and 2, respectively. These data are plotted in Figure 1 together with the $p-T$ data of the L_w + H + V three-phase equilibrium conditions reported by Villard[12] in 1890 and with the saturated vapor pressure of methylfluoride.[9] The new data for the three-phase equilibrium conditions do not well agree with the data reported by Villard.[12] This disagreement might be ascribed to the impurities in the laboratory-made methyfluoride sample and/or to the unspecified uncertainties of the pressure and temperature measurements in the Villard's study.[12]

The equilibrium pressures in the water + methylcyclohexane + methylfluoride system are lower by approximately 0.1 MPa than the corresponding values in the methylcyclohexane-free system at $T = 278$ K. This reduction in the equilibrium pressure due to the addition of methylcyclohexane to the water + methylfluoride system indicates the formation of a double hydrate containing methylfluoride and methylcyclohexane as guests instead of the structure I simple methylfluoride hydrate.[11,12] Considering the molecular size and shape of methylfluoride and methylcyclohexane, the double hydrate is estimated to be a structure H hydrate with methylfluoride molecules in the 5^{12} and $4^35^66^3$ cages and methycyclohexane molecules in the $5^{12}6^8$ cages. The crystallographic structure of the hydrate was identified on the basis of the PXRD measurements. Figure 2 depicts the PXRD profile obtained with the hydrate−crystal sample prepared in the water + methylcyclohexane + methylfluoride system. From this profile, the crystallographic structure is identified to be structure H for the methylfluoride + methylcyclohexane double hydrate. The lattice constants of this hydrate were determined to be $a = 1.218$ nm and $c = 0.999$ nm (Note that the two lattice constants, a and c, are defined for the structure H hydrates). These values are comparable with those for the structure H hydrates formed with methane.[17]

At temperatures below 289 K, the equilibrium pressures in the system with methylcyclohexane are lower than those in the system without methylcyclohexane. But at temperatures above 289 K, the equilibrium pressures in the system with methylcyclohexane overlap with those in the system without methylcyclohexane. These phase equilibria suggest that the stable hydrate changes from the structure H methylfluoride + methycyclohexane double hydrate to the structure I simple methylfluoride hydrate at temperatures above 289 K, as previously shown in several studies reporting similar phase equilibrium data.[18−22]

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