Phase Equilibrium and Crystallographic Structures of Clathrate Hydrates Formed in Methane + 2,2-Dimethylpentane + Water System

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This article reports the pressure−temperature conditions for the four-phase methane vapor + aqueous liquid + hydrocarbon liquid + hydrate equilibrium in the methane + water + 2,2-dimethylpentane system. The pressure and temperature ranges are from (2.430 to 4.823) MPa and from (273.7 to 279.3) K, respectively. The four-phase equilibrium pressures of this system at temperatures below 278.5 K are lower than the three-phase methane vapor + aqueous liquid + hydrate equilibrium pressures in the 2,2-dimethylpentane free system, whereas the four-phase and three-phase equilibrium pressures are equal at temperatures above 278.5 K. This difference in the equilibrium pressures due to the addition of 2,2-dimethylpentane indicates the formation of a structure-H hydrate at temperatures below 278.5 K. The crystallographic structures of the hydrates formed in this system have been identified by powder X-ray diffraction measurements.

Introduction

Clathrate hydrates are crystalline solid compounds that consist of water molecules forming cage structures by hydrogen bonds with guest molecules, such as methane and ethane, enclosed in the cage structures. Depending on the chemical species of the guest substances, water molecules form several different cage structures that interconnect to yield various hydrates of different crystallographic structure, such as structures I, II, and H.[1] Among these hydrates, the structure-H hydrates are unique because they always form with two different guest substances. One is a small-molecule guest substance such as methane and xenon, and the other is a relatively large molecule guest substance such as methylcyclohexane and dimethylbutanes. The latter molecules are called LMGSs (large molecule guest substances). The phase equilibrium conditions in the hydrates forming systems also depend on the chemical species of guest substances. In particular, structure-H hydrates often form under thermodynamic conditions (i.e., the equilibrium pressure is lower and the equilibrium temperature is closer to room temperature) that are milder than those of structure-I and -II hydrates that form exclusively with small-molecule guest substances.

Hydrates may offer the characteristics of high density gas storage media. The amount of a guest gas stored in 1 m^3 of a hydrate may be over 160 m^3. Specifically, hydrates may be utilized as media for natural gas storage and transportation.[2−4] The crystallographic structure of a hydrate formed from natural gas is considered to be structure I, structure II, or structure H depending on the composition of the natural gas and the pressure−temperature conditions of the system. An LMGS may be added to the system of natural gas and water to ensure the formation of a structure-H hydrate. Measurement of the phase equilibrium conditions for the structure-H hydrates and the discovery of effective LMGS to reduce the hydrate equilibrium pressure while not significantly reducing the natural gas storage capacity should contribute to the development of an efficient hydrate-based natural gas storage/transportation technology.

A large amount of phase equilibrium data has been reported for various LMGSs that form structure-H hydrates together with methane. Among such LMGSs, one of the most effective LMGSs with which the lowest equilibrium pressure is available is 1,1-dimethylcyclohexane. Thomas and Behar were the first to report the phase equilibrium data of the structure-H hydrate formed with 1,1-dimethylcyclohexane and methane.[5] Later, Hara et al. reported another data set for the same system.[6] According to the data reported by Thomas and Behar, the equilibrium conditions of the structure-H hydrate formed with 2,2-dimethylpentane is as mild as that of the 1,1-dimethylcyclohexane system.[5] Mehta and Sloan and Østergaard et al. also reported the phase equilibrium data for the 2,2-dimethylpentane system.[7,8] These data are significantly different from the data of Thomas and Behar. In their thermodynamic modeling study, Ballard and Sloan examined, the data from the above-mentioned three research groups. They concluded that the data of Thomas and Behar are accurate because the data from the other two groups represent the equilibrium data for the simple structure-I methane hydrate that is less stable than the structure-H hydrate but may form if the system pressure is set above the equilibrium pressure of the simple methane hydrate at a given temperature.[9] The predictions obtained with the various phase equilibrium calculation programs also differ from each other. The prediction with CSMGem[10] represents the data by Thomas and Behar, whereas those with HWHYD[11] and CSMHYD[12] provide the prediction representing the data by Mehta and Sloan and Østergaard et al., as summarized in Figure 1. To rationalize the controversy about the phase equilibrium of the structure-H hydrate formed with methane and 2,2-dimethylpentane, we have performed accurate measurements of the phase equilibrium data as well as powder X-ray diffraction (PXRD) measurements to identify the crystallographic structure of the hydrate.

Experimental Section

Materials. The fluid samples used in the experiments were deionized, and liquid water, methane of 99.99 % (mass fraction

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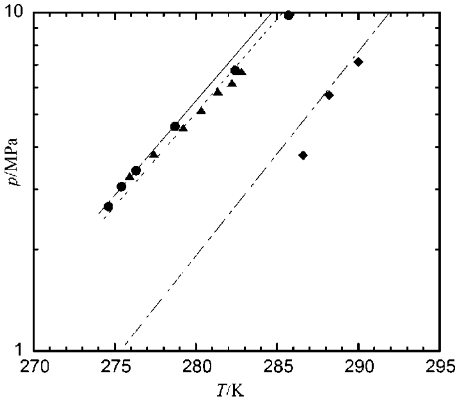

Figure 1. Equilibrium conditions in the system of methane + water + 2,2-dimethylpentane calculated with the phase equilibrium calculation programs and literature data: —, calculated with HW-HYD program;[12] ---, calculated with CSMHYD program;[11] —-—, calculated with CSMGem program,[10] ◆, Thomas and Behar;[5] ▲, Mehta and Sloan;[7] ●, Østergaard et al.[8]

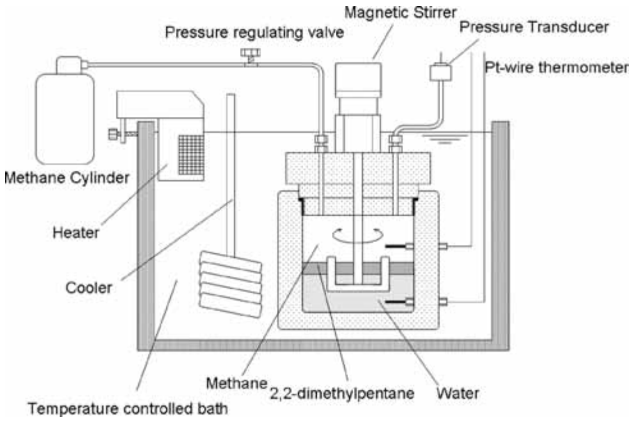

Figure 2. Schematic of the experimental apparatus used for phase equilibrium measurements using the isochoric procedure.

Table 1. Methane-Rich Vapor + Water-Rich Liquid + 2,2-Dimethylpentane-Rich Liquid + Hydrate Four-Phase Equilibrium Pressure−Temperature Conditions in the Methane + Water + 2,2-Dimethylpentane System

T / K	P / MPa	T / K	P / MPa
273.7	2.430	277.1	3.697
274.2	2.592	277.7	3.991
274.9	2.811	278.1	4.202
275.5	3.04	278.3	4.306
276	3.248	278.7	4.559
276.5	3.434	279.3	4.823

basis) certified purity from Takachiho Chemical (Japan), and 2,2-dimethylpentane of 99 % (mass fraction basis) purity from Sigma-Aldrich were obtained. The distilled water was laboratory-made.

Apparatus and Procedure. Figure 2 is a schematic diagram of the apparatus and procedure for measuring temperature−pressure conditions of the four-phase equilibrium: water-rich liquid (L_w) + hydrate (H) + methane-rich vapor (V) + 2,2-dimethylpentane (L_g). The test section was a stainless steel cylindrical vessel with inner dimensions of 50 mm diameter and 120 mm height. In the vessel, a magnetic stirrer was driven through its lid at 400 rpm to agitate the fluids and hydrate. The vessel was immersed in a bath filled with aqueous ethylene glycol solution. The temperature of the vessel (T) was controlled at a prescribed value by the use of a PID-controlled heater and cooler set in the bath. Two platinum resistance thermometers were inserted into the vessel to measure the gas and liquid temperatures. The pressure in the vessel (P) was measured with a strain-gauge pressure transducer (model PHB-A-5MP Kyowa Electric, Japan). The estimated uncertainty of the temperature measurements was ± 0.1 K and that of the pressure measurements was ± 0.015 MPa.

The four-phase equilibrium conditions were measured by the batch isochoric procedure described by Danesh et al.[13] We started each run by placing 30 g of water and 5 g of 2,2-dimethylpentane in the vessel. The vessel was then immersed in the bath. Methane gas was supplied from a high-pressure cylinder through the pressure-regulating valve to the vessel after the air in the vessel was evacuated by a vacuum pump. After P and T were set at the prescribed values in the range of 2.4 to 5.0 MPa and 274 to 280 K, respectively, T was decreased to form a hydrate. When the hydrate formation in the vessel was detected by the decreasing P and the increasing T, the temperature of the bath was maintained to be constant. After a steady state was achieved in the vessel, we recorded the pressure. T was then incrementally increased in steps of 0.1 K. At each temperature step, T was maintained for (10 to 30) h until P had stabilized. By repetition of this incremental temperature increase, a P versus T plot diagram for each run was obtained and a four-phase equilibrium condition was determined from the diagram. When the hydrate was dissociated by the increasing temperature in the vessel, the pressure in the vessel increased. If all of the hydrate was entirely dissociated, then the increase in the pressure became quite low because of the change in the phase equilibrium of the fluids in the vessel. Consequently, the point on the changing P versus T slope was considered to be the four-phase equilibrium point. This operation was repeated under different initial conditions to obtain the four-phase equilibrium data over the desired temperature−pressure range.

X-ray Diffraction. To identify the crystallographic structures of the hydrates, we prepared two hydrate crystal samples under two different conditions using the experimental apparatus described in our previous studies.[14,15] These hydrate samples were formed at 275.1 K (sample A) and 279.3 K (sample B). For the preparation of sample A, the pressure was set at 3.2 MPa to avoid the formation of the structure-I simple methane hydrate that may form at $P > 3.2$ MPa. During the period of hydrate formation in the vessel, a line connecting the vessel and the methane cylinder was intermittently closed. If the pressure decreased from (3.2 to 2.95) MPa, then the equilibrium pressure at this temperature (see Results and Discussion and Table 1 for the equilibrium conditions) was observed after the line was closed; this pressure reduction indicated that the hydrate formation in the vessel was still continuing. Almost complete conversion from water to a hydrate was suggested if no pressure reduction was observed. Agitation in the vessel was continued at 400 rpm over 24 h after the nucleation of the hydrate. After it was confirmed that no further pressure reduction was observed, the vessel was subsequently removed from the temperature-controlled bath and immediately immersed in a liquid nitrogen bath. After T decreased below 160 K, the vessel was removed from the liquid nitrogen pool. The vessel was quickly disassembled at room temperature before the temperature of the hydrate sample increased to 170 K. Then, the lower part of the vessel containing the hydrate sample was again placed in a liquid nitrogen pool, and the hydrate sample was taken out of the vessel. A similar procedure was employed to prepare sample B at the highest system pressure of 4.95 MPa. These prepared samples were stored in a container that was kept at a temperature of below 90 K and was then later subjected to PXRD measurements.

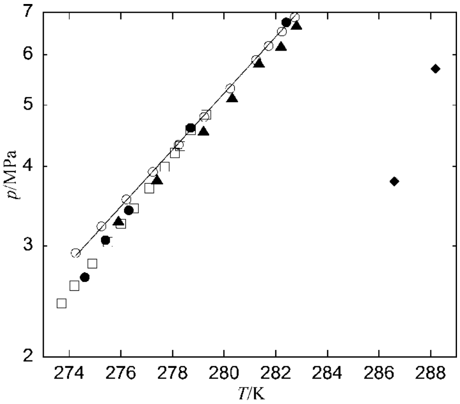

Figure 3. Equilibrium *P* versus *T* conditions for four phases involving clathrate hydrate in the methane + water + 2,2-dimethylpentane system: □, present study; ◆, Thomas and Behar;[5] ▲, Mehta and Sloan;[7] ●, Østergaard et al;[8] ○, three-phase equilibrium *P* versus *T* conditions for the structure-I simple methane hydrate reported in the literature.[17] Solid line is exponential function fit to the data.

For the PXRD measurements, the hydrate samples were 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. The PXRD measurements were done using Cu Kα radiation by parallel beam optics (40 kV, 40 mA; Rigaku model Ultima III). The PXRD measurements were performed in the $\theta/2\theta$ step scan mode with a step width of 0.02° at 93 K. Determination of the unit cell parameter was done by a full-pattern fitting method using the RIETAN-2000 program.[16]

Results and Discussion

The four-phase ($L_w + H + L_g + V$) equilibrium data obtained in the system (methane + water + 2,2-dimethylpentane) are tabulated in Table 1 and depicted in Figure 3. At temperatures below 278.3 K, the data obtained in the present study coincide with the literature data measured by Mehta and Sloan and Østergaard et al. within ± 0.2 K and ± 0.03 MPa. In Figure 3, the three-phase equilibrium data for the structure-I simple methane hydrate[17] are also indicated to demonstrate the pressure depression due to the addition of 2,2-dimethylpentane to the methane + water system. The equilibrium pressure of the hydrate formed with methane + 2,2-dimethylpentane is approximately 0.35 MPa lower than that of the structure-I simple methane hydrate at 274.2 K. The difference in the equilibrium pressures decreases with the increasing *T*. The temperature at which the four-phase equilibrium pressure is equal to the three-phase equilibrium pressure for the structure-I methane hydrate is estimated to be 278.5 ± 0.2 K on the basis of the data shown in Figure 3. At temperatures above 278.5 K, the four-phase equilibrium data obtained in the present study coincide with the three-phase equilibrium data for the structure-I simple methane hydrate[17] within ± 0.1 K and ± 0.02 MPa. These phase equilibrium data suggest that the crystallographic structure of the stable hydrate in the system of methane + water + 2,2-dimethylpentane is structure H at temperatures below 278.5 K, whereas the stable hydrate changes to the structure-I simple methane hydrate at temperatures above 278.5 K.

The crystallographic structures of the hydrates in this system were identified by PXRD measurements. Figure 4 depicts the PXRD profiles of each hydrate sample. From these profiles, sample a is identified to be structure H, and the sample b is identified to be structure I. Accordingly, it is indicated that the hydrate formed at the lower temperature is structure H. The lattice constants of structure-H hydrate in sample a was determined to be $a = 1.223$ nm and $c = 1.008$ nm, and the lattice constant of the structure-I hydrate in sample b was determined to be $a = 1.1869$ nm at 93 K. In conclusion, the stable hydrate in this system is structure H with methane + 2,2-dimethylpentane at temperatures below 278.5 K, whereas the structure-I simple ethane hydrate is stable at temperatures above 278.5 K.

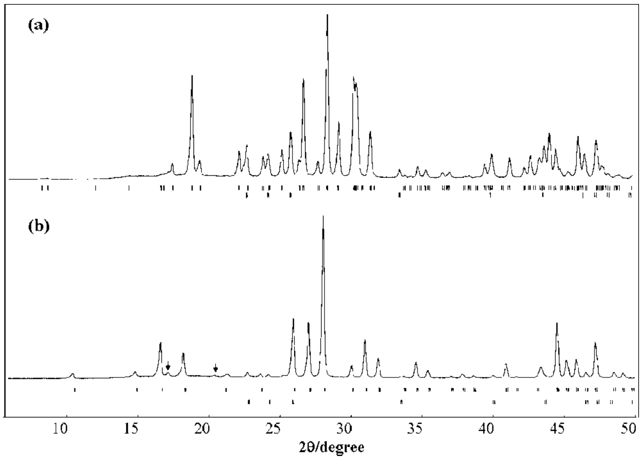

Figure 4. Powder X-ray diffraction profiles obtained from the hydrate samples prepared in methane + water + 2,2-dimethylpentane system. (a) Structure-H hydrate prepared at $P = 2.955$ MPa, $T = 275.1$ K and (b) structure-I hydrate prepared at $P = 4.860$ MPa, $T = 279.3$ K. In the lower part, each upper and lower stick pattern corresponds to hydrate and hexagonal ice, respectively. The arrows indicate the diffraction peak of unknown crystals that would be the solid 2,2-dimethylpentane.

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