Phase Equilibrium for Structure-H Hydrate Formed with Krypton and 2,2-Dimethylbutane

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The temperature and pressure conditions for vapor + liquid + liquid + hydrate four-phase equilibrium in the krypton + 2,2-dimethylbutane + water system have been measured over the temperatures from 273.5 K to 285.6 K. The four-phase equilibrium pressure at a given temperature is lower by 1 MPa to 2.1 MPa than the corresponding equilibrium pressure of structure-II hydrate-forming krypton + water system without 2,2-dimethylbutane. This reduction in the equilibrium pressure due to the addition of 2,2-dimethylbutane suggests the formation of a structure-H hydrate containing krypton as a small-molecule guest and 2,2-dimethylbutane as a large-molecule guest substance. The formation of structure-H hydrate has been confirmed by means of X-ray diffraction measurement.

Introduction

Clathrate hydrates are crystalline compounds consisting of the hydrogen-bonded water molecules forming cages that enclose molecules of guest substances (i.e., species other than water). Depending on the chemical species of the guest substances and their combinations, water molecules configure into different cages that interconnect to form hydrates of various different crystallographic structures such as structure-I, -II, and -H. Formation of a structure-H hydrate requires two different guest substances: one being a small-molecule guest substance like xenon or methane and the other being a large-molecule guest substance like methylbutanes, whereas structure-I or structure-II hydrates may form with a single guest substance. The phase equilibrium conditions for a structure-H hydrate are generally milder (i.e., the equilibrium pressure is lower and the equilibrium temperature is closer to room temperature) than those for a structure-I or structure-II hydrate formed with only a small-molecule guest substance. For example, the equilibrium pressures for structure-H hydrates formed with methane are approximately (1 to 2) MPa lower than those for structure-I methane hydrate.[1] Such milder phase equilibrium property of structure-H hydrate-forming systems is favorable for developing technologies utilizing hydrates. In fact, in recent years, a number of studies related to the utilization of structure-H hydrates formed with methane for natural gas storage and transportation have been reported.[2−8]

In the present study, we investigated the possibility of structure-H hydrate formation with krypton as a small-molecule guest substance, which was previously mentioned by Ripmeester and Ratcliffe[9] but not experimentally confirmed. If a structure-H hydrate forms with krypton under phase equilibrium conditions milder than those of a structure-II simple-krypton hydrate, the structure-H hydrate-forming system may find some industrial applications in hydrate-based technologies such as a working medium in a hydrate-based refrigeration system[10] and a secondary working medium in a refrigeration system[11] because krypton is nonflammable, nontoxic, and not subject to regulations related to greenhouse effect or ozone-depleting potential. Moreover, a structure-H hydrate formed with krypton could be a substitute, to be used safely under low pressure in laboratory studies, for structure-H hydrates formed with methane that require a relatively high pressure and caution due to the flammability/combustibility of methane.

This paper presents four-phase equilibrium temperature−pressure data measured in a krypton + 2,2-dimethylbutane + water system for temperatures from 273.5 K to 285.6 K and the result of X-ray diffraction measurement to indicate that the hydrate formed in this system is of structure-H.

Experimental Section

Materials. Fluid samples used in the experiments were deionized and distilled liquid water; krypton of 99.999 % (volume fraction basis) certified purity from Spectra Gases, Inc., Branchburg, NJ; and 2,2-dimethylbutane of 99 % (mass fraction basis) from Tokyo Kasei Kogyo, Tokyo. Distilled water was laboratory-made. The krypton and 2,2-dimethylbutane were used as supplied by the manufacturers.

Apparatus and Procedure. The experimental apparatus to measure the temperature−pressure conditions for the four phases [water-rich liquid (L_w), hydrate (H), 2,2-dimethylbutane-rich liquid (L_g), and krypton-rich vaporous phase (V)] are the same as those used in our previous studies[12,13] to measure the phase equilibria in the structure-I, -II, or -H hydrate-forming systems with methane. Figure 1 shows the schematic of the apparatus. The main part of the apparatus is a stainless steel cylinder with inner dimensions of 80 mm in diameter and 40 mm in height. A magnetic stirrer is installed in the vessel through its lid to agitate fluids and hydrate crystals inside the vessel at 400 rpm. The vessel is immersed in a temperature-controlled bath to maintain the temperature inside the vessel (T) at a prescribed value. Two platinum-wire resistance thermometers are inserted into the vessel to measure T. The pressure in the vessel (p) is measured with a strain-gauge pressure transducer (model PH-20KB, Kyowa Electric Co. Ltd). The estimated uncertainties

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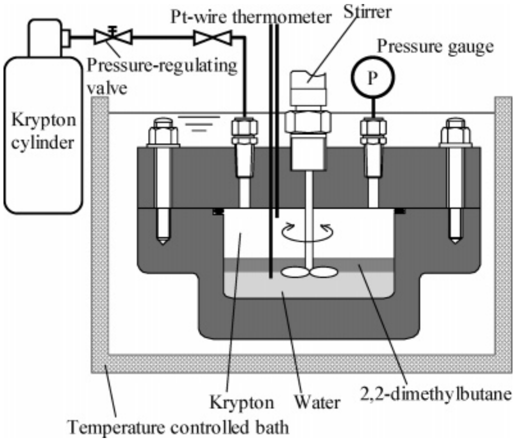

Figure 1. Schematic of the experimental apparatus used for phase equilibrium measurements.

of temperature and pressure measurements are ± 0.1 K and ± 0.004 MPa, respectively.

The equilibrium conditions were measured with the batch, isochoric procedure as described by Danesh et al.[14] Each run was initiated by charging the vessel with 35 cm^3 of liquid water and 20 cm^3 of 2,2-dimethylbutane. The vessel containing the liquid was then immersed into the temperature-controlled bath, and T was set at 290 K. The krypton 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 a prescribed level between 0.4 MPa and 2.1 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 increased T incrementally in steps of 0.1 K. At every temperature step, T was kept 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 $p-T$ data plots changes sharply 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 a temperature range from 273.5 K to 285.6 K. It should be noted that there is possibility of the formation of a metastable structure-II simple-krypton hydrate in the above-mentioned experimental procedure, but we did not observe any experimental sign of the formation of the metastable hydrate.

A hydrate crystal sample for powder X-ray diffraction measurement was prepared with liquid water, liquid 2,2-dimethylbutane, and krypton gas using the same experimental apparatus as used for the phase-equilibrium measurements. The amounts of the liquid samples were the same as those in the phase-equilibrium measurements. The pressure and temperature were set at $p = 1.2$ MPa and $T = 274.0$ K, outside the conditions for structure-II krypton hydrate formation to avoid the possible formation of structure-II krypton hydrate, which may occur at $p > 1.6$ MPa at this temperature. The line connecting the test cell and the high-pressure krypton cylinder was opened during the hydrate formation in the test cell to keep p constant by continuously supplying krypton gas to compensate for 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 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 ≈170 K and then disassembled the vessel to remove the hydrate crystals inside. The samples thus prepared were stored in a container kept at a temperature of ≈170 K and were subjected to X-ray diffraction measurements. For powder X-ray diffraction measurements, the hydrate sample was finely powdered in nitrogen atmosphere at a temperature below 100 K. Powder X-ray diffraction measurements were made using Cu Kα radiation (40 kV, 40 mA; Rigaku model Ultima III) at 93 K.

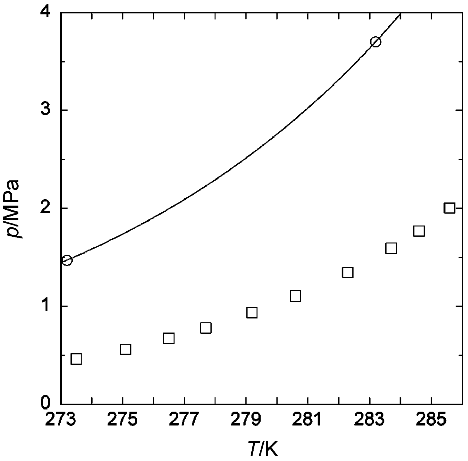

Figure 2. Water-rich liquid + hydrate + 2,2-dimethylbutane-rich liquid + krypton-rich vapor four-phase equilibrium $p-T$ conditions in water + 2,2-dimethylbutane + krypton system: □, present study. Water-rich liquid + hydrate + krypton-rich-vapor three-phase equilibrium conditions in the water + krypton system are also indicated: ○, Holder et al.[16] Solid line is an exponential-function curve best-fitted to the three-phase equilibrium data.

Table 1. Water-Rich Liquid + Hydrate + 2,2-Dimehtylbutane-Rich Liquid + Krypton-Rich Vapor Four-Phase Equilibrium $p-T$ Conditions in Water + 2,2-Dimethylbutane + Krypton System

T/K	p/MPa	T/K	p/MPa
273.5	0.460	280.6	1.103
275.1	0.560	282.3	1.345
276.5	0.673	283.7	1.594
277.5	0.775	284.6	1.768
279.2	0.932	285.6	2.002

Results and Discussion

The $p-T$ data of the $L_w + H + L_g + V$ four-phase equilibrium in the water + 2,2-dimethylbutane + krypton system are listed in Table 1. These data are plotted in Figure 2 together with the $p-T$ data of the $L_w + H + V$ three-phase equilibrium conditions in the water + krypton system without 2,2-dimethylbutane.[16] The four-phase equilibrium pressure in the system with 2,2-dimethylbutane is lower by 1 MPa to 2.1 MPa than the three-phase equilibrium pressure in the system without 2,2-dimethylbutane. The reduction of the equilibrium pressure due to the addition of 2,2-dimethylbutane to the krypton + water system is approximately 60 % for the temperature range of the present measurements. This reduction in the equilibrium pressure

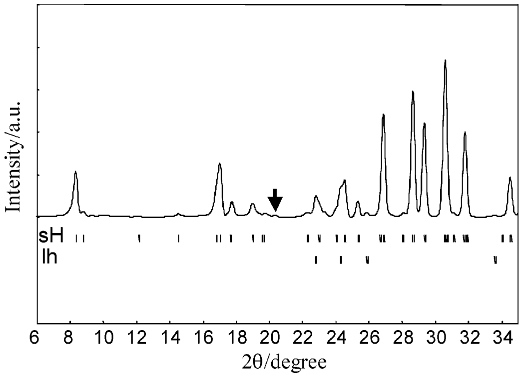

Figure 3. X-ray diffraction profile obtained from hydrate samples prepared in water + 2,2-dimethylbutane + krypton system at $p = 1.2$ MPa and $T = 274.0$ K. The measurement was performed at 93 K. The crystallographic structure of the hydrate was determined to be structure-H. In the lower part, the stick patterns corresponding to the structure refinement result of structure-H hydrate (sH) and hexagonal ice (Ih). The arrow indicates the diffraction peak of solid 2,2-dimethylbutane.

suggests the formation of a double hydrate with krypton and 2,2-dimethylbutane, instead of a structure-II simple krypton hydrate. Considering the molecular size and shape of krypton and 2,2-dimethylbutane, the double hydrate is estimated to be a structure-H hydrate with krypton molecules enclosed in 5^{12} and $4^35^66^3$ cages and 2,2-dimethylbutane molecules enclosed in $5^{12}6^8$ cages. The crystallographic structure of this hydrate was determined by means of X-ray diffraction. Figure 3 depicts the X-ray diffraction profile obtained with the hydrate−crystal sample prepared in the krypton + 2,2-dimethylbutane + water system. This profile indicates that the hydrate is structure-H with unit cell parameters of $a = 1.216$ nm and $c = 0.9972$ nm.

The equilibrium pressures of the structure-H hydrate formed with krypton + 2,2-dimethylbutane, exceeding 0.4 MPa at $T > 274$ K, are not necessarily low as compared to some known hydrates such as those formed with fluorocarbons,[15] propane, and isobutane,[1] which form at temperatures of ≈273 K to 283 K even under a pressure of 0.1 MPa. Thus, the structure-H hydrate formed with krypton may not be a practical candidate for a working medium in the refrigeration systems as mentioned in the Introduction. However, the equilibrium pressures for the structure-H hydrate formed with krypton are substantially lower than the equilibrium pressures of structure-H hydrates formed with methane, which are typically 1 MPa to 2 MPa at 274 K.[1] The structure-H hydrate formed with krypton may be a low-pressure substitute to be used in scientific and engineering studies (e.g., studies to investigate mechanisms of the structure-H hydrate formation) for structure-H hydrates formed with methane.

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