Phase Equilibrium for Structure II Hydrates Formed with Krypton Co-existing with Cyclopentane, Cyclopentene, or Tetrahydropyran

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This paper reports the pressure−temperature conditions for the vapor + liquid + liquid + hydrate four-phase equilibrium in the systems of krypton and water plus each of the following substances: cyclopentane, cyclopentene, and tetrahydropyran. The pressure ranges of the present measurements in the three systems are (0.116 to 7.664) MPa at temperatures from (283.8 to 308.5) K in the cyclopentane system, (0.121 to 2.047) MPa at temperatures from (280.2 to 297.1) K in the cyclopentene system, and (0.118 to 2.075) MPa at temperatures from (278.8 to 296.7) K in the tetrahydropyran system. These equilibrium pressures are lower by at least 4 MPa than those in the binary krypton + water system. The crystallographic structures of the hydrates are identified to be structure II based on the powder X-ray diffraction measurements.

Introduction

Clathrate hydrates are crystalline solid compounds consisting of hydrogen-bonded water molecules configured into cage structures that enclose molecules of *guest* substances. Depending on the molecular structures of the guest substances, the configuration of the water molecules changes to form different cages that interconnect to yield hydrates of different crystallographic structures such as structures I, II, and H. The phase equilibrium conditions in the hydrate-forming systems also depend on the chemical species of the guest substances. For example, methane with a molecular size of 0.4 nm forms the structure I hydrate in the binary methane + water system with the equilibrium pressures of (3 to 10) MPa at temperatures from (275 to 285) K. If cyclopentane having a 0.6 nm molecular size is added to the methane + water system, the crystallographic structure of the resulting hydrate is changed to structure II, and the equilibrium pressure is reduced to the range of (0.5 to 3) MPa at the same temperatures.[1] Such a decrease in the equilibrium pressure (or increase in the equilibrium temperature) of the hydrate-forming systems is favorable for developing novel technologies utilizing hydrates.

Recently, Imai et al.[2] reported their attempt to increase the hydrate equilibrium temperature by adding cyclopentane to the difluoromethane + water system for the development of a hydrate-based refrigeration system, in which the hydrate−equilibrium temperature must be higher than that of a warm environment (such as air, river water, seawater, etc.) for discharging the heat of hydrate formation. This attempt resulted in increasing the maximum equilibrium temperature by approximately 6 K. The maximum equilibrium temperature available with the cyclopentane + difluoromethane double hydrate is reported to be 299.75 K at 1.544 MPa. This hydrate-forming system may be a good candidate for use in a hydrate-based residential air conditioning refrigeration system in which the heat is discharged into the river water or groundwater. However, the equilibrium temperature of approximately 300 K is still insufficient for discharging the heat to the warmer environment such as air in the summer season. In the hydrate-forming system with difluoromethane (or any other guest substances that are not supercritical fluids), the hydrate equilibrium temperature higher than the temperature at which the hydrate equilibrium pressure become equal to the saturated vapor pressure of difluoromethane cannot be practically available. Therefore, there is an upper limit to the equilibrium temperature as long as we utilize guest substances that are not supercritical fluids. This limitation related to the saturated vapor pressure (or liquefaction) of a gaseous guest substance may be avoided by using a guest substance that is in the supercritical state at the temperatures of interest. Relatively small-molecule substances, such as methane, nitrogen, and krypton, are examples of guest substances that are in the supercritical state at the temperatures of interest related to the development of hydrate-based refrigeration system (i.e., 278 K to 310 K).

In this study, we evaluated krypton as a candidate guest substance to be practically applied for the hydrate-based refrigeration system because krypton is known to form a structure II hydrate at relatively mild temperature−pressure conditions as compared to those for the hydrates formed with methane or nitrogen and is less costly than xenon. As the second guest substance used together with krypton to form a double hydrate, cyclopentane, cyclopentene, and tetrahydropyran were tested to increase the equilibrium temperatures. Each of these three substances is known to form a structure II hydrate under atmospheric pressure.[3] Thus, we expected that the equilibrium temperature of the double hydrates formed with krypton and cyclopentane, cyclopentene, or tetrahydropyran would be higher than that of a simple krypton hydrate. The crystallographic structures of the double hydrates were identified using a powder X-ray diffraction method.

Experimental Section

Materials. The 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.

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(Branchburg, NJ), cyclopentane of 99 % (mass fraction basis) certified purity from Aldrich Chemical (Milwaukee, WI), cyclopentene of 98 % (mass fraction basis) certified purity from Tokyo Chemical Industry (Tokyo), and tetrahydropyran of 99 % (mass fraction basis) certified purity from Aldrich Chemical (Milwaukee, WI). The distilled water was laboratory-made. The other fluid samples were used as received by the manufacturers.

Apparatus and Procedure. The experimental apparatus used to measure the pressure−temperature conditions for the four phases [i.e., the krypton-rich vapor phase (V), cyclopentane (or cyclopentene or tetrahydropyran)-rich liquid (L_g), water-rich liquid (L_w), and hydrate (H)] are the same as those used in our previous studies[4−6] to measure the phase equilibria in the system with the structure I, II, or H hydrate. The main part of the apparatus was 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. Two platinum-wire resistance thermometers were inserted into the vessel to measure T. The pressure in the vessel, p, is measured by a strain-gauge pressure transducer (model PH 100 KB, Kyowa Electric Co., Ltd., Tokyo) when p was higher than 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 was ± 0.1 K. The uncertainty of the pressure measurements was ± 0.016 MPa for $p > 2.1$ MPa and ± 0.006 MPa for $p < 2.1$ MPa.

The equilibrium conditions were measured using the batch, isochoric procedure, described by Danesh et al.[7] In each experimental run, the vessel was first charged with liquid water and each of cyclopentane, cyclopentene, or tetrahydropyran. We used 35 g of liquid water and 15 g of each of the liquid guests to ensure the presence of two liquid phases in the test vessel. Liquid water formed a pool approximately 7 mm deep in the vessel. The liquid guest formed an approximately 4 mm layer overlying the water pool. The vessel containing the liquids was then immersed in the temperature-controlled bath. 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 the prescribed level between (0.11 and 7.7) 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 maintained 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 kept constant for (6 to 30) 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 lower 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 the hydrate crystals dissociate and hence is the four-phase equilibrium point. This operation was repeated at several different initial pressures to obtain the four-phase equilibrium data over the temperature range from (283.8 to 308.5) K for the cyclopentane system, from (280.2 to 297.1) K for the cyclopentene system, and from (278.8 to 296.7) K for the tetrahydropyran system. During the course of these phase equilibrium measurements, we found that the equilibrium temperature at a given pressure in the cyclopentane system was higher than the corresponding temperature in the other two systems; hence, the measurements in the cyclopentane system were performed over a wider temperature−pressure range.

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

T/K	p/MPa	T/K	p/MPa	T/K	p/MPa
283.8	0.116	295.5	1.041	304.4	3.955
285.4	0.173	298.0	1.505	305.6	4.689
288.0	0.291	300.1	2.059	306.9	5.828
289.5	0.396	301.3	2.434	308.2	7.286
292.6	0.653	303.0	3.150	308.5	7.664

Hydrate crystal samples for the powder XRD measurements were prepared with liquid water, krypton, and a liquid guest substance (cyclopentane, cyclopentene, or tetrahydropyran) using the same experimental apparatus 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 $p = 1$ MPa and $T = 279$ K, outside the conditions for the structure II simple krypton hydrate formation to avoid the possible formation of the structure II simple krypton hydrate, which may occur at $p > 3$ 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 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 maintained constant for over 50 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 in order to remove the hydrate crystals. The prepared samples were stored in a container kept at a temperature of ≈100 K and were later subjected to XRD measurements.

For the XRD 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 measurements were done using the parallel beam method (40 kV, 40 mA; Rigaku model Ultima III). The XRD measurements were performed in the $\theta/2\theta$ step scan mode with a step width of 0.02° using Cu Kα radiation. The diffraction measurements were performed at 93 K. Determination of the unit cell parameter was done by a full-pattern fitting method using RIETAN-2000.[8]

Results and Discussion

The p, T data of the V + L_g + L_w + H four-phase equilibrium in the systems each containing the cyclopentane, cyclopentene, and tetrahydropyran are listed in Tables 1 to 3. These data are plotted in Figure 1 together with the p, T data of the V + L_w + H three-phase equilibrium conditions in the krypton + water system.[9,10] The four-phase equilibrium pressures measured in the present study are lower by approximately 4 MPa at 283 K than the three-phase equilibrium pressure for the simple krypton hydrate system. This reduction in the equilibrium pressures

Table 2. Krypton-Rich Vapor + Water-Rich Liquid + Cyclopentene-Rich Liquid + Hydrate Four-Phase Equilibrium *p, T* Conditions in Krypton + Cyclopentene + Water System

T/K	*p*/MPa	*T*/K	*p*/MPa	*T*/K	*p*/MPa
280.2	0.121	288.0	0.518	294.4	1.373
281.3	0.148	290.1	0.723	296.2	1.785
284.6	0.296	292.2	0.989	297.1	2.043

Table 3. Krypton-Rich Vapor + Water-Rich Liquid + Tetrahydropyran-Rich Liquid + Hydrate Four-Phase Equilibrium *p, T* Conditions in Krypton + Tetrahydropyran + Water System

T/K	*p*/MPa	*T*/K	*p*/MPa	*T*/K	*p*/MPa
278.8	0.118	288.1	0.606	295.0	1.648
281.1	0.190	291.4	0.992	296.7	2.079
284.4	0.336	293.2	1.277		

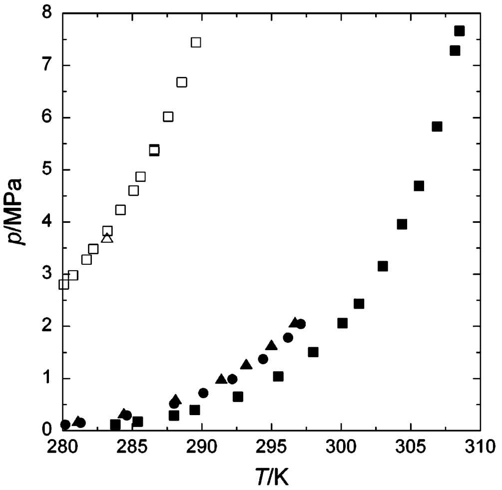

Figure 1. Equilibrium $p-T$ conditions for four phases involving clathrate hydrate formed with krypton and each of the following guest substances: ■, cyclopentane; ●, cyclopentene: ▲, tetrahydropyran (present study). Open symbols indicate three-phase equilibrium $p-T$ conditions in krpton + water system: △, ref 9; □, ref 10.

increases with the increasing temperature and is more than 8 MPa at 290 K. This change in the phase equilibria due to the addition of cyclopentane, cyclopentene, or tetrahydropyran to the krypton + water system suggests the formation of a double hydrate with krypton and cyclopentane, cyclopentene or tetrahydropyran, instead of a structure II simple krypton hydrate.

Considering the molecular size and shape of krypton and cyclopentane, cyclopentene or tetrahydropyran, the double hydrate is estimated to be a structure II hydrate with krypton molecules mainly enclosed in 5^{12} cages and with molecules of the second guests in $5^{12}6^4$ cages. The crystallographic structure of these hydrates was identified on the basis of the XRD measurements. Figure 2 depicts the XRD profiles obtained with the hydrate−crystal samples each prepared in the three systems. From these profiles, the crystallographic structures of the hydrates are all identified to be structure II. These profiles indicate that the lattice constants of each hydrate are 1.726 nm for the cyclopentane + krypton hydrate, 1.722 nm for the cyclopentene + krypton hydrate, and 1.726 nm for the tetrahydropyran + krypton hydrate. These slight differences in the lattice constants would be caused by the different guest molecules.

Among the three systems tested in the present study, the highest equilibrium temperature (or the lowest equilibrium pressure) was found with cyclopentane whereas the lowest was with tetrahydropyran. The equilibrium temperature in the cyclopentane system exceeded 304 K at 4 MPa. The highest equilibrium temperature we measured in the cyclopentane system was 308.5 K at 7.664 MPa. These temperatures are comparable with or higher than the typical ambient temperature in the summer season of most urban areas in the world. Thus, the mixture of krypton gas + liquid cyclopentane + liquid water may be used as the working medium of a hydrate-based residential air conditioning refrigeration system.

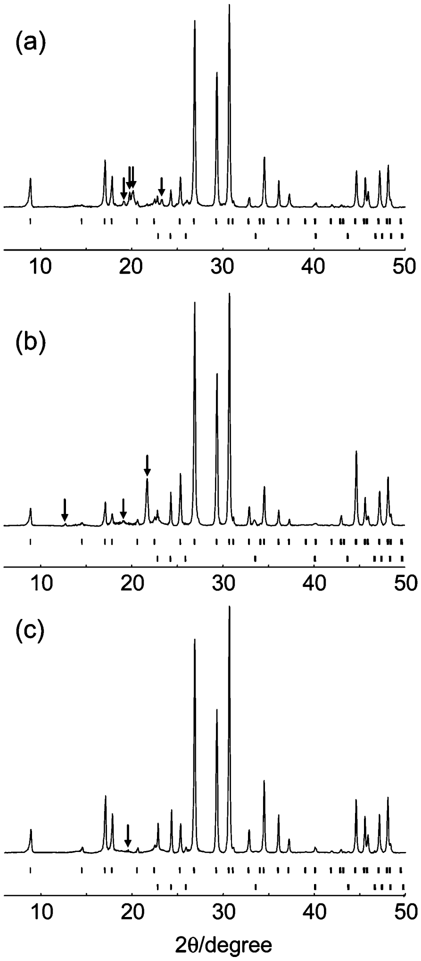

Figure 2. XRD profiles obtained from hydrate samples prepared in the systems of water and krypton plus each of the following substances: (a) cyclopentane; (b) cyclopentene; (c) tetrahydropyran. The crystal samples were prepared at $p = 1$ MPa and $T = 279$ K. The diffraction measurements were performed at 93 K. The crystallographic structure of the hydrate was determined to be structure II. In the lower part, the upper stick patterns correspond to the structure refinement result of structure II hydrate, and the lower stick patterns correspond to those of hexagonal ice that was transformed from interstitial water. The arrows indicate diffraction peaks of unknown crystals that would be formed from second guest substances and water.

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