Phase Equilibrium for Clathrate Hydrates Formed with Difluoromethane or Krypton, Each Coexisting with Fluorocyclopentane

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This paper presents phase-equilibrium pressure−temperature data for the clathrate hydrates formed in two three-component systems—the difluoromethane + fluorocyclopentane + water system and the krypton + fluorocyclopentane + water system. The vapor + liquid + liquid + hydrate four-phase equilibrium in the former system was measured at pressures from (0.110 to 1.040) MPa and at temperatures from (288.65 to 299.55) K, while that in the latter system was measured at pressures from (0.111 to 4.866) MPa and at temperatures from (286.55 to 308.45) K. The temperature in the former four-phase equilibrium was found to exceed that in the three-phase equilibrium in the two-component difluoromethane + water system by 9 K or more over the pressure range up to 1.040 MPa. The temperature in the latter four-phase equilibrium was found to be higher than that in the three-phase equilibrium in the two-component krypton + water system by more than 23 K over the pressure range up to 4.866 MPa.

Introduction

Clathrate hydrates are crystalline solid compounds consisting of hydrogen-bonded water molecules (host molecules) and guest molecules of a different substance, or substances, which we call a guest substance (or guest substances) in this paper. Hydrates are stable only at pressures higher than the water + guest + hydrate equilibrium pressure at a given system temperature or, if the system pressure is given, at temperatures lower than the water + guest + hydrate equilibrium temperature. Thus, it is of engineering importance to know accurately such phase-equilibrium conditions for each hydrate-forming system that can possibly be utilized in some hydrate-based technologies such as the natural gas storage in the form of hydrates or cool-energy storage based on the endothermic nature of hydrate dissociation. Obviously, it is desirable that the phase-equilibrium pressures at temperatures of engineering concerns (typically from 0 °C to 35 °C) are moderate because of economical and safety reasons. Thus, there is a consistent demand for finding hydrate-forming systems that can be safely handled and provide moderate phase-equilibrium pressures. This study was stimulated by this demand.

On the basis of some previous studies,[1−3] we can expect that the phase-equilibrium pressure of a system containing a guest substance of approximately 0.4 nm in molecular size, which forms a hydrate of structure I or structure II by itself, is decreased by the addition of a second guest substance of approximately 0.6 nm in molecular size like a cycloalkane such that a double hydrate of structure II should form. Under ordinary pressure−temperature conditions, the guest substance of smaller molecules is most commonly in the state of supercritical gas or vapor (like methane or carbon dioxide), while the second guest substance is a liquid that may be miscible or immiscible with liquid water (like tetrahydrofuran or cyclopentane). In view of the above nature of mixed-hydrate forming systems, we planned a series of phase-equilibrium measurements using specific mixed-hydrate forming systems each containing a smaller molecule guest substance that is known to form, in the absence of any second guest substance, a hydrate of structure I (sI) or structure II (sII) under relatively low pressures. Our first effort used sI-forming difluoromethane (HFC-32) coupled with sII-forming cyclopentane. The phase-equilibrium temperatures up to 299.75 K were observed in the difluoromethane (HFC-32) + cyclopentane + water system at pressures up to 1.544 MPa.[4] A further increase in the phase-equilibrium temperature is hardly expected in this system because the highest pressure−temperature condition mentioned above is close to the quadruple point at which the four phases—difluoromethane-rich vapor (V) + cyclopentane-rich liquid (L_g) + water-rich liquid (L_w) + hydrate (H)—are in equilibrium. Any pressure increase beyond the quadruple point will not yield any practical increase in the phase-equilibrium temperature.

The phase-equilibrium pressure−temperature conditions observed in the difluoromethane (HFC-32) + cyclopentane + water system[4] barely meet the requirements for the working medium of a hydrate-based refrigeration system[5] now under development, in which the heat generated by hydrate formation needs to be discharged to a moderately warm environment such as air, river water, or groundwater; hence, the phase-equilibrium temperature must be higher than the temperature of the environment. In order to ensure the heat discharge to the environment, particularly into the air in the summer season, hydrate-forming systems having phase-equilibrium temperatures up to 308 K under moderate pressures are desirable.

Very recently, Takeya and Ohmura[6] performed phase-equilibrium measurements involving a krypton + cyclopentane + water system, the system in which an sII-forming gas, krypton, substituted for difluoromethane used in our previous study.[4]

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10.1021/je060309j CCC: $33.50

In addition, Takeya and Ohmura[6] obtained phase-equilibrium data using cyclopentene or tetrahydropyran as the substitute for cyclopentane. Because krypton is a supercritical gas, the phase-equilibrium temperature for a hydrate-forming system containing krypton is not limited by its liquefaction irrespective of the system pressure. The substitution of krypton for difluoromethane extends the possible temperature range for hydrate formation at the cost of a moderate increase in pressure at each temperature level. In fact, Takeya and Ohmura[6] observed equilibrium temperatures up to 308.6 K under pressures up to 7.664 MPa when krypton was coupled with cyclopentane.

This paper reports our more recent phase-equilibrium measurements in which we employed fluorocyclopentane as the second guest substance, which was reported to form, in the absence of any other guest substance, an sII hydrate at 283.7 K under a pressure exerted by its own saturated vapor.[7] Because this temperature exceeds 280.9 K, the phase-equilibrium temperature for the sII cyclopentane hydrate under atmospheric pressure,[8] we expected that the phase-equilibrium for the mixed-hydrate-forming system is shifted in the direction of increasing temperature or decreasing pressure by substituting fluorocyclopentane for cyclopentane. As the smaller molecule guest substance to be coupled with fluorocyclopentane, we employed both difluoromethane and krypton. In the difluoromethane + fluorocyclopentane + water system, we obtained phase-equilibrium temperatures up to 299.55 K under pressures nearly two-thirds of the corresponding pressures in the difluoromethane + cyclopentane + water system tested in our previous study.[4] In the krypton + fluorocyclopentane + water system, phase-equilibrium temperatures up to 308.45 K were obtained under pressures from 58 % to 67 % of the corresponding pressures in the krypton + cyclopentane + water system reported by Takeya and Ohmura.[6]

Experimental Section

Materials. The samples used in the experiments were deionized and distilled water, difluoromethane of 99.9 % (volume basis) certified purity (Asahi Glass Co., Tokyo), krypton of 99.995+ % (mass basis) certified purity (Japan Fine Products Corp., Oyama, Tochigi-ken), and fluorocyclopentane of 99 % (mass basis) certified purity (SynQuest Laboratories, Inc., Alachua, FL). Except for water, the above materials were used as received from their respective manufacturers.

Apparatus and Procedure. The apparatus and procedure that we used in the phase-equilibrium measurements were essentially the same as those detailed in our previous paper.[4] Therefore, they are only briefly outlined here. The test cell, in which a hydrate may be formed and dissociated, was a vertically oriented stainless steel cylinder with a 70.7 cm^3 internal volume. A magnetically driven helical impeller was inserted into the test cell along its axis. The test cell was immersed in a thermostated water bath for controlling the temperature T inside the test cell. For measuring T, a platinum-wire resistance thermometer was inserted into the cell. The pressure p inside the test cell was detected by a strain-gauge pressure transducer (model VPRC-VPRT when 0.1 MPa $\leq p \leq$ 2.0 MPa and model C34GV-VPRT when $p <$ 2.0 MPa; both manufactured by Valcom, Inc., Toyonaka-shi, Osaka, Japan). The estimated uncertainty of the temperature measurements was ± 0.1 K. As for the pressure measurements, the uncertainty was estimated to be ± 0.006 MPa for 0.1 MPa $\leq p <$ 2.0 MPa and ± 0.014 MPa for 2.0 MPa $\leq p <$ 5.0 MPa.

Table 1. V + L_w + L_g + H Four-Phase Equilibrium (*p*, *T*) Conditions in the Difluoromethane + Fluorocyclopentane + Water System

T/K	*p*/MPa	*T*/K	*p*/MPa	*T*/K	*p*/MPa
288.65	0.110	294.15	0.324	297.75	0.657
290.75	0.170	295.45	0.407	298.95	0.857
292.55	0.242	296.55	0.512	299.55	1.040

The operation of each experimental run devoted to obtaining one $p-T$ data point for the V + L_g + L_w + H four-phase equilibrium followed the procedure described by Danesh et al.[9] Each run was commenced by supplying prescribed amounts of liquids, 30 g of liquid water and 10 g of liquid fluorocyclopentane, to the test cell, thereby forming two separate liquid phases inside the cell. After p was set at a prescribed level in the range from (0.1 to 5.0) MPa by supplying the guest gas (difluoromethane or krypton) from a high-pressure gas cylinder through a pressure regulating valve, T was decreased in a stepwise fashion in order to form a hydrate. If we detected a rapid and substantial reduction in p presumably due to the hydrate formation in the test cell, T was held constant at the current level for (5 to 6) h. Subsequently, T was incrementally increased in steps of 0.1 K. At each step, T was held constant for (5 to 6) h. If a hydrate had been formed in the test cell in advance of this temperature-increase process, we could detect a stepwise increase in p, responding to the stepwise increase in T, due to the partial dissociation of the hydrate. The stepwise temperature-increase process was continued until p no longer responded to a further increase in T due to the completed hydrate dissociation. We determined the (p, T) condition recorded during the step beyond which p had leveled off as the four-phase equilibrium condition.

Results and Discussion

The (p, T) data for the V + L_g + L_w + H four-phase equilibrium in the difluoromethane + fluorocyclopentane + water system are compiled in Table 1 and plotted in Figure 1. For comparison, the corresponding data obtained using the difluoromethane + cyclopentane + water system in our previous study[4] and the empirical correlation for the V + L_w + H three-phase equilibrium in the difluoromethane + water system given by Akiya et al.[10] are also plotted in Figure 1. The equilibrium

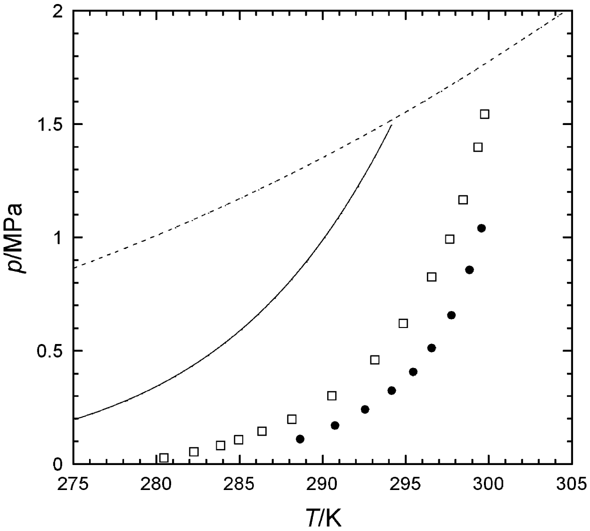

Figure 1. Pressure vs temperature data for the V + L_g + L_w + H four-phase equilibrium and the V + L_w + H three-phase equilibrium in difluoromethane-containing systems: ●, difluoromethane + fluorocyclopentane + water system (this study); □, difluoromethane + cyclopentane + water system (Imai et al.[4]); —, difluoromethane + water system (Akiya et al.[10]). The dotted curve indicates the saturated vapor pressure of difluoromethane.[11]

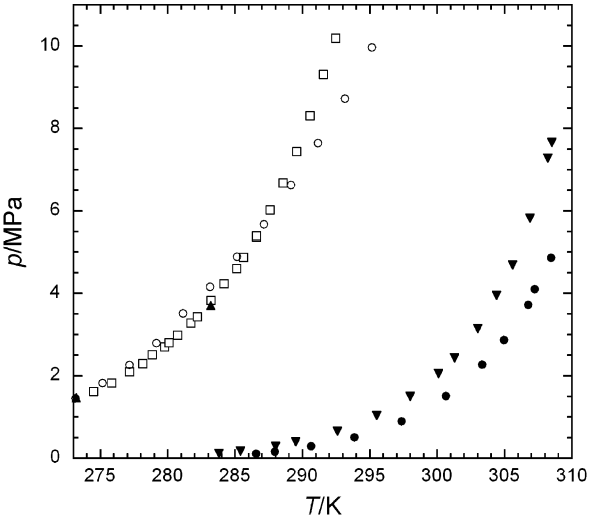

Figure 2. Pressure vs temperature data for the V + L_g + L_w + H four-phase equilibrium and the V + L_w + H three-phase equilibrium in krypton-containing systems: ●, krypton + fluorocyclopentane + water system (this study); ▼, krypton + cyclopentane + water system (Takeya and Ohmura[6]); □, krypton + water system (Sugahara et al.[12]); ○, krypton + water system (Berecz and Balla-Achs[13]); ▲, krypton + water system (Holder et al.[14]).

Table 2. V + L_g + L_w + H Four-Phase Equilibrium (*p*, *T*) Conditions in the Krypton + Fluorocyclopentane + Water System

T/K	*p*/MPa	*T*/K	*p*/MPa	*T*/K	*p*/MPa
286.55	0.111	297.35	0.895	306.75	3.717
287.95	0.162	300.65	1.512	307.25	4.102
290.65	0.288	303.35	2.269	308.45	4.866
293.85	0.521	304.95	2.868		

temperature in the difluoromethane + fluorocyclopentane + water system is higher than that in the difluoromethane + water system by 9 K or more over the pressure range up to 1.040 MPa and is higher than that in the difluoromethane + cyclopentane + water system by (1.5 to 3.5) K over the pressure range from (0.110 to 1.040) MPa. The highest equilibrium temperature we measured in the difluoromethane + fluorocyclopentane + water system is $T = 299.55$ K at pressure $p = 1.040$ MPa. This temperature is 5.5 K higher than the V + L_g + L_w + H quadruple-point temperature for the binary difluoromethane + water system, $T = 294.1$ K at $p = 1.489$ MPa,[10] and is nearly equal to the highest temperature, 299.75 K, that we obtained in the difluoromethane + cyclopentane + water system at a higher pressure, $p = 1.544$ MPa.[4]

The (*p*, *T*) data for the V + L_g + L_w + H four-phase equilibrium in the krypton + fluorocyclopentane + water system are given in Table 2 and plotted in Figure 2. The corresponding data for the V + L_w + H three-phase equilibrium in the krypton + water system[12−14] and for the V + L_g + L_w + H four-phase equilibrium in the krypton + cyclopentane + water system[6] reported in the literature are also plotted in Figure 2 for comparison. The temperature increase due to the addition of fluorocyclopentane to the krypton + water system is more than 23 K over the pressure range up to 4.866 MPa. Compared to the krypton + cyclopentane + water system, an upward shift in the four-phase equilibrium temperature by (2.5 to 3) K is obtained in the krypton + fluorocyclopentane + water system at a given pressure up to about 5 MPa. The highest equilibrium temperature we measured in this system, $T = 308.45$ K at $p = 4.866$ MPa, exceeds the typical summer-season atmospheric temperatures in most urban districts around the world by several degrees or more. This fact indicates that a krypton + fluorocyclopentane + water mixture may be used as the working medium of hydrate-based residential refrigeration systems[5] equipped with simple radiators for directly discharging the heat generated by the hydrate formation into the atmospheric air.

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Received for review July 7, 2006. Accepted August 23, 2006. This study was performed as a part of a joint research project organized by the Tokyo Electric Power Co., Ishikawajima-Harima Heavy Industries Co., Keio University, and the National Institute of Advanced Industrial Science and Technology (AIST) for the purpose of searching for hydrate-forming systems suitable for use in a hydrate-based refrigeration system, a novel piece of residential air-conditioning equipment currently under preliminary development. We are indebted to the project staff of TEPCO and IHI for their encouragement during the course of this study. The financial support by TEPCO and IHI is gratefully acknowledged.

JE060309J