Phase Equilibrium for Clathrate Hydrates Formed with Difluoromethane or Krypton, Each Coexisting with Propan-2-ol, 2-Methyl-2-propanol, or 2-Propanone

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This paper presents phase-equilibrium pressure−temperature data for the clathrate hydrates formed in six three-component systems each consisting of a hydrate-forming gas, a water-soluble freezing-point depression material, and water. These systems are difluoromethane + propan-2-ol + water, difluoromethane + 2-methyl-2-propanol + water, difluoromethane + 2-propanone + water, krypton + propan-2-ol + water, krypton + 2-methyl-2-propanol + water, and krypton + 2-propanone + water. The temperature range over which the phase-equilibrium measurements were performed using each system extended to (268.65 to 266.75) K on the lower side and (284.05 to 293.35) K on the higher side. The phase-equilibrium temperatures in the three difluoromethane-containing systems were found to be lower than that in the binary difluoromethane + water system at the same system pressure above 0.2 MPa at which the equilibrium temperature in the binary system is nearly 275 K. On the contrary, the phase-equilibrium temperatures in the three krypton-containing systems were found to be substantially higher than that in the binary krypton + water system throughout the measurement range for each system.

Introduction

Clathrate hydrates are crystalline solid compounds consisting of water molecules hydrogen-bonded into cage-like lattices and guest molecules encaged in the lattices. The substances that provide such guest molecules in clathrate hydrates (abbreviated as hydrates hereafter) are generally called hydrate formers or, as termed in this paper, guest substances or guests. Thermodynamically, 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, the knowledge of such phase-equilibrium conditions for each hydrate-forming system is of primary importance in any engineering concern involving hydrates. Although numerous phase-equilibrium data are now available for simple hydrates formed by single guest substances, only limited data are available on double hydrates, each formed from two guest substances substantially different from each other in molecular size; i.e., one substance is about 0.4 nm in molecular size and in the state of a supercritical gas or vapor under ordinary pressure−temperature conditions, while the other is about 0.6 nm in molecular size and in the liquid state. Expecting the possible application to hydrate-based refrigeration systems for residential air-conditioning use,[1] we have reported phase-equilibrium data for seven double-hydrate-forming systems in three previous papers.[2−4] These double-hydrate-forming systems were selected expecting their capability of forming hydrates at temperatures exceeding atmospheric temperature in the summer season (typically 300 to 303 K) under moderate pressures, because the heat released by hydrate formation in the higher pressure portion of a refrigeration cycle needs to be discharged to the atmosphere, while heat is to be removed from indoor air by hydrate dissociation (typically at a temperature from 280 to 283 K) in the lower pressure portion of the cycle.

If we envision the use of hydrate-based refrigeration systems in order to generate freezing conditions for, for example, food preservation or ice manufacturing, double-hydrate-forming systems different from any of those tested in our previous studies[2−4] are required. This is because, in the case of freezing applications, hydrates are required to dissociate at a temperature about 268 K under moderate pressures without forming ice. That is, the larger molecule guest substance in each double-hydrate-forming system for the freezing application is required to be water-soluble and to give, when dissolved in the aqueous phase to the stoichiometric concentration (i.e., to the guest-to-water ratio equal to that in the hydrate), a freezing-point depression of about 5 K or over. Some types of alcohols or ketones can be candidates for such guest substances. For example, propan-2-ol (isopropyl alcohol) and 2-propanone (acetone) each coupled with methane were experimentally confirmed to form double hydrates, respectively, at pressures less than the equilibrium pressure for the structure-I methane hydrate at a given temperature above the normal freezing point of water, 273.15 K.[5−7] Propane-2-ol and 2-propanone are also known to yield freezing-point depressions by (6.4 and 5.2) K, respectively, when dissolved in the aqueous phase to the corresponding hydrate stoichiometric concentrations.[8] Therefore, we can expect that propan-2-ol and 2-propanone, each coupled with an appropriate hydrate-forming gas, will provide a guest gas (V) + aqueous liquid (L_w) + hydrate (H) equilibrium at temperatures down to about 268 K at moderate pressures. 2-Methyl-2-propanol (*tert*-butyl alcohol), which was reported to form a structure-II double hydrate with D_2S,[9] is also expected to provide such a phase-equilibrium behavior.

Having been stimulated by the above-described interest, we performed V + L_w + H equilibrium measurements for six

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Table 1. V + L_w + H Three-Phase Equilibrium (*p*, *T*) Conditions in Difluoromethane + Propan-2-ol + Water System

T/K	*p*/MPa	*T*/K	*p*/MPa
268.35	0.138	281.75	0.578
270.15	0.167	284.05	0.757
272.45	0.213	285.55	0.894
275.35	0.289	288.45	1.225
278.85	0.422		

Table 2. V + L_w + H Three-Phase Equilibrium (*p*, *T*) Conditions in Difluoromethane + 2-Methyl-2-Propanol + Water System

T/K	*p*/MPa	*T*/K	*p*/MPa
268.85	0.105	281.55	0.542
271.95	0.154	285.15	0.818
274.95	0.228	287.85	1.105
278.95	0.385		

Table 3. V + L_w + H Three-Phase Equilibrium (*p*, *T*) Conditions in Difluoromethane + 2-Propanone + Water System

T/K	*p*/MPa	*T*/K	*p*/MPa
268.75	0.068	278.65	0.368
271.75	0.120	280.85	0.484
275.05	0.206	282.65	0.610
276.75	0.278	284.05	0.727

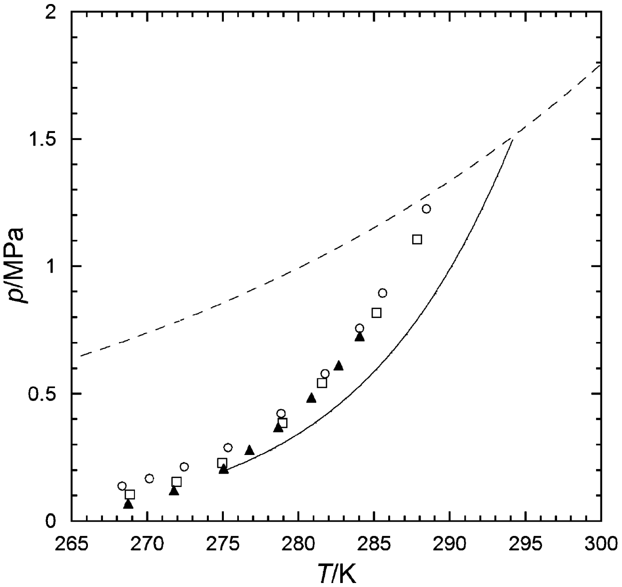

Figure 1. Pressure vs temperature data for the V + L_w + H three-phase equilibrium in difluoromethane-containing systems: ○, difluoromethane + propan-2-ol + water system (this study); □, difluoromethane + 2-methyl-2-propanol + water system (this study); ▲, difluoromethane + 2-propanone + water system (this study); —, difluoromethane + water system (ref 11). The dashed curve indicates the saturated vapor pressure of difluoromethane.[12]

double-hydrate-forming systems, each consisting of difluoromethane or krypton (i.e., a small-molecule guest gas) and one of the three larger molecule water-soluble guest substances—propan-2-ol, 2-methyl-2-propanol, and 2-propanone—besides water. The temperature range over which the phase-equilibrium data were obtained with each system extends to (268.65 to 266.75) K on the lower side and (284.05 to 293.35) K on the higher side. It was confirmed that the V + L_w + H equilibrium was available at a temperature about 268 K with any of the six tested systems. Hence, we can claim their thermodynamic applicability to hydrate-based refrigeration systems for generating water-freezing conditions. All the V + L_w + H equilibrium pressure versus temperature data obtained in these measurements are presented in this paper.

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), propan-2-ol of 99.5+ % (mass basis) certified purity (Aldrich Chemical Co., Milwaukee, WI), 2-methyl-2-propanol of 99+ % (mass basis) certified purity (Aldrich Chemical Co.), and 2-propanone of 99.9+ % (mass basis) certified purity (Aldrich Chemical Co.). 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 used in our previous studies.[2,4] They were detailed in the first paper of this series.[2] 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 VPMC-VHR3-100AN when $p < 0.1$ MPa, model VPRC-VPRT when 0.1 MPa $\leq p <$ 2.0 MPa, and model C34GV-VPRT when 2.0 MPa $\leq p <$ 5.0 MPa; 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 ± 0.001 MPa for $p <$ 0.1 MPa, ± 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.

The operation of each experimental run devoted to obtaining one (*p*, *T*) data point for the V + L_w + H three-phase equilibrium followed the procedure described by Danesh et al.[10] Each run was commenced by supplying 30 g of water and some prescribed amount of a larger molecule guest substance (i.e., propan-2-ol, 2-methyl-2-propanol, or 2-propanone) to the test cell. Assuming that the larger molecule guest substance fully occupies $5^{12}6^4$ cages in a structure-II hydrate, we adjusted the molar ratio of water to the larger molecule guest substance in the test cell to 17:1 such that the composition of the aqueous phase in the test cell would remain constant irrespective of the hydrate formation or dissociation during the experiment. After *p* was set at a prescribed level in the range of (0.06 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 that 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 V + L_w + H equilibrium condition.

Table 4. V + L_w + H Three-Phase Equilibrium (p, T) Conditions in Krypton + Propan-2-ol + Water System

T/K	p/MPa	T/K	p/MPa
267.35	0.380	281.55	1.967
270.25	0.534	285.05	2.982
272.55	0.700	286.95	3.708
275.75	1.018	289.35	4.943

Table 5. V + L_w + H Three-Phase Equilibrium (p, T) Conditions in Krypton + 2-Methyl-2-Propanol + Water System

T/K	p/MPa	T/K	p/MPa
266.75	0.197	281.15	1.130
268.25	0.234	285.65	1.886
270.25	0.289	288.65	2.742
271.95	0.381	291.15	3.630
276.35	0.632	293.35	4.744

Table 6. V + L_w + H Three-Phase Equilibrium (p, T) Conditions in Krypton + 2-Propanone + Water System

T/K	p/MPa	T/K	p/MPa
268.45	0.109	284.25	1.346
271.25	0.193	289.05	2.533
274.85	0.362	291.95	3.741
279.95	0.759	290.45	4.958

Results and Discussion

The (p, T) data for the V + L_w + H three-phase equilibrium in the three difluoromethane-containing systems are separately compiled in Tables 1 to 3 and are plotted together in Figure 1. For comparison, the empirical correlation for the three-phase equilibrium in the binary difluoromethane + water system given by Akiya et al.[11] is also plotted in Figure 1. The phase-equilibrium temperatures in the three-component systems tested in this study are found to be lower than that in the binary difluoromethane + water system under the same pressure above 0.2 MPa, at which the equilibrium temperature in the latter system is nearly 275 K. As expected, the freezing-point depression effect due to propan-2-ol, 2-methyl-2-propanol, or 2-propanone satisfactorily functioned even under the hydrate-forming conditions. We successfully obtained the equilibrium (p, T) data that smoothly extended down to the temperatures of (268 to 269) K from the higher temperature range above the normal water-freezing point. Even at the lowest temperatures mentioned above, we did not detect any sign of water-ice formation about the behavior of impeller rotation in the test cell and also the evolution of p and T, or the (p, T) locus, recorded during the temperature-traversing procedure for determining each equilibrium (p, T) point. The pressures in the V + L_w + H three-phase equilibrium at temperatures of (268 to 269) K in the difluoromethane + propan-2-ol + water and difluoromethane + 2-methyl-2-propanol + water systems are slightly higher than atmospheric pressure, which well meets the requirement for the working medium to be used in refrigeration systems for some freezing applications such as those indicated in the Introduction. The corresponding pressure in the difluoromethane + 2-propanone + water system is somewhat lower than atmospheric pressure; hence, the utility of this system may be more or less restricted. (Note that refrigeration systems are generally designed such that no negative gauge pressure occurs inside the working-medium loops in order to avoid any risk of air leakage into the loops.)

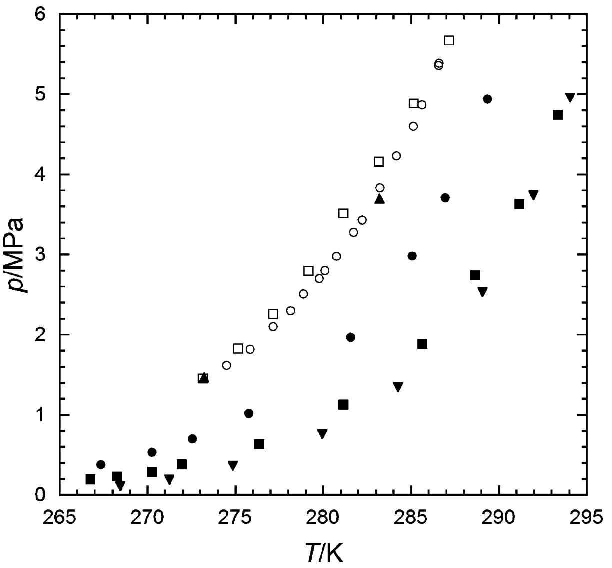

Figure 2. Pressure vs temperature data for the V + L_w + H three-phase equilibrium in krypton-containing systems: ●, krypton + propan-2-ol + water system (this study); ■, krypton + 2-methyl-2-propanol + water system (this study); ▼, krypton + 2-propanone + water system (this study); ○, krypton + water system (ref 13); □, krypton + water system (ref 14); ▲, krypton + water system (ref 15).

The (p, T) data for the V + L_w + H three-phase equilibrium in the three krypton-containing systems are separately compiled in Tables 4 to 6 and are plotted together in Figure 2. The corresponding data for the V + L_w + H three-phase equilibrium in the binary krypton + water system reported in the literature[13−15] are also plotted in Figure 2 for comparison. In contrast to the case of the difluoromethane-containing systems, the phase-equilibrium temperatures in the krypton-containing three-component systems are found to be substantially higher than that in the binary krypton + water system throughout our measurement range for each of the former systems. Again, the freezing-point depression effect due to propan-2-ol, 2-methyl-2-propanol, or 2-propanone satisfactorily functioned in the relevant experiments. We confirmed the V + L_w + H three-phase equilibrium at temperatures down to (267 to 269) K for all the three krypton-containing three-component systems. The pressures in the V + L_w + H three-phase equilibrium at these temperatures in all the three systems more or less exceed atmospheric pressure. The excess of these pressures over atmospheric pressure is relatively small (less than 0.1 MPa) in the krypton + 2-methyl-2-propanol + water and krypton + 2-propanone + water systems as compared to that in the krypton + propan-2-ol + water system; hence, the former two systems may be more advantageous than the latter system for their possible application in refrigeration systems.

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