J. Chem. Eng. Data **2005,** *50,* 1783−1786

Phase Equilibrium for Clathrate Hydrates Formed with Difluoromethane + either Cyclopentane or Tetra-*n*-butylammonium Bromide

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This paper presents phase equilibrium data for the clathrate hydrates formed in two three-component systems—a difluoromethane + cyclopentane + water system and a difluoromethane + tetra-*n*-butylammonium bromide + water system. The vapor + liquid + liquid + hydrate four-phase equilibrium in the former system was measured at pressures from 0.027 MPa to 1.544 MPa and at temperatures from 280.45 K to 299.75 K, while the vapor + liquid + hydrate three-phase equilibrium in the latter system was measured at pressures from 0.175 MPa to 1.215 MPa and temperatures from 286.45 K to 289.95 K. The pressure in the former four-phase equilibrium was found to be lower than that in the two-component difluoromethane + water system by an extent from 0.3 MPa to 0.9 MPa over the temperature range from 280.45 K to 294.1 K, the upper quadruple point for the two-component system. The three-phase equilibrium pressure of the difluoromethane + tetra-*n*-butylammonium bromide + water system has a strong temperature dependency such that, with an increase in the system temperature, it overtakes the three-phase equilibrium pressure of the two-component system, while the former is lower than the latter at temperatures below 289.4 K.

Introduction

Clathrate hydrates are crystalline solid compounds consisting of hydrogen-bonded water molecules that form lattices encaging guest molecules. The guest molecules held in each hydrate may be of a single species or multiple species. The phase-equilibrium conditions in a hydrate-forming system and the crystallographic structure of the hydrate formed in the system depend on the species of the substance (or substances) supplying the guest molecules to the hydrate, which we will call the guest substance. For example, if a guest substance of a ≈0.6 nm molecular size is added to a hydrate-forming methane + water system, the possible structure of the hydrate may be altered from structure I to structure II, resulting in an appreciable reduction in pressure of the gas + liquid + hydrate three-phase equilibrium. Such an extension of the hydrate-formable thermodynamic region may be a problem in the oil and gas industry. Tohidi et al.[1,2] measured the pressure−temperature conditions for the four-phase equilibrium in a system composed of methane and water plus another guest substance having a ≈0.6 nm molecular size (such as cyclopentane, cyclohexane, or neopentane) in order to have an insight into the possible hydrate formation in natural gas + condensate systems. On the other hand, the extension of the hydrate-formable thermodynamic region is favorable for developing hydrate-based technologies such as the natural gas storage in the form of hydrates, the cool energy storage utilizing the endothermic (or exothermic) nature of hydrate dissociation (or formation), etc. There are several examples in the literature describing the attempt at lowering the phase-equilibrium pressure for a methane-containing hydrate by the simultaneous use of a second guest substance, thereby facilitating the natural gas storage and transportation in the form of hydrates.[3−5]

The present study was motivated by an idea of utilizing the above-described possibility of extending the hydrate-formable thermodynamic region with the aid of a second guest substance for the purpose of developing a new technology, i.e., a hydrate-based refrigeration system.[6,7] This system is expected to extract heat from a cooler region (i.e., a space to be refrigerated) by the endothermic hydrate dissociation at a lower pressure and to discharge heat to a warmer region by the exothermic hydrate formation at a higher pressure. To apply this refrigeration system to residential air-conditioning, the heat of hydrate formation needs to be discharged to a moderately warm environment such as air, river water, groundwater, etc. The temperature of river water, for example, in an urban area in or around Tokyo in the summer season is typically ≈298 K; hence, the temperature of the hydrate formation in the refrigeration system must be higher than ≈298 K, desirably under a moderate pressure, to discharge heat to the river water. However, no hydrate-forming system is currently known that satisfies this requirement. If we employ xenon, hydrogen sulfide, chlorine, methane, or nitrogen as a guest substance, an equilibrium temperature of 300 K or even higher is available.[8,9] Nevertheless, none of these guest substances is suitable for practical systems because of the following reasons: the high cost of xenon, the toxicity of hydrogen sulfide and chlorine, and the high equilibrium pressures for the hydrates of methane and nitrogen. Having surveyed many other guest substances based on these requirements, we conceived the possibility of using difluoromethane (HFC-32) and a second guest substance

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10.1021/je050212h CCC: $30.25

to form a mixed hydrate. HFC-32 itself is known to form a structure I hydrate at moderately elevated pressures and at a room temperature. To be more exact, the vaporous HFC-32 + liquid HFC-32 + liquid water + hydrate quadruple point was reported to be at 1.489 MPa and 294.1 K.[10] This temperature is considered to be the upper limit for the equilibrium temperature that we can obtain simply using HFC-32 as the guest substance. If the range of the equilibrium temperature is raised by several degrees Kelvin by the simultaneous use of HFC-32 and a second guest substance, the temperature requirement for the refrigeration system described above should be satisfied. To induce such an effect on the equilibrium condition, the second guest substance needs to form a double hydrate together with HFC-32. We have tested two candidates as the second guest substance—cyclopentane and tetra-*n*-butylammonium bromide (abbreviated TBAB). Cyclopentane is known to form a structure II hydrate by itself at 280.9 K under atmospheric pressure[11] and to form a structure II double hydrate with methane at a pressure significantly lower than that for a structure I methane hydrate.[2] Thus, we expected that, when used together with HFC-32, cyclopentane would play a role analogous to that when used with methane. TBAB is known to form a semi-clathrate hydrate at 285.6 K under atmospheric pressure[12,13] and to form a double hydrate with methane.[14] Therefore, we also expected that the use of TBAB with HFC-32 would yield a reduction in equilibrium pressure and thereby extend the hydrate-formable region in the direction of increasing temperature.

This paper presents the pressure versus temperature data of the HFC-32-rich vapor + cyclopentane-rich liquid + water-rich liquid + hydrate four-phase equilibrium and the HFC-32-rich vapor + TBAB-dissolved aqueous liquid + hydrate three-phase equilibrium that we have measured to confirm our expectations described above. The data obtained with cyclopentane meet our expectations, while those obtained with TBAB show a totally unexpected shift in the equilibrium line from that for the structure I HFC-32 hydrate. However, the latter data may be of scientific interest, because they are the first to show the phase-equilibrium conditions in a hydrate-forming ammonium salt guest + gaseous guest + water system.

Experimental Section

Materials. The samples used in the experiments were deionized and distilled water, difluoromethane (HFC-32) of 99.9 % (volume basis) certified purity (Asahi Glass Co., Tokyo), cyclopentane of 99.9+ % (mass basis) certified purity (Aldrich Chemical Co., Milwaukee, WI), and tetra-*n*-butylammonium bromide (TBAB) of 98+ % (mass basis) certified purity (Aldrich Chemical Co., Milwaukee, WI). Except for water, the above materials were used as received from their respective manufacturers.

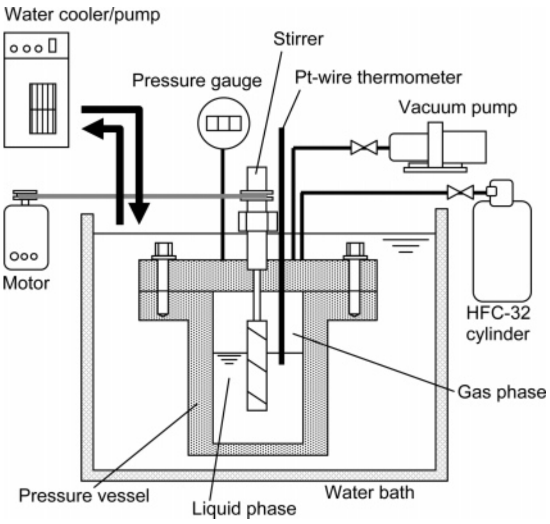

Figure 1. Experimental setup.

Apparatus. Figure 1 shows a schematic of the experimental setup. The major portion of the setup was the test cell, a cylindrical stainless steel cell, in which a hydrate may be formed and dissociated. The inside dimensions of this test cell was 30 mm in diameter and 100 mm in height. A magnetically driven helical impeller was inserted into the cell to allow the radial and axial mixing of the multiphase contents of the cell. The test cell was immersed in a water bath equipped with a PID-controlled water cooling/pumping unit. For measuring the temperature *T* inside the test cell, a platinum wire resistance thermometer was inserted into the cell. A strain-gauge pressure transducer (model VPRC-VPRT, Valcom Inc., Toyonaka-shi, Osaka) was used to measure the pressure *p* inside the test cell when $p \geq 0.1$ MPa. For measuring *p* less than 0.1 MPa, a strain-gauge absolute pressure transducer (model VPRC-VHR3, Valcom Inc., Toyonaka-shi, Osaka) was used instead. 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 $p \geq 0.1$ MPa and ± 0.001 MPa for $p < 0.1$ MPa.

Procedure. The equilibrium $p-T$ conditions that we measured were for the four phases—HFC-32-rich vapor (V) + cyclopentane-rich liquid (L_g) + water-rich liquid (L_w) + hydrate (H)—and for the three phases—HFC-32-rich vapor (V) + TBAB-dissolved aqueous solution (L_w) + hydrate (H). To determine each equilibrium $p-T$ condition, we followed the procedure described by Danesh et al.[15] Each experimental run was started by supplying prescribed amounts of liquids to the test cell. We adjusted the water-to-cyclopentane and water-to-TBAB molar ratios to 17:1 and 24:1, respectively. The former ratio coincides with the stoichiometric water-to-cyclopentane ratio in a structure II hydrate with $5^{12}6^4$ cages fully occupied by cyclopentane molecules. The latter ratio coincides with the stoichiometric water-to-TBAB ratio in a particular type of TBAB semi-clathrate hydrates, which is reported in the literature[13] to give the highest equilibrium temperature under atmospheric pressure. The air inside the test cell was flushed three times by HFC-32 supplied from a high-pressure gas cylinder through a pressure-regulating valve, repeating the pressurization of the cell with HFC-32 and its evacuation from the cell. HFC-32 was then supplied to the cell until the pressure inside the cell (*p*) was increased to the desired level in the range from 0.1 MPa to 1.6 MPa. When this level was below 0.1 MPa, the cell was evacuated with the aid of a vacuum pump. After *p* was adjusted to the desired level, the valve in the line connecting the cell and the gas cylinder was closed to stop the supply of HFC-32.

After both *p* and *T* became constant, we started the operation of decreasing *T* in a stepwise fashion. The magnitude of the drop in *T* from one step to the next was 1 K to 2 K, while the isothermal period between the succeeding two temperature drops was approximately 30 min. 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 h to 6 h. Subsequently, *T* was incrementally increased in steps of 0.1 K. At each step, *T* was held constant for 5 h to 6 h. If a hydrate had been formed in the test cell in advance of

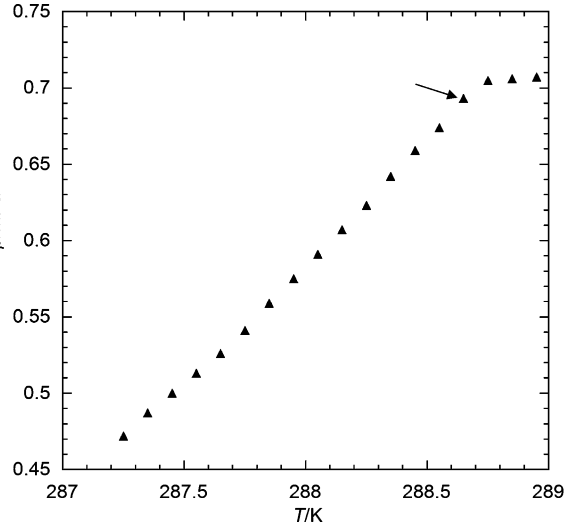

Figure 2. Typical $p-T$ data obtained in an experimental run to determine the $V + L_w + H$ three-phase equilibrium condition in the HFC-32 + TBAB + water system. The data points in this diagram show a $p-T$ locus during a stepwise increase in the temperature T. Whenever a hydrate is present in the test cell, p is increased with an increase in T due to a partial dissociation of the hydrate. The increase in p stops once the hydrate has been completely dissociated. The data point obtained just before p leveled off is indicated by the arrow. This point is assumed to represent a three-phase equilibrium condition, which is read as $p = 0.693$ MPa and $T = 288.55$ K.

Table 1. $V + L_w + H$ Three-Phase Equilibrium $p-T$ Conditions in HFC-32 + Water System

T/K	p/MPa	T/K	p/MPa
278.15	0.270	289.05	0.893
283.15	0.463	290.95	1.084
285.95	0.648		

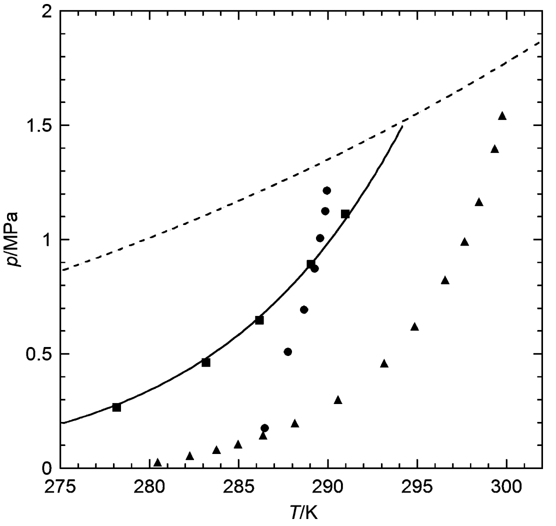

Figure 3. Collected $p-T$ data for the $V + L_w + H$ three-phase equilibrium in the systems of HFC-32 + water (■) and HFC-32 + tetra-*n*-butylammonium bromide + water (●) and for the $V + L_g + L_w + H$ four-phase equilibrium in the system of HFC-32 + cyclopentane + water (▲). The solid curve is due to the empirical correlation for the $V + L_w + H$ three-phase equilibrium in the HFC-32 + water system.[10] The dashed curve indicates the saturated vapor pressure of HFC-32.[16]

Table 2. $V + L_g + L_w + H$ Four-Phase Equilibrium $p-T$ Conditions in HFC-32 + Cyclopentane + Water System

T/K	p/MPa	T/K	p/MPa
280.45	0.027	294.85	0.621
282.25	0.055	296.55	0.825
283.75	0.082	297.65	0.992
286.35	0.145	298.45	1.166
288.05	0.198	299.35	1.398
290.65	0.302	299.75	1.544
293.15	0.459		

this temperature increase process, we could detect a stepwise increase in p, responding to the stepwise increase in T, due to a partial dissociation of the hydrate. The stepwise temperature increase process was continued until p no longer responded to further increases in T because of complete hydrate dissociation. We determined the $p-T$ condition recorded during the step beyond which p had leveled off as the four- or three-phase equilibrium condition. Figure 2 shows a typical set of $p-T$ data obtained in such a stepwise temperature increase process as that outlined above. On the basis of this data set, only one equilibrium data point ($p = 0.693$ MPa and $T = 288.55$ K) was obtained. By repeating the stepwise temperature increase process but with different settings of the initial level of p, we finally obtained a set of $p-T$ data representing the phase-equilibrium line for each guest + water system in a pressure range below the vapor−pressure curve (i.e., the vapor + liquid equilibrium line) for HFC-32.

Results and Discussion

To confirm the reliability of the experimental system that we had newly developed, we first measured the $p-T$ conditions for the $V + L_w + H$ three-phase equilibrium of the binary HFC-32 + water system and compared the obtained data to the empirical correlation reported by Akiya et al.[10] The obtained $p-T$ data are given in Table 1 and plotted in Figure 3 together with the prediction due to the correlation of Akiya et al. The deviation in p at a given temperature between our data and the correlation is within ± 0.03 MPa. Because Akiya et al.[10] did not report their $p-T$ data, to which the correlation was fitted, and stated neither the estimated uncertainty in their $p-T$ measurements nor the deviations of the data from the correlation, we cannot discern whether the above-mentioned deviations between our data and the correlation are in their mutual uncertainties. Nevertheless, we find neither any unusual $p-T$ behavior in our data nor systematic deviations between the data and the correlation. On the basis of these facts, we concluded that our $p-T$ measurements performed in the present study were technically sound.

The $p-T$ data of the $V + L_g + L_w + H$ four-phase equilibrium in the HFC-32 + cyclopentane + water system are given in Table 2 and plotted in Figure 3. We can recognize in Figure 3 that the equilibrium pressure in this system is lower than that in the HFC-32 + water system from 0.3 MPa to 0.9 MPa over the temperature range from 280.45 K to 294.1 K, the upper quadruple point for the latter system. The highest equilibrium temperature we measured in the HFC-32 + cyclopentane + water system is $T = 299.75$ K at $p = 1.544$ MPa. This temperature is 5.7 K higher than the $V + L_g + L_w + H$ quadruple-point temperature for the binary HFC-32 + water system, $T = 294.1$ K at $p = 1.489$ MPa,[10] and it almost meets the temperature requirement for the hydrate-based refrigeration system outlined in the Introduction of this paper.

The $p-T$ data of the $V + L_w + H$ three-phase equilibrium in the HFC-32 + TBAB + water system are given in Table 3 and plotted in Figure 3. We now observe an unexpectedly strong temperature dependency of the equilibrium pressure (p). Contrary to our expectation that the equilibrium $p-T$ curve for the HFC-32 + TBAB + water system would be

Table 3. V + L$_w$ + H Three-Phase Equilibrium $p-T$ Conditions in HFC-32 + Tetra-*n*-butylammonium Bromide + Water System

T/K	p/MPa	T/K	p/MPa
286.45	0.175	289.55	1.007
287.75	0.509	289.85	1.125
288.55	0.693	289.95	1.215
289.25	0.873		

entirely shifted from that for the HFC-32 + water system in the direction of decreasing pressure or increasing temperature, the former crosses the latter at $T = 289.4$ (± 0.1) K. This fact means that at temperatures above 289.4 K, TBAB in the HFC-32 + TBAB + water system plays the role of a thermodynamic inhibitor for hydrate formation, while it serves as a promoter at temperatures below 289.4 K. Because the highest equilibrium temperature for the HFC-32 + TBAB + water system available at pressures below the saturated-vapor pressure line for HFC-32 must be lower than the quadruple-point temperature for the HFC-32 + water system by ~4.0 K (see Figure 3), we find no potential advantage of using the former system in the hypothetical refrigeration system outlined in the Introduction. On the other hand, the potential of the HFC-32 + TBAB + water system to exert a substantial pressure change responding to a small temperature change may find some other applications.

Acknowledgment

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 for the purpose of finding 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 Dr. Kenji Watanabe, Tomonari Ito, and Tomohiro Ogawa (TEPCO); Ken-ichi Tahara and Ryuzo Hiraoka; and Dr. Jun-ichi Ochiai (IHI) for their suggestions and encouragement during the course of the project.

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Received for review May 30, 2005. Accepted June 25, 2005. The financial support by TEPCO and IHI is gratefully acknowledged.

JE050212H