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Clathrate Phase Equilibria for the Water + Deuterium Oxide + Carbon Dioxide and Water + Deuterium Oxide + Chlorodifluoromethane (R22) Systems

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Clathrate phase equilibria for two ternary water + deuterium oxide + carbon dioxide and water + deuterium oxide + chlorodifluoromethane (R22) systems were measured at several different mass % of water and deuterium oxide mixtures. Equilibrium dissociation pressures of these two ternary systems at the three-phase (clathrate−liquid−vapor) boundaries range (1.43 to 4.86) MPa and (0.141 to 0.886) MPa, respectively. The temperature range occupied by the three-phase boundary of the water + deuterium oxide + R22 system is a little larger than that of the water + deuterium oxide + carbon dioxide system. The dissociation pressures at the quadruple points were found to steadily increase with deuterium oxide composition.

Introduction

Clathrates are crystalline compounds formed from guest molecules and host water molecules under suitable conditions of temperature and pressure. The water molecules are linked together with hydrogen bonds and form a three-dimensional structure containing cavities capable of entrapping guest molecules. The hydrate structure is stabilized only through the physical interaction between the encaged gas molecules and the water lattice. It has been recognized that the plugging problem of gas pipelines in natural gas transportation was primarily due to the gas hydrate formation between water and natural gases composed of methane, ethane, propane, and other light hydrocarbons. The phase behavior of the gas hydrate formation has been of considerable significance to the natural gas industry. On the other hand the gas hydrate formation has offered the possibility for the development of a seawater desalination process and gas storage and separation processes (Sloan, 1990; Berecz and Balla-Achs, 1983).

The hydrate phase equilibria for the binary water + carbon dioxide system have been investigated in detail by many researchers (Larson, 1955; Robinson, 1971; Adisasmito, 1991; Unruh, 1949). On the other hand, only a few investigators have been reported on hydrate phase equilibria for the binary water + R22 system (Berecz and Balla-Achs, 1983). No experimental data of clathrate phase equilibria for the systems containing deuterium oxide as a host molecule have been, however, reported in the literature. In this work, the ternary water + deuterium oxide + carbon dioxide and water + deuterium oxide + R22 systems containing two host and one guest components were studied in order to investigate the effect of other hosts besides water on the overall clathrate phase equilibria.

Experimental Section

Materials. The carbon dioxide with a minimum purity of 99.9 mol % was supplied by World Gas Co. The R22 used for the present study was supplied by Ulsan Chemical Co. and had a stated purity of 99.5 mol %. Deionized distilled water was used, and the deuterium oxide was from Aldrich Chemical Co. with a purity of 99.9 atom %. All chemicals were used without further purification.

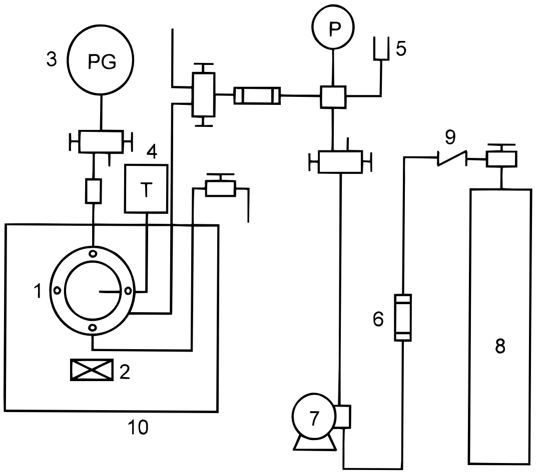

Figure 1. Schematic diagram of the experimental apparatus used in this work: 1, equilibrium cell; 2, magnet; 3, pressure gauge; 4, thermometer; 5, rupture disk; 6, check valve; 7, high-pressure pump; 8, CO_2 cylinder; 9, line filter; 10, water bath.

Apparatus. A schematic diagram of the experimental apparatus is shown in Figure 1. The equilibrium cell was made of 316 stainless steel and had an internal volume of about 50 cm^3. Two sight glasses equipped at the front and back of the cell allowed visual observation of phase transitions. The cell contents were vigorously agitated by a magnetic spin bar with an external magnet immersed in a water bath. The temperature of the water bath was controlled by an externally circulating refrigerator/heater. The temperature in the cell was measured by the K-type thermocouple with a digital thermometer (Cole-Parmer, 8535-26) with a resolution of ±0.1 K. This thermometer was calibrated with the ASTM D900 mercury thermometer. A Heise gauge (CMM 44307) ranging (0 to 200) bar with a maximum error of ±0.1 bar was used to measure the relatively high dissociation pressures of the water + deuterium oxide + carbon dioxide system. For the water + deuterium oxide + R22 system, a pressure gauge supplied from Ujin Instrument Co. (W1081, 0 to 10 bar range) was used since the expected dissociation pressures of this system were below 0.9 MPa.

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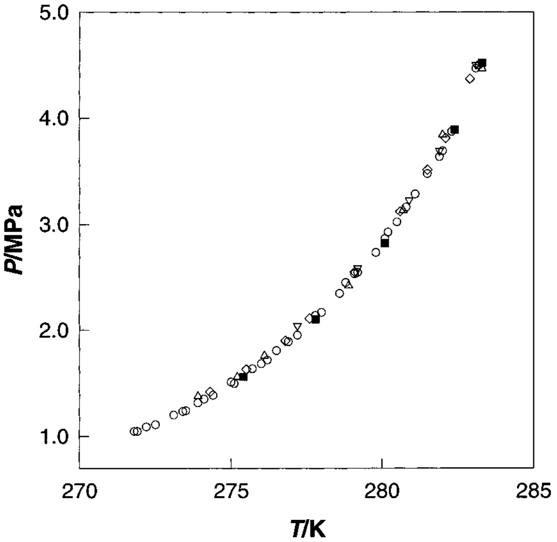

Figure 2. Hydrate equilibrium conditions of carbon dioxide for assuring the validity of the apparatus: (■) this work; (○) Larson (1955); (△) Robinson (1971); (▽) Unruh (1949); (◇) Adisasmito et al. (1991).

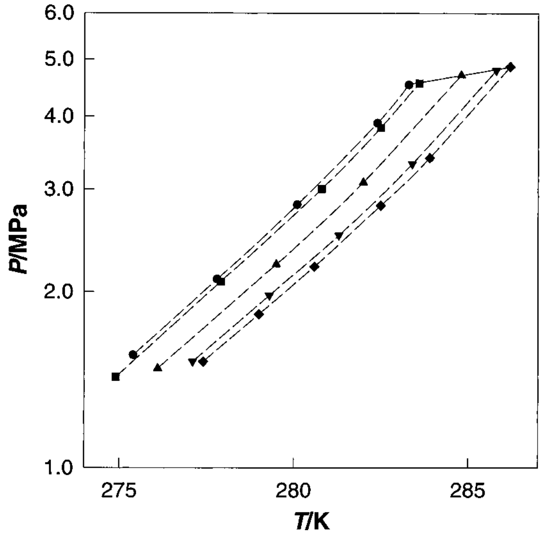

Figure 3. Experimental dissociation pressures for the water + deuterium oxide + carbon dioxide system: (●) 0 mass % D_2O; (■) 10 mass % D_2O; (▲) 50 mass % D_2O; (▼) 80 mass % D_2O; (◆) 100 mass % D_2O.

Table 1. Equilibrium Dissociation Pressures for the Water + Deuterium Oxide + Carbon Dioxide System

mass % of D_2O	T/K	P/MPa
0	275.4	1.56
	277.8	2.10
	280.1	2.82
	282.4	3.89
	283.3[a]	4.52[a]
10	274.9	1.43
	277.9	2.08
	280.8	3.00
	282.5	3.82
	283.6[a]	4.55[a]
50	276.1	1.48
	279.5	2.23
	282.0	3.08
	284.8[a]	4.70[a]
80	277.1	1.52
	279.3	1.97
	281.3	2.50
	283.4	3.31
	285.8[a]	4.79[a]
100	277.4	1.52
	279.0	1.83
	280.6	2.21
	282.5	2.81
	283.9	3.39
	286.2[a]	4.86[a]

[a] Quadruple point (clathrate + liquid mixture of H_2O and D_2O + liquid CO_2 + vapor).

Table 2. Equilibrium Dissociation Pressures for the Water + Deuterium Oxide + Chlorodifluoromethane (R22) System

mass % of D_2O	T/K	P/MPa
0	276.3	0.141
	279.4	0.207
	283.1	0.329
	287.4	0.587
	290.1[a]	0.830[a]
10	279.2	0.186
	282.6	0.294
	285.0	0.397
	288.4	0.620
	290.5[a]	0.840[a]
50	278.7	0.159
	284.4	0.344
	287.1	0.492
	288.5	0.580
	290.3	0.747
	291.2[a]	0.863[a]
100	279.9	0.165
	282.8	0.237
	285.4	0.337
	288.2	0.485
	290.8	0.699
	292.4[a]	0.886[a]

[a] Quadruple point (clathrate + liquid mixture of H_2O and D_2O + liquid R22 + vapor).

Procedure. The experiment begins by charging the equilibrium cell with about 20 cm^3 of the mixtures of water and deuterium oxide. After the cell was pressurized to a desired pressure with either carbon dioxide or R22, the system was then cooled to about 5 K below the anticipated clathrate-forming temperature. Once the system temperature becomes constant, clathrate nucleation was induced by agitating the magnetic spin bar with the immersed magnet in the water bath. When the clathrates formed and the system pressure reached a steady-state condition, the cell temperature increased at a rate of about 1 K/h until the clathrate phase was in coexistence with the liquid and vapor phases. The system temperature was then slowly raised at a rate of 0.2 K/h. The nucleation and dissociation steps were repeated at least two times in order to reduce the hysteresis phenomenon. When a very small amount of crystals existed, by visual observation, without significantly increasing or decreasing its size, and the system temperature was kept constant at least for 8 h after stabilizing the system pressure, the pressure was considered as an equilibrium clathrate dissociation pressure at the specified temperature.

Results and Discussion

In order to investigate clathrate dissociation behavior for the mixtures containing two host and one guest components, the two ternary water + deuterium oxide + carbon dioxide and water + deuterium oxide + R22 systems were chosen and the experiments were performed at several concentration ratios of the water and deuterium oxide mixtures. In order to verify the experimental apparatus and procedure, the clathrate dissociation pressures of the water + carbon dioxide system measured in this work were compared with those of Larson (1955), Robinson and Mehta (1971), Unruh and Katz (1949), and Adisasmito

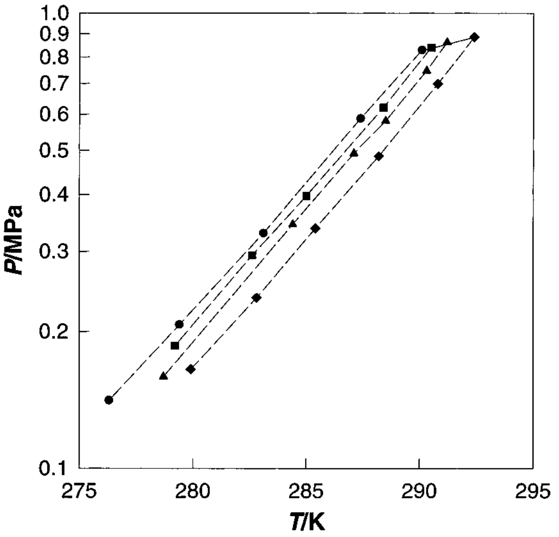

Figure 4. Experimental dissociation pressures for the water + deuterium oxide + chlorodifluoromethane (R22) system: (●) 0 mass % D_2O; (■) 10 mass % D_2O; (▲) 50 mass % D_2O; (♦) 100 mass % D_2O.

et. al. (1991), as shown in Figure 2. Both results were found to be in good agreement within a maximum deviation of about ±0.12 MPa. Three-phase, clathrate, liquid, and vapor, equilibrium measurements of the water + deuterium oxide + carbon dioxide system are illustrated in Figure 3, and the clathrate dissociation pressure values are listed along with the corresponding temperatures and deuterium oxide compositions in Table 1. As the mass % of deuterium oxide increased, the clathrate dissociation temperature increased at a specific pressure. The clathrate equilibrium dissociation pressure lines show the same pattern of behavior over the entire range of the three-phase boundary.

The clathrate equilibrium measurements for the water + deuterium oxide + R22 system are presented in Table 2 and depicted in Figure 4. The clathrate dissociation pressures for the binary water + R22 system were compared with those of Berecz and Balla-Achs (1983). They were found to be in good agreement within a maximum deviation of about ±0.0067 MPa. The overall pattern of the water + deuterium oxide + R22 system is similar to that of the water + deuterium oxide + carbon dioxide system, as shown in Figures 3 and 4.

The quadruple points of the two ternary systems are also presented in Tables 1 and 2 along with the corresponding deuterium oxide compositions, and the quadruple loci were expressed by the solid lines in Figures 3 and 4.

The equilibrium dissociation pressures of the water + deuterium oxide + R22 system range from 0.141 MPa up to 0.886 MPa, considerably lower than those of the water + deuterium oxide + carbon dioxide system. The highest dissociation pressure, 0.886 MPa, corresponds to the quadruple point of the binary deuterium oxide + R22 system at 292.4 K. The pressure range occupied by the three-phase clathrate–liquid–vapor boundary of the water + deuterium oxide + R22 system was found to be quite lower than that of the water + deuterium oxide + carbon dioxide system. On the other hand, the corresponding temperature range of the water + deuterium oxide + R22 system is a little higher than that of the water + deuterium oxide + carbon dioxide system.

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