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Fluid Phase Equilibria

Phase equilibrium relations for binary mixed hydrate systems composed of carbon dioxide and cyclopentane derivatives

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ARTICLE INFO

ABSTRACT

Thermodynamic stability boundaries of carbon dioxide + cyclopentane, carbon dioxide + cyclopentanone, and carbon dioxide + fluorocyclopentane mixed hydrates have been investigated in the range of 274.19–293.72 K and up to 4.88 MPa. The phase equilibrium curves of the structure-II mixed hydrates are located at a temperature remarkably higher than that of the structure-I simple carbon dioxide hydrate. The highest temperature point of each four-phase (hydrate, aqueous, cyclopentane derivative-rich, and gas phases) equilibrium curve was 292.60 K (for the first system), 284.78 K (for the second system), and 293.72 K (for the third system)

1. Introduction

Clathrate hydrate is a solid crystalline, which has an ice-like appearance. Guest species like hydrocarbons and noble gases construct clathrate hydrates with host water molecules. There are several kinds of hydrate cages and some of them are combined to form specific hydrate structures. The unit cell of the structure-I (s-I) hydrate consists of two 5^{12}-cages (S-cages) and six $5^{12}6^2$-cages (M-cages). In the same manner, that of the structure-II (s-II) hydrate is formed with sixteen S-cages and eight $5^{12}6^4$-cages (L-cages). Crystal structures and thermodynamic stabilities of gas hydrates mainly depend on the kind of guest species [1].

Gas hydrate is suggested to be utilized for some applications such as gas storage and transport, gas isolation, gas separation, refrigeration, and so on. However, high pressure and low temperature are naturally required for its formation and stabilization. Wherever hydrate is operated practically, therefore, it is necessary to moderate the working conditions. The reasonable way to moderate these conditions is the addition of the second guest species which is called thermodynamic promoters [1–6].

In the present study, three five-membered cyclic hydrocarbon molecules (cyclopentane (c-C_5H_{10}), cyclopentanone (c-C_5H_8O), and fluorocyclopentane (c-C_5H_9F)) were selected as a candidate for thermodynamic promoter. Five-membered cyclic hydrocarbons

have a suitable molecular size for the L-cage occupancy of s-II hydrates, and they may work as thermodynamic promoters [2–6]. The pressure–temperature relations for carbon dioxide (CO_2) + c-C_5H_{10} derivative + water systems were measured under four-phase equilibrium conditions (hydrate, aqueous, c-C_5H_{10} derivative-rich, and gas phases). The crystal structure of gas hydrate was analyzed by means of powder X-ray diffractometry (PXRD). Furthermore, the dissociation enthalpies of the CO_2 + c-C_5H_{10} derivative mixed hydrates were roughly estimated with Clapeyron equation under the assumption of full compartmental occupancy in S- and L-cages.

2. Experimental

2.1. Apparatus

The high-pressure cell (inner volume: 10 cm^3, maximum working pressure: 5 MPa) is the same as the one used previously [7]. The temperature was controlled with the thermocontroller (Taitec, CL-80R) and the program unit (Taitec, PU-5). The equilibrium temperature was measured with the thermistor thermometer (Takara, D632, reproducibility: 0.02 K). The equilibrium pressure was measured with the pressure gauge (Valcom, VPRT, maximum uncertainty: 0.02 MPa). PXRD pattern was measured using a diffractometer (Rigaku, Ultima IV) with a Rigaku D/teX ultra high-speed position sensitive detector and CuKα X-ray (generation power: 40 kV, 50 mA).

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Table 1
Four-phase equilibrium conditions (temperatures T and pressures p) for $CO_2 + c$-C_5H_{10} derivative + water systems. Asterisks indicate the maximum equilibrium temperatures.

T (K)[a]	p (MPa)[a]	T (K)[a]	p (MPa)[a]	T (K)[a]	p (MPa)[a]
$CO_2 + c$-C_5H_{10} + water system		$CO_2 + c$-C_5H_8O + water system		$CO_2 + c$-C_5H_9F + water system	
280.16	0.08	274.19	0.47	283.18	0.05
280.76	0.11	274.49	0.48	284.21	0.13
281.22	0.15	275.42	0.56	285.20	0.22
283.17	0.34	276.46	0.66	286.22	0.33
284.04	0.45	277.36	0.77	287.24	0.46
285.11	0.60	278.39	0.91	288.24	0.61
286.09	0.76	279.36	1.07	289.23	0.81
287.07	0.96	280.34	1.26	290.23	1.04
288.03	1.20	281.34	1.50	291.25	1.36
289.03	1.49	282.31	1.79	292.15	1.76
290.03	1.85	283.24	2.17	293.19	2.46
291.01	2.36	284.30	2.64	293.56	2.84
291.21	2.45	284.78*	3.21	293.72*	3.21
291.95	2.82	284.60	3.68	293.66	3.60
292.45	3.31			293.47	4.09
292.57	3.71			292.62	4.49
292.60*	4.10			291.89	4.79
292.55	4.36				
292.29	4.71				
291.57	4.88				

[a] Uncertainties u are $u(T) = 0.02$ K, $u(p) = 0.02$ MPa.

2.2. Procedure

A desired volume (each is approximately $2\,cm^3$) of distilled water and c-C_5H_{10} derivative was introduced into the evacuated high-pressure glass cell. The contents were pressurized with CO_2 up to a desired pressure. The cell was immersed into a thermostatic cooling bath. The contents were cooled and agitated to generate mixed hydrates. A magnetic stirrer was moved up and down for agitation. After that, temperature and pressure was gradually increased and decreased respectively to establish four-phase (HL_1L_3G; H: hydrate phase, L_1: aqueous phase, L_3: c-C_5H_{10} derivative-rich phase, G: gas phase) coexistence condition. When the pressure change was within 0.01 MPa and four-phase coexistence was confirmed visually, we determined that the system reached a four-phase equilibrium.

Phase equilibrium curves stand vertically or rather retrograde at a pressure above the maximum temperature point. Temperature was increased very gradually (0.1 K every 1 h) to allow the amount of hydrate to decrease and the system to reach equilibrium at each step. The temperature and pressure where negligible amount of gas hydrates exists were determined as a four-phase equilibrium condition.

The structure of the $CO_2 + c$-C_5H_8O mixed hydrate has not been reported. After the $CO_2 + c$-C_5H_8O mixed hydrates were prepared in the high-pressure cell, the contents were pressurized with additional CO_2 so that almost all of free water was converted to mixed hydrate. The hydrate samples were taken from the cell at 263 K and kept at 77 K. Samples were ground and put flatly on the sample stage of the diffractometer. PXRD was performed at 143 K. The measurements were performed in the stepscan mode with scan rate of 10 degree min^{-1} and step size of 0.02 degree. The PXRD pattern indexing and cell refinement were performed with PowderX [8] and Chekcell [9] programs.

2.3. Materials

CO_2 (molar purity: 0.9999) was purchased from Neriki Gas Co., Ltd. c-C_5H_{10} (molar purity: 0.98) was obtained from Tokyo Chemical Industries Co., Ltd. c-C_5H_8O (molar purity: 0.99) was obtained from Merck Ltd. c-C_5H_9F (molar purity: 0.9869) was obtained from SynQuest Laboratories, Ltd. The distilled water was purchased from Wako Pure Chemical Industries, Ltd. All materials were used without further purification.

3. Results and discussion

Table 1 summarizes the four-phase equilibrium relations of the $CO_2 + c$-C_5H_{10} derivative + water systems containing hydrates. The four-phase (HL_1L_3G) equilibrium curves of the $CO_2 + c$-C_5H_{10} derivative mixed hydrate systems are shown in Fig. 1 accompanied with the three kinds of three-phase (HL_1G, HL_2G, and L_1L_2G; L_2: liquefied CO_2-rich phase) equilibrium curves of the simple CO_2 hydrate system [10]. The present four-phase (HL_1L_3G) equilibrium curve of the $CO_2 + c$-C_5H_{10} mixed hydrate system below 3 MPa agrees well with the reported data [11,12]. The
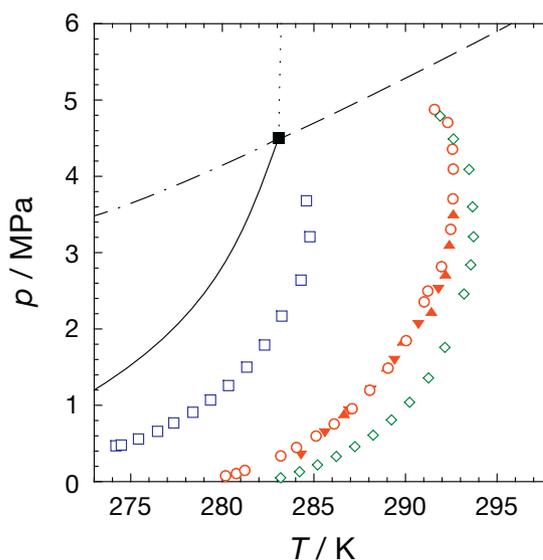
Fig. 1. Phase equilibrium relations of the $CO_2 + c$-C_5H_{10} derivative mixed hydrate systems. Open circles: $CO_2 + c$-C_5H_{10} mixed hydrate (HL_1L_3G), closed triangles: $CO_2 + c$-C_5H_{10} mixed hydrate (HL_1L_3G) [11], closed inverted triangles: $CO_2 + c$-C_5H_{10} mixed hydrate (HL_1L_3G) [12], open squares: $CO_2 + c$-C_5H_8O mixed hydrate (HL_1L_3G), open rhombuses: $CO_2 + c$-C_5H_9F mixed hydrate (HL_1L_3G), solid line: simple CO_2 hydrate (HL_1G) [10], dotted-dashed line: simple CO_2 hydrate (HL_2G) [10], dotted line: simple CO_2 hydrate (HL_1L_2) [10], dashed line: $CO_2 +$ water (L_1L_2G) [10] systems, closed square: quadruple point of simple CO_2 hydrate (HL_1L_2G) [17].