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Four-Phase Equilibrium Relations Including Clathrate Hydrate Phase in Ternary System of Xenon, Benzene, and Water

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ABSTRACT: Thermodynamic stability boundaries of xenon (Xe) + benzene mixed hydrate system were measured in a temperature range of (274.1 to 284.4) K and pressure range up to 0.5 MPa. The four-phase equilibrium curve of structure-II hydrate (H_{sII}), aqueous (L_w), C_6H_6-rich liquid (L_{HC}), and gas (G) phases in the Xe+benzene mixed hydrate system intersects with the three-phase equilibrium curve (H_{sI}+L_w+G) in the structure-I simple Xe hydrate system. The slope of H_{sII}+L_w+L_{HC}+G in the Xe+benzene mixed hydrate system changes around (283.00±0.05) K and (0.420±0.005) MPa. At temperatures above 283.00 K, the structure-II Xe+benzene mixed hydrate collapses and instead, the structure-I simple Xe hydrate is formed.

Keywords. Gas hydrate; Phase equilibria; X-ray diffractometry; Benzene; Help gas

1. INTRODUCTION

Gas hydrates are crystalline substances including guest species (noble gases, natural gas constituents, hydrofluorocarbons, and small cyclic compounds) in the hydrogen-bonded water cages.[1] There are several kinds of hydrate cages and some of them are combined to form the specific hydrate structures, structure-I (sI), structure-II (sII), and structure-H (sH). The size of guest species as well as pressures and temperatures determine which structure is formed. The smallest guest species is hydrogen (H_2).[2,3] One of the largest guest species is a dimethylcyclohexane (DMCH) stereo isomer.[4-8] DMCHs do not generate any gas hydrates by itself without the existence of small gas molecules called help gases. The 1,1-DMCH, *cis*-1,2-DMCH and *cis*-1,4-DMCH generate the sH hydrate with assistance of methane (CH_4), while the other DMCH stereo isomers cannot generate it. In the case of using xenon (Xe) as help gas, the *cis*-1,4-DMCH does not generate the sH hydrate.[8] That is, the help gas affects whether the sH hydrate is formed or not. CH_4 is a superior help gas to Xe.

Benzene (C_6H_6) is an important organic compound for chemical industries and a constituent of crude oil. It has been reported that cyclohexane and C_6H_6 form the sII hydrates with assistance of methane[9,10] and Xe[4]. Neither toluene nor *o*-xylene, which is a benzene derivative, generates any clathrate hydrate even in the presence of CH_4,[11] while both methylcyclohexane (MCH) and *cis*-1,2-DMCH generate the sH hydrate in the presence of CH_4[5] and Xe[8,12]. The benzene ring is larger than the cyclohexane ring, although the number of the cyclic carbons is the same. The size of the C_6H_6 molecule would be little bit too large for $5^{12}6^4$-cage of sII hydrate. There might be a possibility of sH benzene hydrate formation in the presence of Xe, instead of CH_4. To clarify both the C_6H_6 enclathration and the function of Xe as help gas, the thermodynamic stability of the Xe+C_6H_6 mixed hydrate is important. The purpose of the present study is to confirm the crystal structure of the Xe+C_6H_6 mixed hydrate and to measure thermodynamic stability boundaries of the Xe+C_6H_6 mixed hydrate in a temperature range from 274 K to a temperature where the Xe+C_6H_6 mixed hydrate collapses.

2. EXPERIMENTAL

Materials used in the present study are summarized in Table 1. All of them were used without further purification.

The experimental apparatus for phase equilibrium measurement used in the present study is almost the same as ones used in the previous work.[12,13] The pressure-proof glass cell (Taiatsu Techno, HPG-10-1) with the transparent polycarbonate supporter was used. The inner volume and maximum working pressure of the glass cell were 10 cm^3 and 5 MPa, respectively. These materials allowed visual observation of the phase behavior in the hydrate, C_6H_6-rich oil (or solid C_6H_6), and aqueous phases under high-pressure conditions. All parts of the high-pressure cell were immersed in a temperature-controlled bath with the thermocontroller (Taitec, CL-80R). The distilled water (approximately 4 cm^3) and C_6H_6 (approximately 1 cm^3) were introduced in the cell. The air dissolved in both phases was purged with Xe three times. After pressurizing with Xe up to the desired pressure, the contents were subcooled to approximately (3 to 5) K below the anticipated equilibrium temperature. Hydrate nucleation was induced by vigorously agitating the contents by the up-and-down movement of a magnetic stirrer bar driven by an exterior permanent magnetic ring. This up-and-down mixing method is most efficient in the preparation of the s-H hydrate because gas, C_6H_6-rich oil (or solid C_6H_6), and aqueous phases effectually keep in touch with each other. After the hydrate nucleation, the bath temperature was increased up to 1 K lower than the anticipated equilibrium temperature. The cell temperature was then slowly (with a rate of 0.1 K for 60 min) elevated to dissociate the formed hydrates. When a very small amount of hydrate crystals remained and the system pressure and temperature were stabilized, the resulting temperature and pressure were measured as an equilibrium condition. An equilibrium point was determined after several repetitions of formation and dissociation. In addition, the same equilibrium measurements using the fresh contents of water, C_6H_6, and Xe were also repeated to avoid metastability. 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: 0.004 MPa). To verify the crystal structure of the Xe+C_6H_6 mixed hydrate, the powder X-ray diffraction (PXRD) pattern was measured on a Shimadzu, MAXima_X XRD-7000 diffractometer with Cu radiation (wavelength, 0.154060 nm; generation power, 40 kV, 40 mA) and a cold stage (Anton Paar TTK450). The hydrate sample for the PXRD measurement was prepared at 277.6 K with the Xe repressurization (up to 0.25 MPa) to increase the amount of sample. The hydrate sample was cooled at 253 K in the refrigerator and then depressurized. The sample was taken from the cell in the cold room controlled at 253 K, where the Xe+C_6H_6 mixed hydrate is stable enough because the equilibrium pressure of Xe+C_6H_6 mixed hydrate is below atmospheric pressure at 253 K as shown in the present study. Before the sample is loaded onto the cold stage, the sample was grained in the mortar immersed in liquid nitrogen. The measurement was done at 153 K in the step scan mode with scan rate of 2 deg/min and step size of 0.02 degrees.

3. RESULTS AND DISCUSSION

3.1. Crystal Structure of Xe+C_6H_6 mixed hydrate.

The PXRD pattern of the Xe+C_6H_6 mixed hydrate prepared at 277.6 K and (0.20 to 0.25) MPa is shown in Figure 1. The pattern clearly indicates that the Xe+C_6H_6 mixed hydrate is the sII (cubic, $Fd3m$). The obtained lattice parameter recorded at 153 K and 0.1 MPa is a= (1.732 ± 0.001) nm, which falls into the category of sII hydrates having slightly larger lattice constant, even in view of their thermal expansivities.[14-17]

3.2. Thermodynamic Stability Boundaries.

The four-phase equilibrium curves of {sII hydrate (H_{sII}), aqueous (L_w), C_6H_6-rich liquid (L_{HC}), and gas (G)} phases and {H_{sII}, L_w, solid C_6H_6 (S_{HC}), and G} phases in the Xe+C_6H_6 mixed hydrate system are listed in Table 2 and shown in Figure 2. The broken (blue) curve in Figure 2 corresponds to the three-phase equilibrium curve for the simple Xe hydrate.[12] The sII Xe+C_6H_6 mixed hydrate is more thermodynamically stable than the sI simple Xe hydrate. At (276.65±0.05) K and (0.175±0.005) MPa along the stability boundaries of the Xe+C_6H_6 mixed hydrate, the solid C_6H_6 phase disappears and instead, the C_6H_6-rich liquid phase appears. That is, the quintuple point of (H_{sII}+L_w+L_{HC}+S_{HC}+G) is there. Note that the densities of the Xe+C_6H_6 mixed hydrate and solid C_6H_6 are larger and smaller than that of the aqueous phase, respectively. The density difference makes it possible to distinguish the mixed hydrate from the solid C_6H_6.

The four-phase equilibrium curve $H_{sII}+L_w+L_{HC}+G$ of the $Xe+C_6H_6$ mixed hydrate system intersects with the three-phase equilibrium curve $H_{sI}+L_w+G$ of the simple Xe hydrate system.

The pressure and temperature relations of the simple Xe hydrate are correlated by the following equation:

$$\ln(p/p_0) = a + bT, \quad \text{where } p_0 = 1 \text{ MPa}. \quad (1)$$

The above equation is superior to two-parameter Clausius-type equation. The constants a and b in the simple Xe hydrate system are –29.204 and 0.10004 K^{-1} (the correlation coefficient r is 0.99993), respectively. The slope (dp/dT) of the four-phase equilibrium curve of $H_{sII}+L_w+L_{HC}+G$ in the $Xe+C_6H_6$ mixed hydrate system changes at (283.00±0.05) K and (0.420±0.005) MPa. At temperatures above 283.00 K, the slope of $H+L_w+L_{HC}+G$ is almost the same as that of $H+L_w+G$ in the simple Xe hydrate system. The correlated parameters by eq 1 are listed in Table 3. The phase behavior indicates the sII $Xe+C_6H_6$ mixed hydrate collapses at the temperature and the sI Xe hydrate is formed instead of sII $Xe+C_6H_6$ mixed hydrate. Such phase behavior in the $Xe+C_6H_6$ mixed hydrate system is very similar to that in the sH Xe+MCH,[12] Xe+1,1-DMCH,[8] and Xe+*cis*-1,2-DMCH[8] mixed hydrate systems. There are two different points: one is that the slope in the sII $Xe+C_6H_6$ mixed hydrate is slightly steeper than those in the sH Xe+MCH,[12] Xe+1,1-DMCH,[8] and Xe+*cis*-1,2-DMCH[8] mixed hydrate systems; the other is that benzene works as a very weak thermodynamic inhibitor for the sI Xe hydrate formation, while MCH and DMCHs do not have such effect.

4. CONCLUSIONS

The four-phase equilibrium relations in the ternary system of Xe, C_6H_6, and water were investigated. Compared to the stability boundary (H_{sI}+L_w+G) of the sI Xe hydrate, the stability boundaries (H_{sII}+L_w+S_{HC}+G) and (H_{sII}+L_w+L_{HC}+G) of the sII Xe+C_6H_6 mixed hydrate are shifted to higher temperature and lower pressure side. On the stability boundaries of the sII Xe+C_6H_6 mixed hydrate, C_6H_6 is solidified at a temperature lower than the melting point at atmospheric pressure. The quintuple point of (H_{sII}+L_w+L_{HC}+S_{HC}+G) is located at (276.65±0.05) K and (0.175±0.005) MPa. The curve (H_{sII}+L_w+L_{HC}+G) intersects with the stability boundary (H_{sI}+L_w+G) of the sI Xe hydrate. At (283.00±0.05) K and (0.420±0.005) MPa, which is the upper limit temperature for the existence of the sII Xe+C_6H_6 mixed hydrate, the sII Xe+C_6H_6 mixed hydrate collapses.

Table 1. Information on the Chemicals Used in the Present Study

chemical name	source	mole fraction purity
xenon (Xe)	Air Liquide	> 0.99995
benzene (C6H6)	Kanto Chemical	> 0.995
water	Wako Pure Chemical Industries	> 0.9999

Table 2. Experimental Four-Phase Equilibrium Data for the Ternary System of Xe, C_6H_6, and Water at Temperature *T* and Pressure *p* [a]

T / K	*p* / MPa	*T* / K	*p* / MPa	*T* / K	*p* / MPa
$H_{sII}+L_w+S_{HC}+G$ [b]		$H_{sII}+L_w+L_{HC}+G$ [b]		$H_{sII}+L_w+L_{HC}+G$ [b]	
274.14	0.126	277.92	0.209	281.87	0.362
274.46	0.131	278.11	0.217	281.91	0.363
274.68	0.136	278.28	0.221	281.98	0.367
274.98	0.141	278.49	0.225	282.14	0.373
275.42	0.149	278.73	0.236	282.31	0.384
275.95	0.160	278.96	0.242	282.53	0.389
276.34	0.169	279.22	0.252	282.73	0.403
276.58	0.174	279.42	0.258	282.77	0.406
$H_{sII}+L_w+L_{HC}+S_{HC}+G$ [b,c]		279.73	0.271	282.98	0.419
276.65±0.05	0.175±0.005	280.04	0.281	$H_{sI}+H_{sII}+L_w+L_{HC}+G$ [b,c]	
$H_{sII}+L_w+L_{HC}+G$ [b]		280.26	0.291	283.00±0.05	0.420±0.005
276.68	0.177	280.56	0.305	$H_{sI}+L_w+L_{HC}+G$ [b]	
276.83	0.181	280.87	0.317	283.16	0.427
277.04	0.185	281.16	0.328	283.23	0.433
277.31	0.193	281.37	0.339	283.64	0.453
277.44	0.196	281.45	0.342	283.84	0.460
277.68	0.203	281.64	0.351	284.05	0.471
277.79	0.207	281.75	0.357	284.37	0.489

[a] Uncertainties *u* are *u*(*T*) = 0.02 K and *u*(*p*) = 0.004 MPa.

[b] The symbols H_{sI}, H_{sII}, L_w, L_{HC}, S_{HC}, G stand for the sI hydrate, sII hydrate, aqueous, C_6H_6-rich liquid, solid C_6H_6, and gas phases, respectively.

[c] Quintuple point

Table 3. Coefficients for Eq 1 in the temperature range from T_L to T_H

System	Curve	a	b /K^{-1}	r	T_L / K	T_H / K
Xe+C_6H_6+H_2O	H_{sII}+L_w+L_{HC}+G	-39.424	0.13625	0.99976	276.65	283.00
	H_{sI}+L_w+L_{HC}+G	-31.513	0.10830	0.99834	283.00	284.37
Xe+H_2O	H_{sI}+L_w+ G	-29.204	0.10004	0.99993	273.60	287.81

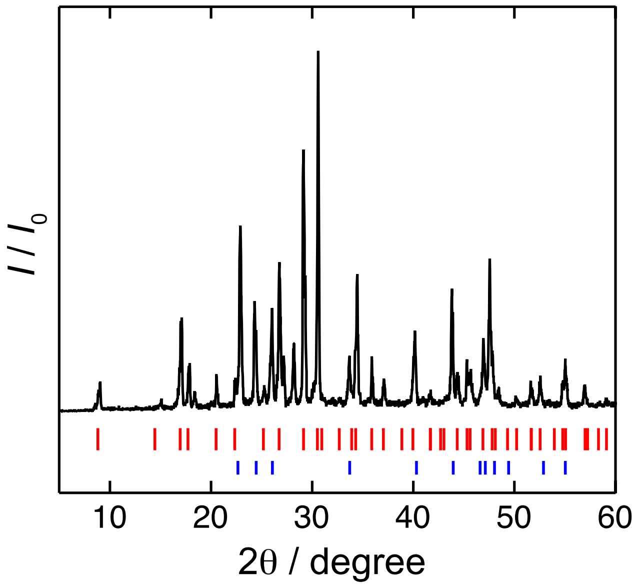

Figure 1. Powder XRD pattern (intensity *I*, diffraction angle θ) obtained from Xe+C_6H_6 mixed hydrate prepared at 277.6 K (recorded at 153 K). The vertical bars represent the contributions from s-II hydrate (red, upper) and hexagonal ice (blue, bottom).

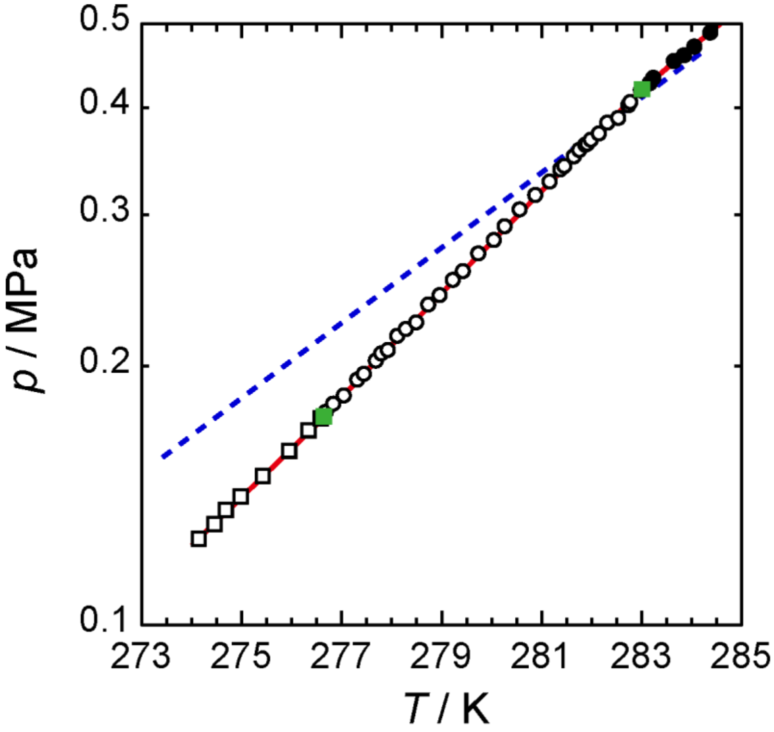

Figure 2. Four-phase equilibrium relations (temperature *T*, pressure *p*) fitted by the red solid curves in the ternary system of Xe, C_6H_6, and water. Open squares and open circles represent the stability boundaries (H_{sII}+L_w+S_{HC}+G) and (H_{sII}+L_w+L_{HC}+G) of the sII Xe+C_6H_6 mixed hydrate, respectively. Closed circles represent the stability boundary of the sI Xe hydrate in the presence of C_6H_6-rich liquid phase. The blue broken-curve stands for the three-phase (H_{sI}+L_w+G) equilibrium curve of the simple Xe hydrate system (in the absence of C_6H_6). The green closed-squares at low and high temperatures are the quintuple points of (H_{sII}+L_w+L_{HC}+S_{HC}+G) and (H_{sI}+H_{sII}+L_w+L_{HC}+G), respectively. The symbols H_{sI}, H_{sII}, L_w, L_{HC}, S_{HC}, G stand for the sI hydrate, sII hydrate, aqueous, C_6H_6-rich liquid, solid C_6H_6, and gas phases, respectively.

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Notes

The author declares no competing financial interest.

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