Thermodynamic Stabilities of Tetra-*n*-butyl Ammonium Chloride + H_2, N_2, CH_4, CO_2, or C_2H_6 Semiclathrate Hydrate Systems

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The thermodynamic stabilities of semiclathrate hydrates were investigated in the tetra-*n*-butyl ammonium chloride (TBAC) aqueous solution (mole fraction of TBAC is 0.0323) + H_2, + N_2, + CH_4, + CO_2, and + C_2H_6 systems. The dissociation temperature of each semiclathrate hydrate is higher than that of the simple TBAC semiclathrate hydrate (hydration number is 30) except for the C_2H_6-containing system in the whole pressure region under the present experimental conditions. Isobaric dissociation temperatures of the TBAC + H_2, + N_2, + CH_4, and + CO_2 hydrates increase in this order. The temperature−pressure projection indicated that the hydrate structural transition occurs around 3 MPa in the TBAC + CH_4 semiclathrate hydrate system, while the three-phase equilibrium curves of the other TBAC hydrate systems do not show any discontinuity in gradient under the present conditions.

Introduction

Clathrate hydrates are icelike crystalline compounds and consist of water molecules and appropriate guest molecules. The water molecules are strongly hydrogen bonded and construct hydrate lattices with cavities, in which guest molecules are encaged. Generally, the guest molecules encaged in the clathrate hydrate do not participate in forming hydrate lattices.[1]

Fowler et al.[2] have discovered the semiclathrate hydrates of the tetra-*n*-butyl ammonium salts. Semiclathrate hydrate is a type of clathrate hydrate. The semiclathrate hydrate generated from the tetra-*n*-butyl ammonium halide (hereafter TBAX) aqueous solution is stable under atmospheric pressure and room temperature. Halide anions are bound to the water molecules through hydrogen bonds and join host frameworks, some of which entrap tetra-*n*-butyl ammonium cations.[3] For example, the tetra-*n*-butyl ammonium bromide (hereafter TBAB) hydrate of which hydration number is 26 consists of 10 dodecahedron, 16 tetrakaidecahedron, and 4 pentakaidecahedron cages.[4] The tetrakaidecahedron and pentakaidecahedron cages are occupied by the tetra-*n*-butyl ammonium cations, while the dodecahedron cage is empty so that only small gas molecules can be encaged in the vacant cage.[5] Gas separation[5,6] and H_2 storage processes[7−9] by using the TBAB hydrate have been proposed because the TBAB hydrate has the moderate stable condition and the empty cavity.

Tetra-*n*-butyl ammonium chloride (hereafter TBAC) is a guest species forming semiclathrate hydrate. Three crystal structures of the TBAC semiclathrate hydrate have been reported: $TBAC\cdot 24H_2O$, $TBAC\cdot 30H_2O$, and $TBAC\cdot 32H_2O$.[11] The melting points under atmospheric pressure are around 288.20 K, 288.30 K, and 287.95 K, respectively.[11,12] That is, the composition−temperature projection for the simple TBAC semiclathrate hydrate system has the maximum temperature (288.30 K) at atmospheric pressure with 3.23 mol % aqueous solution ($TBAC\cdot 30H_2O$).[11,12] The TBAC semiclathrate hydrates also have the dodecahedron cage,[3] in which it is suggested that the tetra-*n*-butyl ammonium cation is not encaged. Therefore, the TBAC hydrate has prospects for a medium for gas separation and gas storage similar to the TBAB and tetra-*n*-butyl ammonium fluoride (TBAF) hydrates.[7−10] However, there are no phase equilibrium data on TBAC + gas semiclathrate hydrate systems. In the present study, we have investigated the thermodynamic stabilities of semiclathrate hydrate for the TBAC + water + H_2, + N_2, + CH_4, + CO_2, and + C_2H_6 systems (the TBAC mole fraction of aqueous solution is 0.0323).

Experimental Methods

a. Experimental Apparatus. Figure 1 is a schematic illustration of an experimental apparatus. The experimental apparatus consisted of the following parts: a high-pressure glass cell (Taiatsu Techno Co., Ltd., HPG), a pressure gauge (Valcom, VPRT), and a temperature control unit (Taitec, CL-80R). The inner volume and maximum working pressure are 10 cm^3 and 5 MPa, respectively. Equilibrium temperature was measured by a Pt resistance thermometer (Thermoprobe Inc., TL-1A). Equilibrium pressure was recorded by the pressure gauge. The uncertainties of equilibrium temperature and pressure were 0.06 K and 0.02 MPa, respectively. In addition, the adaptability of the experimental apparatus was confirmed by the three-phase equilibrium measurement for the simple CH_4 and CO_2 hydrate systems.

b. Experimental Procedure. The thermodynamic stability boundaries were investigated by an ordinary static measurement. TBAC aqueous solution was prepared at stoichiometric composition ($TBAC\cdot 30H_2O$, mole fraction of TBAC aqueous solution was 0.0323) by mass on an electronic balance (uncertainty: 0.0001 g, Mettler, AE 200-S) and introduced into the high-pressure glass cell. The solution was sufficiently

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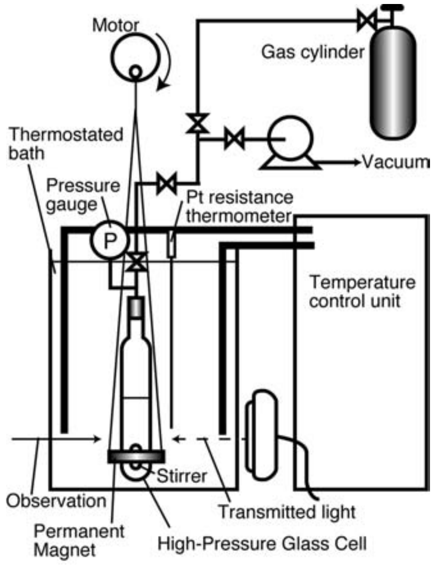

Figure 1. Schematic illustration of the experimental apparatus.

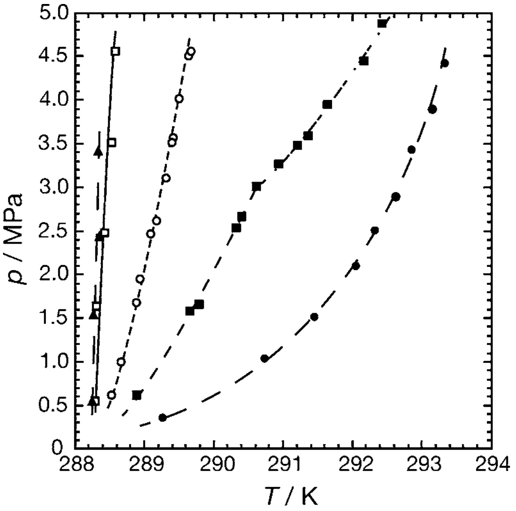

Figure 2. Thermodynamic stabilities of the semiclathrate hydrates (temperature T−pressure p projection) for the tetra-n-butyl ammonium chloride (TBAC) aqueous solution (mole fraction of TBAC is 0.0323) + C_2H_6, + H_2, + N_2, + CH_4, and + CO_2 systems. ▲, TBAC aqueous solution + C_2H_6 system; □, TBAC aqueous solution + H_2 system; ○, TBAC aqueous solution + N_2 system; ■, TBAC aqueous solution + CH_4 system; ●, TBAC aqueous solution + CO_2 system.

degassed with a bubbling method by a gas we were going to measure. The cell was immersed in a thermostated bath to control temperature. A programming thermocontroller circulated the thermostatted water. Next, the contents were cooled and agitated to generate the semiclathrate hydrate. A magnetic stirrer was manipulated in a vertical direction to agitate the contents. The phase behavior was observed straightforwardly under transmitted light. To investigate the phase equilibrium relation including equilibrium composition of aqueous phase accurately, the temperature was increased very gradually (0.1 K step) after the semiclathrate hydrate was annealed to avoid metastability. The temperature was changed when an equilibrium state was established at each temperature step. The temperature where the negligible amount of semiclathrate hydrate existed was determined as the three-phase equilibrium temperature (equilibrium composition of the aqueous phase was the same as that of the initial solution).

c. Materials. TBAC (purity: ≥ 99 %) was purchased from Fluka. H_2 (purity: 99.99 %) was obtained from Fujita Sanso Co., Ltd. Takachiho Chemical Industrial Co., Ltd. supplied N_2 (purity: 99.99 %), CH_4 (purity: 99.99 %), CO_2 (purity: 99.99 %), and C_2H_6 (purity: 99.9 %). Distilled water was produced by an auto still (Yamato, WG 25). All the materials were used without further purification.

Results and Discussion

Figure 2 represents the thermodynamic stability boundaries of the semiclathrate hydrates for the TBAC aqueous solution (mole fraction of TBAC is 0.0323) + H_2, + N_2, + CH_4, + CO_2, and + C_2H_6 systems. Table 1 summarizes the three-phase equilibrium relations. The symbols of p and T stand for the equilibrium pressure and temperature, respectively. Filled triangles, open squares, open circles, filled squares, and filled circles stand for the TBAC + water + C_2H_6, + H_2, + N_2, + CH_4, and + CO_2 system, respectively. The four-phase equilibrium of (hydrate + aqueous + liquid C_2H_6 + gaseous C_2H_6 phases) was established at 3.41 MPa in the TBAC + water + C_2H_6 system. Three-phases of (hydrate + aqueous + gas phases) coexisted under the other equilibrium conditions of the present study.

The dissociation temperatures of the semiclathrate hydrates increase with a rise of pressure in the TBAC + water + H_2, + N_2, + CH_4, and + CO_2 systems, whereas the dissociation temperature is invariant (around 288.30 K) in the TBAC + water + C_2H_6 one. Therefore, the gas molecules except for the C_2H_6 can occupy the dodecahedron cage of the TBAC semiclathrate hydrate under the present experimental conditions (a similar result has been reported in the TBAB semiclathrate hydrate system[6]). Table 2 summarizes the dodecahedron-cage occupancy of each gas in the present study with van der Waals diameters of the guest molecules.[1] In addition, the TBAC + H_2, + N_2, + CH_4, and + CO_2 semiclathrate hydrates are stable under much lower pressure and higher temperature conditions than each simple gas hydrate, i.e., the simple H_2, N_2, CH_4, and CO_2 hydrates.[1]

The isobaric dissociation temperatures of the TBAC + H_2, + N_2, + CH_4, and + CO_2 hydrates increase in this order. This order is the same as that of the isobaric dissociation temperatures of the simple H_2, N_2, CH_4, and CO_2 hydrates.[1] The thermodynamic stabilities of these simple hydrates depend on the guest occupancy of both the dodecahedron and tetrakaidecahedron or hexakaidecahedron cages, whereas those of the present TBAC hydrate systems are affected by only the guest occupancy of the dodecahedron cage. Generally, the dodecahedron cage prefers the occupancy by CH_4 to that by CO_2 because of the molecular sizes and shapes of these guests, which implied that the TBAC + CH_4 hydrate has higher dissociation temperature (higher cage occupancy and lower chemical potential) than the TBAC + CO_2 one. The present results suggest that the empty dodecahedron cage of the TBAC semiclathrate hydrate is more suitable for the CO_2 molecule than that of the structure-I clathrate hydrate.[1] A possible reason is that the participation of the chloride anions in the host framework causes distortion of the hydrogen-bonded network and enlargement of the cavity volume.

The TBAC + CH_4 hydrate system exhibits a discontinuous change in dp/dT around 3 MPa. It is suggested that the crystal structure of the TBAC + CH_4 semiclathrate hydrate transforms from 4/mmm (TBAC·$30H_2O$)[11] to another one so that the semiclathrate hydrate enclathrates a larger amount of CH_4. Sakamoto et al.[10] reported that the TBAF + H_2 hydrate system

Table 1. Thermodynamic Stability Boundaries (Temperature *T*, Pressure *p*) of the Semiclathrate Hydrates for the Tetra-*n*-butyl Ammonium Chloride (TBAC) Aqueous Solution (Mole Fraction of TBAC is 0.0323) + C_2H_6, + H_2, + N_2, + CH_4, and + CO_2 Systems

T/K	*p*/Mpa
TBAC + C_2H_6 system	
288.25	0.55
288.26	1.54
288.34	2.43
288.32	3.41
TBAC + H_2 system	
288.28	0.55
288.30	1.64
288.42	2.47
288.53	3.51
288.58	4.55
TBAC + N_2 system	
288.52	0.61
288.66	0.99
288.89	1.67
288.93	1.94
289.10	2.46
289.18	2.62
289.31	3.09
289.40	3.50
289.42	3.56
289.51	4.01
289.64	4.50
289.68	4.56
TBAC + CH_4 system	
288.89	0.61
289.66	1.57
289.78	1.66
290.33	2.53
290.39	2.66
290.62	3.01
290.93	3.26
291.19	3.47
291.35	3.59
291.64	3.94
292.15	4.45
292.42	4.87
TBAC + CO_2 system	
289.27	0.36
290.73	1.03
291.45	1.51
292.05	2.09
292.32	2.50
292.63	2.88
292.85	3.42
293.16	3.89
293.33	4.42

Table 2. van der Waals Diameters (*d*, Ref 1) and Enclathration in the Tetra-*n*-butyl Ammonium Chloride Semiclathrate Hydrate under the Present Experimental Conditions

	d/nm (ref 1)	enclathration
H_2	0.27	○
N_2	0.41	○
CH_4	0.44	○
CO_2	0.51	○
C_2H_6	0.55	×

shows hydrate structural transition to encage a larger number of H_2 molecules depending on the circumstance conditions. It was claimed in the same report that the hydration number per a TBAF molecule of the semiclathrate hydrate increases—that is, the number of the dodecahedron cage, where H_2 can be enclathrated, increases—after the solid phase transition. Therefore, it is implied that the crystal structure of the TBAC + CH_4 hydrate in the higher pressure region than 3 MPa is of the same structure as the simple semiclathrate hydrate of TBAC·$32H_2O$ (*P*4/*m*)[11] of which the hydration number is larger than that of TBAC·$30H_2O$ (4/*mmm*) similar to the TBAF + H_2 hydrate system.

Conclusion

The thermodynamic stabilities of the semiclathrate hydrates have been investigated for the TBAC + water + H_2, + N_2, + CH_4, + CO_2, and + C_2H_6 systems. These gases except for C_2H_6 are encaged in the dodecahedron cage of the TBAC semiclathrate hydrate under the present experimental conditions. The isothermal dissociation temperatures of the TBAC + H_2, + N_2, + CH_4, and + CO_2 hydrates increase in this order. The empty cage of the TBAC semiclathrate hydrate is smaller than the C_2H_6 molecule and has a more suitable shape for the CO_2 molecule than the dodecahedron cage of the structure-I clathrate hydrate. In addition, the stability boundary of the TBAC + CH_4 hydrate system exhibits the discontinuity in gradient around 3 MPa, indicating the occurrence of solid phase transition around the pressure condition.

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