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Phase Equilibria of Semiclathrate Hydrate for Nitrogen in the Presence of Tetra-*n*-butylammonium Bromide and Fluoride

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Semiclathrate hydrate phase equilibria for N_2 + TBAB (tetra-*n*-butylammonium bromide) + water mixtures were measured in the temperature range of (280 to 290) K and in the pressure range of (4.0 to 9.2) MPa at TBAB, w (weight fraction) = 0.05, 0.20, 0.40, and 0.60. Also, semiclathrate hydrate phase equilibria for N_2 + TBAF (tetra-*n*-butylammonium fluoride) + water mixtures were measured in the temperature range of (293 to 302) K and in the pressure range of (2.0 to 9.7) MPa at TBAF, $w = 0.10$, 0.20, 0.34, and 0.45. The equilibrium dissociation temperatures for each pure TBAB and TBAF semiclathrate were also measured at the same concentrations under atmospheric conditions. The presence of TBAB or TBAF remarkably shifted the equilibrium conditions of the double semiclathrates to higher temperature and lower pressure regions when compared with those of the pure N_2 hydrate. The highest stabilization effect was observed at the stoichiometric concentrations of each semiclathrate (TBAB, $w = 0.40$; TBAF, $w = 0.34$).

Introduction

Gas hydrates are nonstoichiometric crystalline compounds formed when "guest" molecules of suitable size and shape are incorporated into the well-defined cages in the "host" lattice made up of hydrogen-bonded water molecules.[1] In gas hydrates, water molecules form a lattice structure with cages that can capture guest molecules and guest molecules interact with water molecules through van der Waals forces.[1] On the other hand, quaternary ammonium salts (QASs) such as tetra-*n*-butylammonium bromide (TBAB) and fluoride (TBAF) form semiclathrate hydrates with water molecules at atmospheric pressure.[2] In TBAB or TBAF semiclathrates, anions such as Br^- and F^- of the QASs form cage structures with water molecules and the tetra-*n*-butylammonium (TBA) cations occupy four cages.[2−6] In gas hydrates, the guest molecules are not physically bonded to water lattices, while in semiclathrates, guest molecules can both form part of the host lattice and occupy cages after breaking part of the cage structure.[1−6] Recently, semiclathrates have been applied to a method for gas storage and separation because small gas molecules can be captured in empty cages of semiclathrates of TBAB or TBAF at mild conditions.[7−12] Chapoy et al.,[7] Hashimoto et al.,[8] and Sakamoto et al.[9] showed that H_2 can be enclathrated in the TBAB and TBAF semiclathrate hydrates, and thus, semiclathrates could be potential hydrogen storage media. Kamata et al.[10] reported that small gas molecules such as methane and hydrogen sulfide were selectively encaged in dodecahedral cages of TBAB semiclathrate hydrates during clathrate formation, whereas the larger gas molecules such as ethane and propane were not incorporated into the TBAB semiclathrate hydrates. Duc et al.[11] and Fan et al.[12] confirmed that the addition of TBAB or TBAF into the mixed $CO_2 + N_2$ gas hydrates could give a remarkable pressure reduction for hydrate formation in the application to the process for capturing CO_2 from flue gas. Semiclathrate hydrate phase equilibria for H_2, CH_4, and CO_2 in the presence of TBAB or TBAF were well established by other researchers.[13−16] However, to the best of our knowledge, semiclathrate phase equilibria for N_2, which is a main component of flue gas and is small enough to be captured in the empty cages of semiclathrates, have rarely been reported in the literature. In this paper, we present the experimental measurements of semiclathrate phase equilibria for N_2 in the presence of TBAB and TBAF. Moreover, the dissociation temperatures of pure TBAB and TBAF semiclathrates under atmospheric pressure conditions were also measured at four different weight fractions (w) of TBAB and TBAF.

Experimental Section

Materials. The N_2 gas used for the present study was supplied by Praxair and had a stated purity of x (mole fraction) = 0.99999. TBAB with a purity of $w = 0.99$ and TBAF solution with a purity of $w = 0.75$ in water were purchased from Sigma-Aldrich (United States). Doubly distilled, deinonized water was used. All materials were used without further purification.

Apparatus. A schematic diagram and detailed description of the experimental apparatus for the clathrate hydrate phase behavior was given in previous papers.[17−19] The apparatus was specially constructed to accurately measure the hydrate dissociation pressures of multicomponent and multiphase mixtures through both visual observation of phase transitions and the pressure−temperature trace. The equilibrium cell was made of 316 stainless steel and had an internal volume of about 50 cm^3. Two sapphire windows equipped at the front and back of the cell allowed visual observation of the phase transitions occurring inside the equilibrium cell. The cell content was vigorously agitated by a magnetic spin bar with an external magnet immersed in a water bath. A thermometer (Digi-Sense, United States) with an accuracy of ± 0.1 K for full ranges was inserted into the cell to measure the inner content. This thermometer was calibrated using an ASTM 63C mercury thermometer (Every Ready Thermometer, United States) with a resolution of ± 0.1 K. A pressure transducer (VPRT, Valcom, Japan) with

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Table 1. Semiclathrate Hydrate Phase Equilibrium Data for the TBAB + Water System at Atmospheric Pressure

w	T / K	w	T / K
0.05	276.3	0.40	285.2
0.20	282.0	0.60	284.3

an uncertainty of 0.02 MPa was used to measure the cell pressure. The pressure transducer was also calibrated using a Heise Bourdon tube pressure gauge (CMM-137219, (0 to 10) MPa range) having a maximum error of ± 0.01 MPa in the full range.

Procedure. The experiment for clathrate hydrate phase equilibrium measurements began by charging the equilibrium cell with about 20 cm^3 of aqueous solutions containing the desired compositions of TBAB or TBAF. The equilibrium cell with the solution was flushed with N_2 at least three times to remove any residual air. After the equilibrium cell was pressurized to the desired pressure with N_2, the whole main system was cooled to about 5 K below the expected clathrate hydrate-forming temperature. Clathrate hydrate nucleation and growth was then induced in the aqueous solution, and the system pressure continuously decreased due to clathrate hydrate formation. When the system pressure reached a steady-state condition, the cell temperature was increased at a rate of about 1 $K \cdot h^{-1}$ until a clathrate hydrate phase was in coexistence with the liquid and vapor phases. The system temperature was then slowly raised at a rate of 0.1 $K \cdot h^{-1}$. The nucleation and dissociation steps were repeated at least two times to reduce the hysteresis phenomenon. When a very small amount of crystals was found to exist by visual observation without significantly increasing or decreasing its size, the system temperature was kept constant for at least 8 h after stabilization of the system pressure. Then the pressure was considered as an equilibrium clathrate hydrate dissociation pressure at the specified temperature. To confirm the visual observation method, a pressure−temperature plot was also used to determine the equilibrium conditions. If the temperature was increased below the hydrate equilibrium condition, a substantial increase of the system pressure was observed due to the dissociation of the solid hydrate phase, resulting in the release of N_2. However, when the temperature was increased above the hydrate equilibrium condition, a very slight increase of the system pressure was detected due to only the thermal expansion of the gas phase. Therefore, the intersection point between the hydrate dissociation line and thermal expansion line from the pressure−temperature plot was considered as the three-phase hydrate equilibrium condition.

Results and Discussion

It has been reported that pure TBAB semiclathrate has two crystal structures (type A and type B), which have different transmittances, refractions, and crystal morphologies, depending on the mass fraction of aqueous solution.[6,20] In the region of w (weight fraction) < 0.2, type B semiclathrate forms preferentially, while type A semiclathrate is more stable in the region of w > 0.2. In the present study, the phase equilibrium relation of temperature−composition for the pure TBAB semiclathrate system was also measured at $w = 0.05$, 0.20, 0.40, and 0.60 under atmospheric conditions. The equilibrium data are listed in Table 1 and shown in Figure 1. The equilibrium data for TBAB at $w = 0.05$, 0.20, 0.40, and 0.60 are in good agreement with the literature values. As can be seen in Figure 1, TBAB semiclathrate is most stable at the stoichiometric concentration ($w = 0.40$) of type A TBAB semiclathrate where the equilibrium temperature is 285.2 K and hydration number is 26 ($TBAB \cdot 26H_2O$).[20]

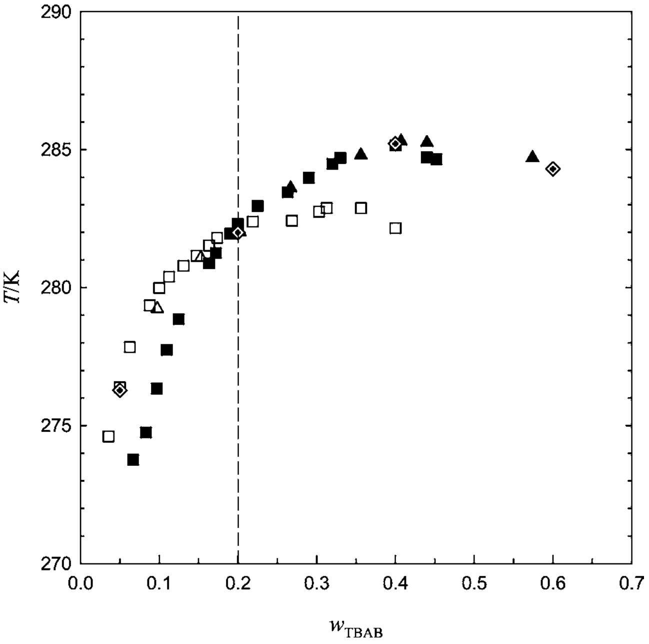

Figure 1. Phase diagram of the TBAB semiclathrate under atmospheric pressure conditions. ■, type A, Oyama et al.;[20] ▲, type A, Hashimoto et al.;[8] □, type B, Oyama et al.;[20] △, type B, Hashimoto et al.;[8] ◇, this work.

Table 2. Semiclathrate Hydrate Phase Equilibrium Data for the N_2 + TBAB + Water System

$w = 0.05$		$w = 0.20$		$w = 0.40$		$w = 0.60$	
T / K	p / MPa	T / K	p / MPa	T / K	p / MPa	T / K	p / MPa
281.3	4.12	286.6	4.24	286.8	4.04	285.2	5.12
282.1	5.24	287.4	5.37	287.4	4.97	285.9	6.52
282.6	6.05	287.9	6.60	288.3	6.26	286.5	7.72
283.5	7.55	288.5	7.83	288.8	7.59	287.2	9.15
284.3	9.18	289.2	9.49	289.4	8.97		

The three-phase equilibria (hydrate (H)−liquid water (L_W)−vapor (V)) for the N_2 + TBAB + water systems were measured to determine the stability region of the N_2 + TBAB semiclathrate hydrates at four different concentrations of TBAB, $w = 0.05$, 0.20, 0.40, and 0.60, and the overall results are summarized in Table 2 and shown in Figure 2 along with the three-phase equilibrium data of the pure N_2 hydrate.[21] The presence of even a small amount of TBAB induced the hydrate stability condition to become more favorable by lowering the pressure and raising the temperature for N_2 + TBAB semiclathrates. In the N_2 + TBAB semiclathrates the TBA cation occupies four partially broken cages because of its size and the N_2 molecules occupy dodecahedral cages (5^{12}).[6,13] The N_2 + TBAB semiclathrates were more stabilized when the TBAB concentration increased from $w = 0.05$ to $w = 0.40$. However, at $w = 0.60$, the stabilization effect for the N_2 + TBAB semiclathrate was less than at $w = 0.40$. Accordingly, the maximum stabilization effect of TBAB was observed at $w = 0.40$, which corresponds to the stoichiometric concentration of type A TBAB semiclathrate ($TBAB \cdot 26H_2O$), as can be expected from the phase diagram of the pure TBAB semiclathrate in Figure 1. At $w = 0.60$, the stoichiometric amount of TBAB participates in forming the TBAB semiclathrate with N_2; however, the excess amount of TBAB remains as free ions of TBA^+ and Br^-, not acting as a semiclathrate former but acting

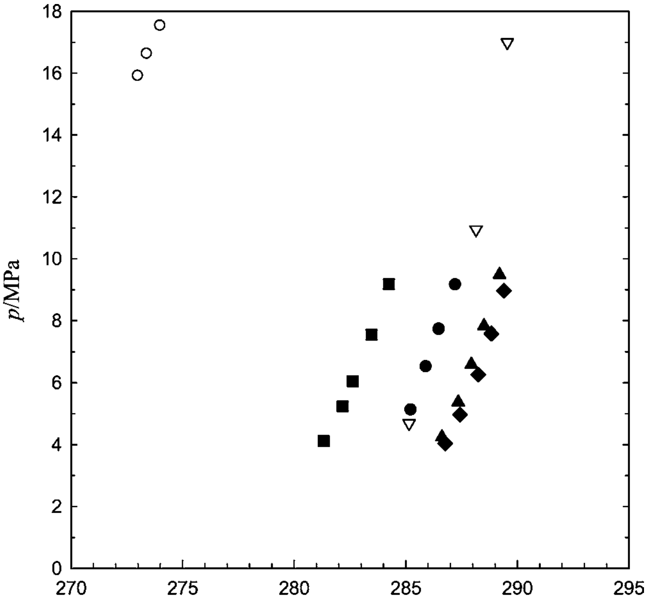

Figure 2. Semiclathrate hydrate phase equilibria of the N_2 + TBAB + water systems. ○, pure N_2, van Cleeff and Diepen;[21] ■, TBAB $w = 0.05$; ▲, TBAB $w = 0.20$; ◆, TBAB $w = 0.40$; ●, TBAB $w = 0.60$; ▽, TBAB $w = 0.10$, Arjmandi et al.[13]

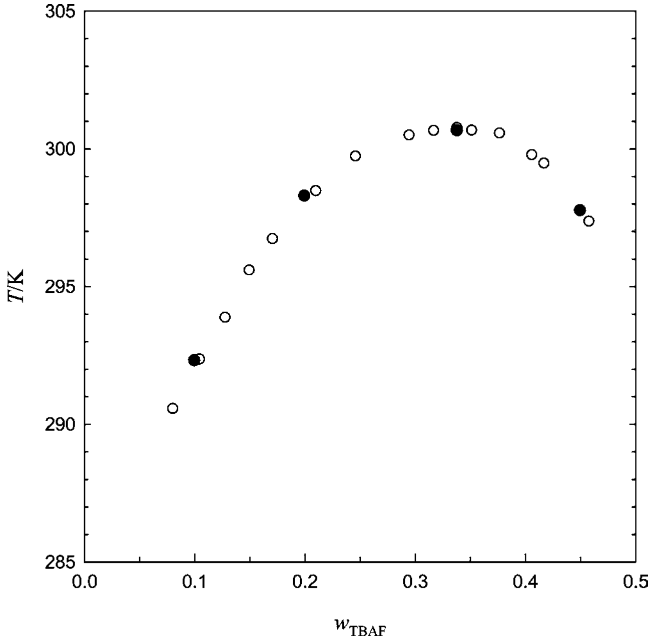

Figure 3. Phase diagram of the TBAF semiclathrate under atmospheric pressure conditions: ○, Sakamoto et al.;[9] ●, this work.

as an inhibitor. Therefore, at a specified temperature, the semiclathrate equilibrium pressure at $w = 0.60$ was higher than that at $w = 0.40$.

It has also been reported that pure TBAF forms semiclathrate hydrate structures, where small cages may be partially occupied with water molecules or left vacant.[22,23] TBAF semiclathrate has two crystal structures: One is a cubic structure with a hydration number of 28.6 ($TBAF \cdot 28.6H_2O$), and the other is a tetragonal structure with a hydration number of 32.3 ($TBAF \cdot 32.3H_2O$), which seems to be metastable.[5,22,23] As Sakamoto et al.[9] indicated and can be seen in Figure 3, the maximum dissociation temperature for TBAF semiclathrate under atmospheric pressure conditions was observed at the stoichiometric concentration ($w = 0.34$) of TBAF semiclathrate, where the equilibrium temperature is 300.65 K and hydration number is 28.6 ($TBAB \cdot 28.6H_2O$). The equilibrium data are listed in Table 3 and shown in Figure 3. The equilibrium data for TBAF at w = 0.10, 0.20, 0.34, and 0.45 are in good agreement with the literature values.

Table 3. Semiclathrate Hydrate Phase Equilibrium Data for the TBAF + Water System at Atmospheric Pressure

w	T/K	w	T/K
0.10	292.3	0.34	300.7
0.20	298.3	0.45	297.8

Table 4. Semiclathrate Hydrate Phase Equilibrium Data for the N_2 + TBAF + Water System

$w = 0.10$		$w = 0.20$		$w = 0.34$		$w = 0.45$	
T/K	p/MPa	T/K	p/MPa	T/K	p/MPa	T/K	p/MPa
293.1	2.05	299.1	2.17	301.9	2.44	299.2	2.11
294.2	3.90	299.6	3.95	302.4	3.94	299.7	3.94
294.8	5.72	300.4	5.86	302.7	6.26	300.4	5.85
295.4	7.60	300.8	7.77	303.1	7.80	300.8	7.75
296.1	9.42	301.0	9.64	303.4	9.44	300.9	9.59

The three-phase equilibria ($H-L_W-V$) for the N_2 + TBAF + water systems were measured to determine the stability region of the N_2 + TBAF semiclathrate hydrates at four different concentrations of TBAF, w = 0.10, 0.20, 0.34, and 0.45. The overall experimental results are summarized in Table 4 and shown in Figure 4 along with the three-phase equilibrium data of the pure N_2 hydrate.[21] The presence of TBAF caused the $H-L_W-V$ equilibrium conditions to be shifted to the stabilized region represented by higher temperature and lower pressure when compared with those of the pure N_2 hydrate. The stabilization effect was increased with increasing TBAF concentration from $w = 0.10$ to $w = 0.34$. However, less stabilization effect for the N_2 + TBAF semiclathrate was observed at $w = 0.45$. As can be expected from the results of

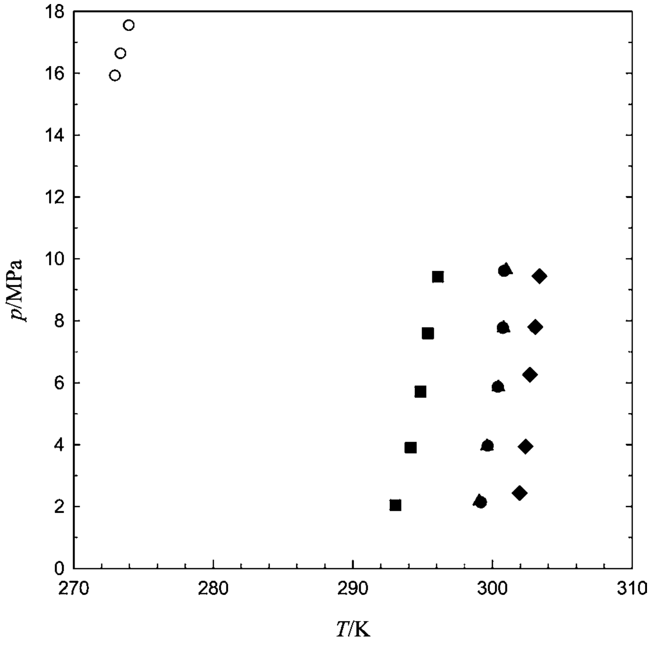

Figure 4. Semiclathrate hydrate phase equilibria of the N_2 + TBAF + water systems: ○, pure N_2, van Cleeff and Diepen;[21] ■, TBAF $w = 0.10$; ▲, TBAF $w = 0.20$; ◆, TBAF $w = 0.34$; ●, TBAF $w = 0.45$.

N_2 + TBAB semiclathrate equilibria, the excess amount of TBAF, which cannot participate in semiclathrate formation, remains as free ions of TBA^+ and F^- and then acts as an inhibitor. Accordingly, TBAF $w = 0.34$, which corresponds to the stoichiometric concentration of TBAF semiclathrate ($TBAF \cdot 28.6H_2O$) showed the maximum stabilization effect.

TBAF generally showed more remarkable pressure reduction for the semiclathrate formation with N_2 at a specified temperature than TBAB. More investigation on the structural details of N_2 + TBAF semiclathrate should be achieved in the near future through sophisticated analysis methods and wider experimental ranges.

Conclusions

In this paper we presented the $H-L_W-V$ phase equilibria for the N_2 + TBAB + water and N_2 + TBAF + water systems. The presence of TBAB or TBAF caused the $H-L_W-V$ equilibrium line of the N_2 + TBAB or N_2 + TBAF semiclathrates to be greatly shifted to higher temperature and lower pressure regions when compared to that of pure N_2 hydrate. The highest stabilization effect was observed at the stoichimetric concentrations corresponding to the hydration number of each semiclathrate, which are $w = 0.\ 40$ for TBAB and $w = 0.34$ for TBAF, respectively. TBAF appeared to be more favorable for stabilizing the semiclathrate than TBAB in the temperature and pressure ranges of the present study. The overall experimental results obtained from this study can be used for understanding the fundamental phase behavior of the N_2 + QAS semiclathrates and, thus, could be applied as valuable key information in gas storage and separation using QAS semiclathrates.

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