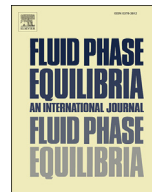




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Phase equilibrium and characterization of ionic clathrate hydrates formed with tetra-*n*-butylammonium bromide and nitrogen gas

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ABSTRACT

We report the three-phase (gas–hydrate–aqueous) equilibrium measurements and phase characterization of ionic clathrate hydrates formed in a nitrogen + tetra-*n*-butylammonium bromide (TBAB) + water system. The measurement conditions used were $0.0029 \leq x_{\text{TBAB}} \leq 0.0257$ ($0.05 \leq w_{\text{TBAB}} \leq 0.32$), $280 \text{ K} < T < 291 \text{ K}$, and $1 \text{ MPa} < P < 12 \text{ MPa}$, where x_{TBAB} , w_{TBAB} , T , and P denote the mole fraction of TBAB in the aqueous phase, mass fraction of TBAB in the aqueous phase, temperature, and pressure, respectively. We also performed single-crystal structure analyses of the crystals formed at 2.1 and 5.8 MPa, which indicated that they possessed the same orthorhombic *Pm* hydrate phase but significantly different gas capacities. We also showed that the low nitrogen gas pressure supply extends the melting point of the simple TBAB hydrate formed in the absence of gas. CO₂ may be efficiently captured from flue gas when the partial pressure of N₂ is maintained below 4 MPa.

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1. Introduction

The development of capture technologies for various gases will allow for new applications of previously unused resources. N₂ and CO₂ gases are the main components of flue gases in various fields, such as power plants, iron mills, and heating. Separation of these gases, especially CO₂, is necessary for storage, transport, and use in other fields. There is high demand for CO₂ in the agricultural industry for use in crop fertilizers to enhance photosynthesis [1,2]. Since combustion heating during cold months is still widely used in greenhouse horticulture, onsite gas separation and storage with low energy consumption would allow for a new distributed energy recycling system. For this purpose, a separation and storage medium that can rapidly capture and release gases is required. Furthermore, this system can be extended to a large-scale sustainable energy system, i.e., industrial carbon emissions utilized in agriculture [3,4].

Ionic clathrate hydrates are potential candidate media for the separation and storage of gases. They are crystalline guest–host compounds composed of water and ionic guest substances with or

without small guest gases such as CH₄, N₂, and CO₂. In the structure of ionic clathrate hydrates, ionic guest cations can occupy the four-cage fused space, and the small guest anions can replace water molecules composing the hydrate framework through hydrogen bonds [5–10]. Ionic clathrate hydrates can rapidly form and dissociate through small changes in temperature or pressure. Tetra-*n*-butylammonium bromide (TBAB) is a nontoxic and widely used ionic guest substance. TBAB hydrates have melting points of ~285 K [11–13]. The empty pentagonal–dodecahedral (D) cages in the TBAB hydrate structure can incorporate a guest gas and the hydrates are more stable than the simple TBAB hydrates formed in the absence of gas [14]. Based on the phase equilibrium data [15–20], CO₂ molecules are more suitable for hydrate cages than N₂ molecules; therefore, ionic clathrate hydrates can be used for CO₂ capture from flue gases as well as canonical clathrate hydrates [21–23]. Recently, efficient incorporation of CO₂ molecules in the D cages of the TBAB hydrate structure was revealed [14], where CO₂ molecules were encapsulated by the D cages in a complex manner. While vast experimental data is available for the TBAB + CO₂ hydrate formation system [24–27], there have been minimal reports regarding the equilibrium data for the TBAB + N₂ hydrate system [28–30]. Most of these reports use a pressure measurement range over 3 MPa. However, it is also necessary to investigate formation of the gas-containing TBAB hydrate in the low pressure region, which may

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reduce the compression work of the system.

In this study, we report the three-phase (gas–hydrate–aqueous) equilibrium measurements of the $N_2 + TBAB + H_2O$ system. The experimental conditions used were $0.0029 \leq x_{TBAB} \leq 0.0257$ ($0.05 \leq w_{TBAB} \leq 0.32$), $280\text{ K} < T < 291\text{ K}$, $1\text{ MPa} < P < 12\text{ MPa}$, where x_{TBAB} , w_{TBAB} , T , and P denote the mole fraction of TBAB in the aqueous phase, the mass fraction of TBAB in the aqueous phase, the temperature, and the pressure, respectively. The P – T data trend changed depending on the formation pressure due to phase properties such as gas capacity. We performed phase characterization through X-ray crystal structure analyses of crystals formed at two different pressures.

2. Experimental

2.1. Materials

The raw materials used in this study were water, TBAB, and nitrogen gas. For experiments with $P < 4\text{ MPa}$, water was sterilized with an ultraviolet lamp, purified by activated carbon, and deionized before use. The certified resistivity and total organic content of the water were $18.2\text{ M}\Omega\text{ cm}$ at 298 K and $\leq 5\text{ ppb}$, respectively. For experiments with $P > 4\text{ MPa}$, we used water distilled in our laboratory. These different water treatments satisfied each measurement uncertainty.

The specifications of TBAB and nitrogen gas are summarized in Table 1. These materials were used as received from their respective manufacturers.

2.2. Apparatus

We used two sets of experimental apparatuses for phase equilibrium measurements, which were selected according to pressure range ($P < 4\text{ MPa}$ and $P > 4\text{ MPa}$). For $P < 4\text{ MPa}$, we used a high-pressure cell with a 96 cm^3 volume. A hydrate formation cell was equipped with a strain-gauge pressure sensor (PGR-50KA-P, Kyowa Electronic Instruments Co. Ltd.) and an electromagnetically induced stirrer on the lid. The cell was charged with $\sim 20\text{ g}$ of an aqueous TBAB solution. The apparatus mainly consisted of a water bath, a PID (proportional–integral–derivative) controlled heater, stirrers, a vacuum pump, a pressure sensor, and thermometers. Two platinum resistance thermometers were inserted in the bath; one to control the bath temperature and the other (NRHS1-0; CAB-F201B-2; Chino Co.), which was certified as traceable, to determine the equilibrium temperature. Aqueous solutions were gravimetrically prepared using an electronic balance (GX-6100, A&D Co., 0.02 g uncertainty) and supplied to the cell ($\sim 20\text{ g}$). The residual air was removed from the cell before supplying the prescribed pressure of nitrogen gas with a vacuum pump. The details of this apparatus were reported previously [31].

For $P > 4\text{ MPa}$, we used a 1000 cm^3 high-pressure cell with a different setup. This cell was also equipped with an electromagnetically induced stirrer on the lid to stir the liquid phase. The cell was immersed in a temperature-controlled bath, and $\sim 700\text{ cm}^3$ of

an aqueous solution was supplied to the cell. Aqueous solutions were gravimetrically prepared using an electronic balance (HF-2000, A&D Co.) with 0.01 g resolution. A platinum resistance thermometer (NRDS1, Chino Co.) and a semiconductor pressure transducer (KJ-15, Nagano Keiki Co. Ltd.) were connected to the cell. The residual air was removed from the cell before supplying the prescribed pressure of nitrogen gas through a gas charge and discharge process. The details of this apparatus were reported previously [32].

The measurement uncertainties for $P < 4\text{ MPa}$ were at most 0.079 K for T , 0.007 MPa for P , and 0.00035 for x_{TBAB} . Those for $P > 4\text{ MPa}$ were 0.4 K for T , 0.08 MPa for P , and 0.00001 for x_{TBAB} .

2.3. Equilibrium measurement procedures

We used an isochoric method for the gas–hydrate–aqueous phase equilibrium, for which the detailed procedures can be found elsewhere [31–34]. This method originated from gas hydrate formation upon sufficient decrease in temperature. The system temperature was then increased stepwise by 0.1 K . In response to the temperature increase, the system pressure rose through gas release from the hydrate phase. The system temperature was maintained until the pressure was equilibrated. The longest process was for $x_{TBAB} = 0.0256$ ($w_{TBAB} = 0.32$), which required 60 h for one temperature step. After the hydrates in the system dissociated completely, only a slight pressure increase of $\sim 1\text{ kPa}$ was observed. The temperature and pressure one step prior to dissociation were determined to be the phase equilibrium temperature and pressure, respectively. One data point at phase equilibrium was determined for each gas pressure supply and the above-mentioned procedure was repeated at each pressure and TBAB concentration. We used TBAB solutions with four different compositions, i.e., $x_{TBAB} = 0.0029, 0.0062, 0.0138, \text{ and } 0.0256$ ($w_{TBAB} = 0.05, 0.10, 0.20, \text{ and } 0.32$, respectively). A process for the present equilibrium measurements is provided in Fig. 1. In this case, the system pressure was raised to $\sim 5\text{ kPa}$ by 0.1 K temperature increments. For the last two temperature increments, the increases in pressure were minimal, and the gas hydrates in the system were completely dissociated.

2.4. Hydrate phase characterization

To characterize the hydrate phases for which equilibrium conditions were likely to have different P – T slopes (discussed later), we performed single-crystal X-ray structure analyses. We formed single crystals using high-pressure cells which had glass windows through which the inside could be observed. A pressure sensor (Valcom, Co. Ltd., VPRTF-A2-10MPaW-5) was connected to the cell, and 3 g of a TBAB solution with $x_{TBAB} = 0.0138$ ($w_{TBAB} = 0.200$) was injected. After the residual air was removed using a vacuum pump, nitrogen gas was injected into the cell. The cell was immersed in a temperature-controlled bath of poly(methyl methacrylate) resin, and the bath temperature was monitored with a platinum resistance thermometer (Eutech Instruments Pte Ltd., EcoScan Temp 6).

Table 1
List of materials used in this study.

Name	Chemical formula	Supplier	Purity
<i>Measurements at $P < 4\text{ MPa}$</i>			
Nitrogen	N_2	Taiyo Nippon Sanso, Co., Tokyo, Japan	≥ 0.9999995 in mole fraction
Tetra- <i>n</i> -butylammonium bromide	$(n\text{-C}_4\text{H}_9)_4\text{NBr}$	Sigma–Aldrich, Co.	≥ 0.99 in mass fraction
<i>Measurements at $P > 4\text{ MPa}$</i>			
Nitrogen	N_2	Taiyo Nippon Sanso, Co., Tokyo, Japan	≥ 0.9999995 in mole fraction
Tetra- <i>n</i> -butylammonium bromide	$(n\text{-C}_4\text{H}_9)_4\text{NBr}$	Sigma–Aldrich, Co.	≥ 0.99 in mass fraction

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