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Phase equilibria of tetra-iso-amyl ammonium bromide (TiAAB) semiclathrates with CO_2, N_2, or CO_2 + N_2

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ABSTRACT

This study examined the thermodynamic stability and guest gas inclusion of tetra-iso-amyl ammonium bromide (TiAAB) semiclathrates with CO_2, N_2, or CO_2 (20%) + N_2 (80%), with a primary focus on semiclathrate phase equilibria and Raman spectra. The three-phase (H-L_W-V) equilibria of TiAAB semiclathrates with CO_2, N_2, or CO_2 (20%) + N_2 (80%) were measured at a stoichiometric concentration (TiAAB 3.7 mol%) using both a conventional isochoric method and a stepwise differential scanning calorimeter (DSC) method. The phase equilibria demonstrated that TiAAB (3.7 mol%) semiclathrates with CO_2, N_2, or CO_2 (20%) + N_2 (80%) were significantly stabilized compared with the corresponding CO_2, N_2, or CO_2 (20%) + N_2 (80%) gas hydrates. The enclathration of CO_2 and N_2 molecules in the cages of TiAAB semiclathrates was clearly confirmed via Raman spectroscopy. The experimental results indicate that TiAAB semiclathrates can incorporate CO_2 and N_2 into the cage lattices at elevated temperatures and lowered pressures and are potential materials for CO_2 capture.

1. Introduction

Clathrate hydrates are crystalline inclusion compounds that consist of hydrogen-bonded cage frameworks called “host” and small-sized “guest” molecules [1]. They are generally classified as true clathrates and semiclathrates, depending on the types of interactions between host and guest molecules, even though their strict distinction has blurred [2,3]. True clathrates exhibit van der Waals interactions between encapsulated guest molecules and host water molecules. Well-known gas hydrates belong to true clathrates. On the other hand, semiclathrates have chemical or ionic interactions between host and guest molecules. Quaternary ammonium salts (QASs) such as tetra-n-butyl ammonium bromide (TBAB), tetra-n-butyl ammonium chloride (TBAC), and tetra-n-butyl ammonium fluoride (TBAF) form semiclathrates with water under atmospheric pressure [4–6]. In QAS semiclathrates, TBA cations are captured in the partially broken large cages, while anions (Br^-, Cl^- or F^-) participate in building up host frameworks [2,3,7]. QAS semiclathrates have much higher thermodynamic stability compared to gas hydrates and have vacant small (5^{12}) cages, which are available for encapsulating small-sized gas molecules [7–10]. Due to these unique features of QAS semiclathrates, TBAB, TBAC, and TBAF semiclathrates have been extensively explored for potential gas storage, CO_2 capture, and cold energy storage applications [7–18].

Recently, tetra-iso-amyl ammonium bromide (TiAAB) has been suggested as a promising semiclathrate former for CO_2 capture and gas storage because TiAAB semiclathrate has greater thermodynamic stability than that of TBAB, TBAC, and TBAF semiclathrates [19,20,21]. This indicates that the formation of TiAAB semiclathrates with guest gases can occur at lower pressures and higher temperatures. However, accurate phase equilibria in a wide pressure range and spectroscopic observation of guest enclathration in TiAAB semiclathrates for CO_2 capture applications have rarely been reported in the literature.

In this study, as a first step of TiAAB semiclathrate-based CO_2 capture, semiclathrate phase equilibria of CO_2 + TiAAB + water, N_2 + TiAAB + water, and CO_2 (20%) + N_2 (80%) + TiAAB + water mixtures were experimentally measured using both a conventional isochoric (pVT) method and a stepwise differential scanning calorimeter (DSC) method. The enclathration of CO_2 and N_2 in the TiAAB semiclathrates was confirmed using Raman spectroscopy.

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2. Experimental

2.1. Materials

CO_2 with a purity of 99.999% was provided by Deokyang Co. (Republic of Korea), and N_2 with a purity of 99.99% was supplied by KOSEM Co. (Republic of Korea). The gas mixture of CO_2 (20%) + N_2 (80%) was supplied by MS Gas Co. (Republic of Korea). The tetra-iso-amyl ammonium bromide (TiAAB) used in this study was synthesized using Menschutkin reaction [22]. The ^{1}H NMR (D_2O) spectrum of TiAAB consisted of the following peaks: 0.85–0.87 (m, 24H), 1.46–1.49 (t, 8H), 1.53–1.59 (m, 4H), 3.12–3.16 (t, 8H). The detailed procedure of the TiAAB synthesis was described in a previous paper [20]. Deionized doubly distilled water was used for the experiment. The suppliers and purity of the materials used in this study are presented in Table 1.

2.2. Apparatus and procedures

The equilibrium cell used to measure the semiclathrate phase equilibria was made of 316 stainless steel and had an inner volume of 50 cm^3. An impeller-type mechanical stirrer was used to vigorously agitate the solutions inside the cell to accelerate semiclathrate formation and dissociation. The equilibrium cell was immersed in a circulator (RW-2025G, Jeio Tech, Republic of Korea) to control the temperature. A resistance temperature detector (RTD) sensor was used to measure the cell temperature after being calibrated using an ASTM 63C thermometer (H-B Instrument Company, USA). A pressure transducer (S-10, WIKA, Germany) was used to measure the cell pressure and was calibrated using a Heise Bourdon tube pressure gauge (CMM-140830, 0–20.0 MPa, Ashcroft, Inc. USA). The uncertainties associated with the temperature (T) and pressure (p) measurements were 0.1 K and 0.02 MPa, respectively.

An isochoric (pVT) method with step heating and cooling was adopted to determine the semiclathrate phase equilibria. The cell was charged with approximately 20 cm^3 of TiAAB (3.7 mol%) solution and then pressurized with the CO_2, N_2, or CO_2 (20%) + N_2 (80%) gas to the desired pressure. The cell was cooled down at a rate of 1.0 $K{\cdot}h^{-1}$ to induce semiclathrate formation. After the formation of semiclathrates, which was indicated by an abrupt pressure drop, the cell was slowly heated at a rate of 0.1 K per 90 min for the dissociation. The three-phase (semiclathrate (H) - liquid water (L_W) - vapor (V)) equilibrium point was determined by the intersection of the semiclathrate dissociation curve and the thermal expansion line at each pressure condition.

A high-pressure micro-differential scanning calorimeter (HP μDSC7 evo, Setaram Inc., France) was also used to measure the semiclathrate phase equilibria. The HP μDSC device consists of a reference cell and a sample cell, with an operating pressure range from 0 MPa to 40.0 MPa and an operating temperature range from 228.15 K to 393.15 K. The HP μ-DSC had a resolution of 0.02 μW. The DSC can be used to determine equilibrium dissociation temperature of semiclathrates using either dynamic or stepwise methods [23–25]. In this study, the stepwise DSC method, which was found to be more reliable and accurate, was also employed to confirm the semiclathrate phase equilibrium points measured by the isochoric (pVT) method. For the stepwise DSC experiments, the sample cell was charged with approximately 10 mg of TiAAB (3.7 mol%) solution, whereas the reference cell was left empty. Because stirring was not available, a multi-cycle mode of cooling and heating was applied to the cells in order to completely convert the TiAAB solution to TiAAB semiclathrates. The HP μDSC cells were initially cooled to T = 253 K at a cooling rate of 1.0 $K{\cdot}min^{-1}$, and then, they were firstly heated to a temperature 1 K lower than the expected dissociation temperature in 2 K increments with 3 h intervals. The temperature was further increased in 0.1 K increments with a 3 h isothermal duration at each step until there were no endothermic peaks from semiclathrate dissociation. As shown in Fig. 1, the temperature at the point at which the endothermic peaks disappeared was determined to be the equilibrium dissociation temperature of semiclathrates at a given pressure.

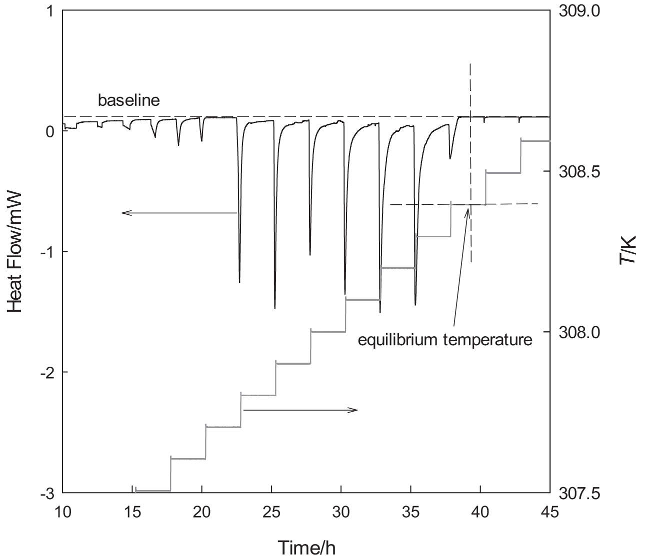

Fig. 1. Heat flow changes during stepwise heating of the CO_2 + TiAAB (3.7 mol%) semiclathrate at 2.9 MPa.

Table 1
Materials used in this study.

Chemical Name	Supplier	Purity	Water in mass fraction/10^{-6}	Analysis
CO_2	Deokyang	0.99999	–	GC[a,b]
N_2	KOSEM	0.9999	–	GC[a,b]
CO_2 (20%) + N_2 (80%)	MS Gas	–	–	GC[a,b]
TiAAB[c]	Synthesis	–	<150	NMR[d], KF[e]

[a] Analysis done by supplier.
[b] Gas chromatography.
[c] TiAAB: tetra-iso-amyl ammonium bromide.
[d] Nuclear magnetic resonance.
[e] Karl Fischer titration.

A fiber-coupled Raman spectrometer (SP550, Horiba, France) with a multichannel air cooled CCD detector and 1800 grooves/mm grating was used to obtain Raman spectra of TiAAB semiclathrates with CO_2, N_2, or CO_2 (20%) + N_2 (80%). A fiber-optic Raman probe was attached to the high-pressure equilibrium cell with a water jacket to allow the collection of the Raman spectra. A more detailed description of the experimental methods and procedure has been provided in our previous papers [20,26,27].

3. Results and discussion

3.1. Thermodynamic stability of TiAAB semiclathrates with CO_2, N_2, or CO_2 + N_2

TiAAB is known to form semiclathrates with a chemical formula of TiAAB·26 H_2O, which has a stoichiometric TiAAB concentration