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Hydration numbers and thermal properties of tetra-*n*-butyl ammonium bromide semiclathrate hydrates determined by ion chromatography and differential scanning calorimetry

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ABSTRACT

The hydration numbers and thermal properties of tetra-*n*-butyl ammonium bromide (TBAB) semiclathrate hydrate crystals formed from TBAB aqueous solutions with TBAB mole fractions (x) in the range of (0.0060–0.0360) were investigated by ion chromatography and differential scanning calorimetry (DSC). The hydration numbers of TBAB hydrates can be estimated from combined ion chromatography and DSC. The hydration number (n) and dissociation enthalpy of orthorhombic TBAB hydrate are constant at $n = 38$ and $\Delta H_{diss} \approx 220$ kJ mol^{-1}, respectively, for $x = $ (0.0060–0.0120). The hydration numbers and the enthalpies of tetragonal TBAB hydrates gradually increase from $n = 26.0$ and $\Delta H_{diss} = 149$ kJ mol^{-1} at $x = 0.0360$ to $n = 28.2$ and $\Delta H_{diss} = 160$ kJ mol^{-1} at $x = 0.0150$, respectively. The dissociation enthalpies of tetragonal TBAB hydrates linearly increase from $n = $ (26 to 32), which indicates that the enthalpies increase because of an increasing number of hydrogen bonds forming the TBAB hydrates. The dissociation temperatures of tetragonal TBAB hydrates decrease with increasing hydration number, and crystals with higher hydration numbers are thermodynamically unstable.

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1. Introduction

Clathrate hydrates are inclusion compounds comprising hydrogen-bonded hydrate cages containing guest molecules. In cases where large ionic guest molecules are included in a crystal, the guest cations are enclathrated over several hydrate cages, and the anions replace part of water molecules in the hydrate cages; such clathrate hydrates are known as "semiclathrate hydrates" [1]. A characteristic of semiclathrate hydrates is that the solid (hydrate)–liquid phase changes occur with relatively high latent heats in the range of (273–301) K [2–18], and small gas molecules (e.g., CO_2, CH_4, H_2, and N_2) can be captured in empty cages under lower pressure conditions than those required for the corresponding pure gas hydrates [15–23]. Fundamental and applied studies have reported using semiclathrate hydrates as phase-change materials (PCMs) for thermal/cold energy storage systems and as gas-capture materials for gas storage and separation systems [7–28].

Tetra-*n*-butyl ammonium bromide (TBAB) is a typical guest molecule involved in the formation of semiclathrate hydrates.

The maximum equilibrium temperature (T) in pure TBAB hydrates is $T = $ (285.2–285.9) K at $x = $ (0.029–0.040) (x indicates the mole fraction of TBAB in aqueous solutions); the different results have been reported by these researchers [4,5,11–16]. The dissociation enthalpies per guest mole are $\Delta H_{diss} = $ (151–153) kJ mol^{-1} at hydration number $n = 26$, 179 kJ mol^{-1} at $n = 32$, and (201–219) kJ mol^{-1} at $n = 38$ [8,14]: the enthalpies were measured by differential scanning calorimetry (DSC). Although it has been reported that TBAB hydrates with various crystal structures and different hydration numbers exist, all relevant details have not yet been provided. For example, Gaponenko et al., Aladako et al., and Lipkowski et al. have reported that a monoclinic TBAB hydrate with $n = 24$, tetragonal hydrates with $n = $ (26 and 32), and an orthorhombic hydrate with $n = 36$ are stable on the basis of X-ray diffraction analysis, chemical analysis (titration with $Hg(NO_3)_2$ using diphenylcarbazone as an indicator), and the T–x phase diagram [4,5,29]. On the other hand, Shimada et al. and Oyama et al. have reported that a tetragonal TBAB hydrate with $n = 26$ and an orthorhombic hydrate with $n = 38$ are stable on the basis of X-ray diffraction analysis and the T–x phase diagram [14,15,19]. It has been confirmed that tetragonal TBAB hydrates formed above $x = 0.014$ are stable crystals under appropriate conditions and orthorhombic hydrate formed below $x = 0.014$ is a stable crystal,

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on the basis of both the T–x phase diagram and spectroscopic measurements [13–16,19]. Recently, Rodionova et al. have reported that tetragonal TBAB hydrates are formed at $x \approx (0.023$ and $0.053)$ on the basis of X-ray diffraction analysis, and the hydration numbers of TBAB hydrates prepared at $x \approx (0.032, 0.023,$ and 0.006–$0.010)$ were respectively confirmed to be $n = (26, 32,$ and $38)$ by chemical analyses with an ion-selective electrode and titration with $Hg(NO_3)_2$ solution in aqueous ethanol with diphenylcarbazone as an indicator [8]. These reports suggest that the thermal properties and crystal structures, including hydration numbers, of pure TBAB hydrates change depending on the formation conditions of the hydrate crystals (e.g., supercooling temperature and mole fraction of the TBAB aqueous solution) and/or procedures (e.g., with or without annealing and agitation).

The hydration numbers and dissociation enthalpies of TBAB hydrate crystals in TBAB aqueous solutions of various mole fractions are important parameters not only for understanding the thermal properties of hydrate crystals but also for industrial applications such as thermal/cold energy storage and gas-capture materials. In addition, a simple and safe method to assess hydration numbers without using $Hg(NO_3)_2$ solution is necessary. In this study, a new assessment method for the hydration numbers of TBAB hydrates using ion chromatography and DSC measurements is proposed: Ion chromatography is used for clathrate hydrate analyses such as the ion removal assessments in sea water desalination [30], and DSC is widely used for the thermal property studies of semiclathrate hydrates. The dependence of the hydration numbers and dissociation enthalpies of TBAB hydrates on TBAB aqueous solution mole fraction is also reported.

2. Experimental

2.1. Materials

Research-grade TBAB (0.99 mass fraction purity, Sigma-Aldrich Co., LLC.) and distilled water (ADVANTEC®, RFD240FC) were used without further purification (as described in Table 1). The mole fraction of the initial TBAB aqueous solutions (x) were 0.0060, 0.0100, 0.0120, 0.0150, 0.0160, 0.0200, 0.0300, and 0.0360, and they were measured by an electronic balance with the reading uncertainty of ±0.1 mg: based on the mass measurement uncertainty, the uncertainties of x are estimated to be within ±0.00005. (10–20) cm^3 of these solutions were placed in plastic test tubes of 50 cm^3 capacity.

2.2. Measurement procedures

The hydrate samples were prepared using cooling baths (Isotemp®, 4100 R20/R28 or EYELA, NCB-3300), and the bath temperatures were measured using calibrated thermocouples (±0.05 K, type K or type T, Chino Co., Japan) at 0.1 MPa (±0.005 MPa, i.e., atmospheric pressure) in air. After crystallizing the samples by cooling to below 273 K, the hydrate samples were prepared with agitation and annealing. The equilibrium temperatures at each mole fraction were taken from Oshima et al. [12,13]; the temperature at $x = 0.0150$ was newly obtained by measuring three times

here using the same procedure. The expanded uncertainty of the obtained hydrate-liquid equilibrium temperature in controlling the sample temperature is considered was estimated to be ±0.1 K with a confidence level of approximately 0.95. The hydrate samples were grown with (0.1–2.0) K sub-cooling for a few to several days. For each mole fraction, two or three samples were prepared under the same conditions. The hydrate crystals were separated from the aqueous solutions (residual solutions) and quickly dried using paper sheets. Small crystalline particles with diameters in the range of (850–1000) μm were collected using metal sieves and cooled with liquid nitrogen for ion chromatography and DSC measurements.

The mole fraction of Br$^-$ in the hydrate crystals and residual solutions were analyzed by ion chromatography (SHIMADZU, SIL-10AI) using an anion-exchange column (SHIMADZU, Shim-pack IC-SA2) and a suppressor-type electric conductance detector (SHIMADZU, CDD-10ASP). The eluent was a mixed aqueous solution of 12 mmol m^{-3} sodium hydrogen carbonate and 0.6 mmol m^{-3} sodium carbonate. The column was held at 40 °C, and the sample volume was 1600 cm^3 for all analyses. The Br$^-$ mole fraction in each sample was determined from a calibration curve for standard TBAB solutions, and the mole fractions in each sample were estimated from the Br$^-$ mole fractions. Samples ≈0.1 g in mass were diluted with 1000 cm^3 ultrapure water (Merck Millipore, Direct-Q UV3), and the mole fractions in each sample were normalized by each sample mass. The samples were analyzed five times, and average values were taken.

The amounts of the residual solution in the hydrate crystals and the dissociation enthalpies of the hydrates were measured by DSC (MAC Science, DSC-3200S). The heat quantities and temperatures of DSC were calibrated by the melting heat and melting point of H_2O ice. Hydrate particle samples (90–200) mg in mass were placed in a sealed aluminum cell. The temperature of the sample cell was increased at a rate of 0.5 K min^{-1} from below 268 K. Measurements were repeated at least five times, and average values were taken.

3. Results and discussion

Fig. 1 shows the hydrate mole fractions (x_{h1}) calculated from the Br$^-$ mole fractions determined by ion chromatography.
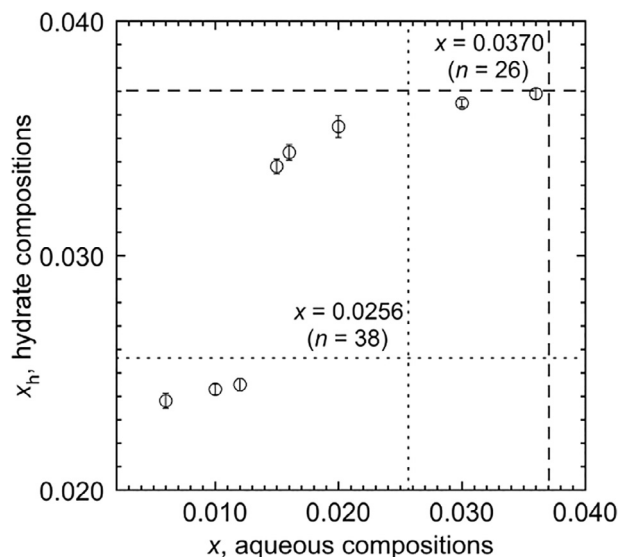
Table 1
Specifications of the materials used in the experiments.

Chemical name	Source	Mass fraction purity
Tetra-*n*-butyl ammonium bromide (TBAB)	Sigma-Aldrich Co. LLC.	0.99[a]
Distilled water (H_2O)	ADVANTEC®, RFD240FC	–

[a] No further purification was done before use.

Fig. 1. The TBAB hydrate mole fraction (x_{h1}) as a function of initial TBAB solution mole fraction (x) estimated from Br$^-$ mole fraction determined by ion chromatography. Dashed and dotted lines indicate $x = 0.0370$ ($n = 26$) and $x = 0.0256$ ($n = 38$), respectively.