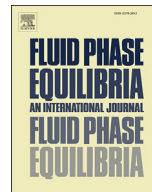




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Phase equilibrium temperature and dissociation heat of ionic semiclathrate hydrate formed with tetrabutylammonium butyrate

Yuji Yamauchi, Yuta Arai, Tatsuro Yamasaki, Fuyuki Endo, Atsushi Hotta, Ryo Ohmura*

Department of Mechanical Engineering, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan

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ABSTRACT

This paper reports the phase equilibrium temperature and dissociation heat of ionic semiclathrate hydrate formed with tetrabutylammonium butyrate (TBABu). The temperature – composition phase diagram of the TBABu hydrate was determined in the mass fraction from 0.10 to 0.44. The highest equilibrium temperature of TBABu hydrate was 15.4 °C in the mass fraction range from 0.35 to 0.37. On the dissociation heat of DSC measurements, a single heat flow peak of TBABu hydrate excluding ice melting peak was observed at all the mass fraction systems. The largest dissociation heat was 184.9 ± 3.1 kJ/kg at the mass fraction 0.36. TBABu hydrate could potentially be used as a thermal energy storage material.

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1. Introduction

Clathrate hydrates are ice-like crystalline compounds consisting of host water molecules forming cages by hydrogen-bonded and enclosing different guest molecules within. There are reports on using clathrate hydrate as phase change material (PCM) [1–7]. In an ionic semiclathrate hydrate, anions of a guest compound partially replace with H₂O molecules forming hydrogen-bonded cages. Ionic semiclathrate hydrates are formed when guest compounds are ionic compounds like tetrabutylammonium (TBA) salts and tetrabutylphosphonium (TBP) salts [8]. Equilibrium temperatures of ionic semiclathrate hydrates are often higher than pure ice melting point under atmospheric pressure. Thermal energy storage technologies using ionic semiclathrate hydrate contribute to moderating imbalance in energy demand.

The coefficient of performance (COP) of a refrigerator may be defined as $\varepsilon = T_L / (T_H - T_L)$ for the inverse Carnot cycle. T_L and T_H are temperatures of low and high grade heat sources. If phase change temperature was close to required temperature, COP is improved. Required temperatures of cooling air are various for applications. For residential air conditioning, required air temperature is 5 °C–15 °C. For data centers, required temperature is 15 °C–32 °C

[9]. Water is widely used as thermal energy storage medium. By using ionic semiclathrate hydrates for thermal energy storage materials, we may expect higher COP of the refrigerator than that of ice system.

Tetrabutylammonium bromide (TBAB) is one of the ionic guest compounds which forms ionic semiclathrate hydrate. TBAB hydrate is being utilized as a thermal energy storage material for residential air conditioning [10]. Thermal properties of TBAB hydrate have been well investigated. The equilibrium temperature of TBAB hydrate is approximately 13 °C, and the dissociation heat is approximately 200 kJ/kg [10–18]. This equilibrium temperature is suitable for a thermal energy storage material of residential air conditioning. However, in the air conditioning for data center, cooling air temperature can be higher. Thermal property data of the hydrates other than TBAB hydrate are required to select suitable thermal energy storage material for various applications.

In addition to tetrabutylammonium bromide, tetrabutylammonium chloride (TBAC), tetrabutylammonium fluorine (TBAF) can be guest compounds. TBAC hydrate forms ionic semiclathrate hydrate with water molecules below approximately 288 K under atmospheric pressure [11,12,19–22]. TBAF also forms ionic semiclathrate hydrate below approximately 301 K [18,23]. There are also the previous studies on thermal properties of tetrabutylphosphonium salt (TBP salt) hydrates. Kobori et al. have mentioned that the equilibrium temperature of TBA salt hydrate tend to be higher than TBP salt hydrate with the common anion [24].

* Corresponding author.

E-mail address: rohamura@mech.keio.ac.jp (R. Ohmura).

Halogens like bromide, chloride, and fluorine can be anions of guest compounds, and their hydrates thermal properties have been well investigated. In addition to them, carboxylic acids can also be anions of guest compounds, like tetrabutylammonium acrylate (TBAAC) [25]. TBAAC is neutralized salt of tetrabutylammonium hydroxide with acrylic acid, one of the carboxylic acid. The knowledge on thermal properties of the ionic semiclathrate hydrates formed with organic salts has been quite limited.

Nakayama et al. [26] and Dyadin et al. [27] reported on the phase equilibrium temperature of many of tetrabutylammonium carboxylates hydrates. According to those reports, the equilibrium temperature of tetrabutylammonium butyrate (TBABu) hydrate was 15 °C–22 °C. Tetrabutylammonium butyrate is neutralized salt of tetrabutylammonium hydroxide with butyric acid. TBABu hydrate is also promising as a thermal energy storage material. However, there is no report on the dissociation heat of TBABu hydrate. Those data are necessary to clarify whether TBABu hydrate can store sufficient thermal energy. In addition to that, uncertainties of measurements of phase equilibrium temperature were not evaluated because these were reported before the Guide to the Expression of Uncertainty in Measurement (GUM) [28] were established.

In this study, the phase equilibrium temperature and the dissociation heat of the ionic semiclathrate hydrate formed with tetrabutylammonium butyrate were measured. The phase equilibrium temperature of TBABu hydrate was measured by the stepwise temperature increasing procedure. The dissociation heat was measured by a differential scanning calorimetry.

2. Experiment methods

2.1. Materials

Tetrabutylammonium butyrate (TBABu) aqueous solutions for forming TBABu hydrate were obtained by neutralizing tetrabutylammonium hydroxide (TBAOH) solution (0.40 mass fraction in aqueous solution, Sigma Aldrich Co. LLC.) with butyric acid (0.99 mass fraction, Sigma Aldrich Co. LLC.). Mass fraction 0.44 of TBABu solution was upper limit that can be obtained by neutralizing those solutions. Distilled and deionized water was used for preparing several different concentrations of TBABu solution. The masses of compounded solution and water were measured by an electronic balance with the expanded uncertainty of ± 0.1 mg (coverage factor $k = 2$). The specifications of the materials used in the experiments are summarized in Table 1. The standard uncertainties of TBABu mass and mole fraction are estimated to be $u(w_{\text{TBABu}}) = 1.0 \times 10^{-4}$ and $u(x_{\text{TBABu}}) = 1.0 \times 10^{-5}$. The mass fraction of impurities in mixed solution is estimated to be less than 2.0×10^{-4} .

2.2. Equilibrium temperature

A schematic of the experimental apparatus was described elsewhere [11,25,29]. The bath was filled with ethylene glycol solution. The system temperature was controlled by a chiller (CTP-3000 EYELA, Tokyo Rikakikai Co. Ltd.), and the temperature was

first kept constant at 1 °C. The temperature in the test tube was measured by a platinum resistance temperature detector with the uncertainty of ± 0.1 °C ($k = 2$). TBABu aqueous solution (approximately 0.5 g) was injected into each glass test tubes (external diameter 10 mm, inside diameter 8 mm). Openings of the test tubes were covered with silicon caps to prevent solution evaporating. These test tubes were previously cooled in a refrigerator for 24 h to ensure that hydrate grow completely before they were set in the bath. To observe hydrate dissociation, a CMOS digital camera attached to a microscope.

In the phase equilibrium temperature measurement, the test section temperature was increased in steps of every 0.1 °C. At each step the temperature was kept constant for at least 5 h. If TBABu hydrate crystals started to dissociate, the temperature was continuously kept for another 5 h. We repeated this 5 h waiting. When the crystals did not visually change, the temperature was increased by 0.1 °C. Typically, the temperature was kept for 10 h in total, but 70 h temperature keeping was necessary at the mass fraction of 0.36. This stepwise temperature increase was continued until all of the TBABu hydrate dissociated. The phase equilibrium temperature was determined as the highest temperature at which the crystals remained in the test tube. These measurements were performed under atmospheric pressure. This stepwise measurement is the same as that performed in the previous studies reported by Sato et al. [11], Suginaka et al. [29] and Sakamoto et al. [25]. The hydrate dissociation behavior observed in the present study is discussed in more detail in the “Results and Discussion” section.

2.3. Dissociation heat

The dissociation heat of TBABu hydrate was measured by a differential scanning calorimetry (DSC-822e METTLER TOLEDO Co., Ltd.). In this measurement, aluminium test pans were used. A reference test pan was filled with the air.

Dry nitrogen was filled in the test section of the DSC with the flow rate of 40 cm³/min under atmospheric pressure. First, the system was kept at 15 °C for 3 min. To form TBABu hydrate in the test pan, the system was cooled to –20 °C and kept for 10 min. Then the temperature was increased constantly by 2 °C/min until 30 °C. By checking heat flow peaks for generating hydrate, it was confirmed that TBABu hydrate formed completely during the cooling process. To ensure the reproducibility of heat flow rate curve and dissociation heat value, triplicate measurements were performed at each mass fraction system.

3. Results and discussion

3.1. Equilibrium temperature

The phase equilibrium temperature of TBABu hydrate was measured in the mass fraction range from 0.10 to 0.44. The results of equilibrium temperature are summarized in Table 2. T_{eq} is equilibrium temperature of TBABu hydrate. The atmospheric pressures shown in Table 2 were measured by the Local

Table 1
Specifications of the materials used in the experiments.

Sample name	Chemical Formula	Supplier	Purity ^a
Tetrabutylammonium hydroxide (TBAOH)	(CH ₃ CH ₂ CH ₂ CH ₂) ₄ N(OH)	Sigma Aldrich Co. LLC.	0.40 mass fraction in aqueous solution
Butyric acid	CH ₃ CH ₂ CH ₂ COOH	Sigma Aldrich Co. LLC.	0.99 mass solution
Water	H ₂ O	Laboratory made	Electrical conductivity was less than 0.1 μS/cm
Tetrabutylammonium butyrate aqueous solution		Laboratory made with above solutions	Impurities mass fraction was less than 2.0×10^{-4}

^a The mass fraction of impurities in TBABu aqueous solution was estimated from the impurities of TBAOH solution, butyric acid, water and neutralizing process.

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