Calorimetric Measurements on Ionic Semiclathrate Hydrate Formed with Tetrabutylammonium Sulfate ($TBASO_4$)

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Abstract: This paper reports the dissociation heats of ionic semiclathrate hydrate formed with tetrabutylammonium sulfate ($TBASO_4$) holding the bivalent anion. The heat flow rates and the dissociation heats of $TBASO_4$ hydrate were measured by the differential scanning calorimetry (DSC) at the mass fractions 0.30, 0.34 and 0.38. On the DSC curves of the heat flow rate, the two peaks were observed at the mass fractions 0.30 and 0.34, and the single peak was observed at the mass fraction 0.38. The largest dissociation heat of $TBASO_4$ hydrate was 190 $kJ \cdot kg^{-1}$ at the mass fraction 0.34.

Key words: Tetrabutylammonium sulfate ($TBASO_4$), ionic semiclathrate hydrate, differential scanning calorimetry, dissociation heat.

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1. Introduction

The phase change materials (PCM) of the thermal energy storage system are useful to advanced utilization of energy. PCM can be categorized into the two types, the organic and the inorganic [1], [2]. The organic PCM consists of the carbon molecule. The disadvantage point utilizing the organic PCM is the low thermal conductivity. On the cooling system for the machines, the sudden generation of heat cannot be managed. The inorganic PCM has two types utilizing the metallic salts and clathrate hydrates. The metallic salts are corrosive in the device. These systems would not be able to be used long time. Clathrate hydrates, or hydrates, are ice-like inclusion compounds consisting of water molecules, host materials, forming the cage surrounding the molecules of other materials, guest materials. They have the large heat of formation and dissociation [3]. The thermal energy storage system can be miniaturized with this property. With the water molecules, hydrates are comparatively hard to flame. In general, the hydrate formation requires high pressure and low temperature. On ionic semiclathrate hydrates, a part of the hydrate cage is replaced with the anion of the guest compound. They can be formed under the atmospheric pressure and at the room temperature [4]-[6]. Thermal energy storage system using ionic semiclathrate hydrate can improve the energy management.

Tetrabutylammonium bromide (TBAB) hydrate is the only hydrate commercialized as PCM. It was reported that the equilibrium temperature of TBAB hydrate was 285.9 K [7]. The equilibrium temperature required for the general air conditioning system is 278 K to 288 K. TBAB hydrate is utilized as PCM for the general air conditioning system [8], [9]. On TBAB hydrate, previous studies reported the dissociation heat was 193 $kJ \cdot kg^{-1}$ [10] and the thermal conductivity was 0.349 $W \cdot m^{-1} \cdot K^{-1}$ [11]. The thermal properties of TBAB hydrate have been reported by a lot of previous studies [7], [10]-[12]. However, the studies about the thermal properties of the other hydrates as PCM are quite limited compared to TBAB hydrate. Thermal properties are required to select the suitable material as PCM for various applications. It is important to put more effort into studying on the other hydrate PCM.

For the thermal energy storage system, the dissociation heat is one of the most important thermal properties to design the actual system. On ionic semiclathrate hydrates, Sakamoto et al. reported the greatest dissociation heat of tetrabutylammonium acrylate (TBAAc) hydrate was 195 kJ·kg^{-1} at $w_{\mathrm{TBAAc}} = 0.33$ (w_{material} denotes the mass fraction of material) and tetrabutylphosphonium chloride (TBPC) hydrate was 194 kJ·kg^{-1} at $w_{\mathrm{TBPC}} = 0.37$ [13]. Suginaka *et al.* reported also the greatest dissociation heat of tetrabutylphosphonium bromide (TBPB) hydrate was 214 kJ·kg^{-1} at $w_{\mathrm{TBPB}} = 0.35$ [14]. Yamauchi et al. reported the greatest dissociation heat of tetrabutylammonium butyrate (TBABu) hydrate was 185 kJ·kg^{-1} at $w_{\mathrm{TBABu}} = 0.36$ [15] and tetrabutylammonium propionate (TBAPr) hydrate was 203 kJ·kg^{-1} at $w_{\mathrm{TBAPr}} = 0.38$ [16]. Arai et al. reported the greatest dissociation heat of tetrabutylphosphonium acetate (TBPAce) hydrate was 192 kJ·kg^{-1} at $w_{\mathrm{TBPAe}} = 0.36$ [17]. The dissociation heats of studied ionic semiclathrate hydrates were approximately 200 ± 15 kJ·kg^{1}. The greatest dissociation heats were measured at $w = 0.35 \pm 0.03$.

Ionic semiclathrate hydrates reported on the dissociation heat consist of the monovalent anions as the halogens or the carboxylic acids. The dissociation heats of ionic semiclathrate hydrates with the bivalent and trivalent anions as the sulfuric acid and the phosphoric acid have not been reported. The bivalent and trivalent anions are larger than the monovalent anions. The cage structures with the bivalent and trivalent anions would be different from that with the monovalent anions. The thermal properties would be changed by the structure change of the hydrate cages. Revealing the new thermal properties can not only develop technology as the thermal energy storage system but also help to clarify variations in the mechanism of the thermal properties.

Tetrabutylammonium sulfate ($TBASO_4$) hydrate has the bivalent anion. In addition to hydrate characteristic, $TBASO_4$ hydrate may be eco-friendly material without halogen molecule. Therefore, $TBASO_4$ hydrate would be suitable as PCM. Nakayama reported the equilibrium temperature of $TBASO_4$ hydrate was 285.6 K at $w_{\mathrm{TBASO4}} = 0.335$ [18]. On $TBASO_4$ hydrate, the other thermal properties are not measured. In this study, the dissociation heat of $TBASO_4$ hydrate holding the bivalent anion was measured. The comparison on the dissociation heats of ionic semiclathrate hydrates holding the monovalent anion and the bivalent anion was discussed.

2. Experiment Methods

2.1. Materials

Tetrabutylammonium sulfate ($TBASO_4$) solution was prepared by neutralizing tetrabutylammonium hydroxide (TBAOH) solution (0.40 mass fraction in aqueous solution made by Sigma-Aldrich CO. LLC.) with sulfuric acid (0.70 mass fraction in aqueous solution made by Sigma Aldrich Co. LLC.). The mass fractions 0.30, 0.34 and 0.38 of $TBASO_4$ aqueous solutions were adjusted by laboratory-made water which was deionized and distilled. The mass of these solutions was measured by an electronic balance (IUW-200D sefi, As One Co. LLC.) with the uncertainty of ± 0.01 mg. The liquid reagents used in this study were summarized on Table 1.

2.2. Dissociation Heat Measurements

The dissociation heat of $TBASO_4$ hydrate was measured by the differential scanning calorimetry (DSC-822e METTLER TOLEDO Co. Ltd.) with the uncertainty of ± 6 kJ·kg^{-1} on Fig. 1. In this study, the aluminum pans of 4.0×10^{-3} cm^3 were used. Approximately 30 mg of the reagents was injected into the pan called the sample test pan. The mass of the pan was then measured. The reference test pan was filled with the air.

The test section of DSC was filled with the dry nitrogen at the flow rate of 40 $cm^3 \cdot min^{-1}$ under 0.1 MPa. The temperatures of two test pans during the measurement could be controlled as shown on Fig. 2. The system was first kept at 293 K for 2 minutes. the temperature was then decreased from 293 K to 253 K by 5 $K \cdot min^{-1}$ to form hydrate. After keeping at 253 K for 5 minutes, the system was heated from 253 K to 303 K by 2 $K \cdot min^{-1}$ to dissociate hydrate. The heat flow rate was measured by DSC. The dissociation heat was obtained by integrating the peak of the heat flow rate during the hydrate dissociation.

Table 1. The Specification of the Liquid Reagents Used in This Study

Sample Name	Chemical Formula	Supplier	Purity
Tetrabutylammonium hydroxide (TBAOH) solution	$(CH_3CH_2CH_2CH_2)_4N(OH)$	Sigma Aldrich Co. LLC.	0.40 mass fraction in aqueous solution
Sulfuric acid	H_2SO_4	Sigma Aldrich Co. LLC.	0.70 mass fraction in aqueous solution
Water	H_2O	Laboratory made	Electrical conductivity was less than 0.1 $\mu S \cdot cm^{-1}$
Tetrabutylammonium sulfate ($TBASO_4$) solution	$((CH_3CH_2CH_2CH_2)_4N)_2SO_4$	Laboratory made with above solutions	-

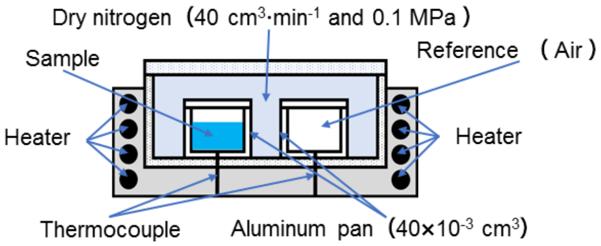

Fig. 1. The schematic diagram of the differential scanning calorimetry.

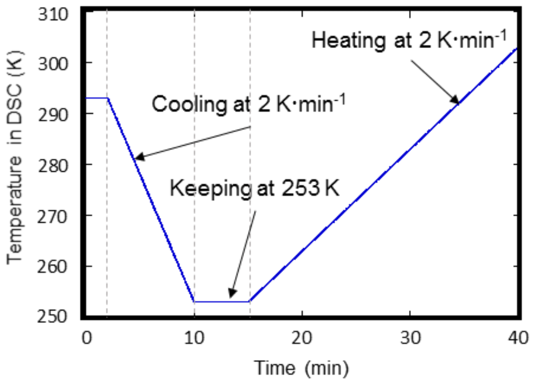

Fig. 2. The schematic diagram of the controlled temperature in DSC.

3. Results and Discussion

3.1. Heat Flow Rate Measurements

On $TBASO_4$ hydrate, the heat flow rates were measured by DSC at the mass fractions 0.30, 0.34 and 0.38. In the measurement process, the DSC curve of the heat flow rate at w_{TBASO4} = 0.38 is presented in Fig. 3 in the form of a heat flow rate – time diagram. The heat flow rates were normalized by the mass of $TBASO_4$ aqueous solution injected into the sample test pan. The exothermic peak of the heat flow rate means that the temperature of the sample test pan was higher than T_r, where T_r denotes the temperature of the reference test pan. On the contrary, when the temperature of the sample test pan was lower than T_r, the endothermic peak of the heat flow rate was observed. The phase changes of hydrate would occur at the start of the heat flow rate peaks. In Fig. 3, the endothermic peak of the heat flow rate was observed on the cooling process. $TBASO_4$ hydrate would be formed then. On the heating process, the endothermic peak of the heat flow rate was observed. It would mean $TBASO_4$ hydrate dissociation.

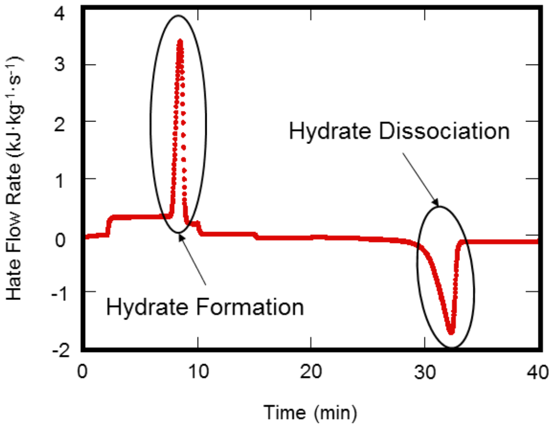

Fig. 3. The DSC curve of the heat flow rate in the measurement process at w_{TBASO4} = 0.38.

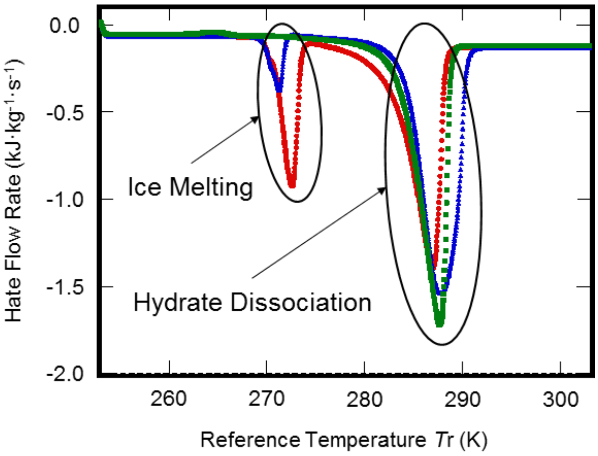

Fig. 4. The DSC curve of the heat flow rate in the heating process.
Red ●, w_{TBASO4} = 0.30; blue ▲, w_{TBASO4} = 0.34; green ■, w_{TBASO4} = 0.38.

The DSC curves on the heating process at the mass fractions 0.30, 0.34 and 0.38 are presented in Fig. 4 in the form of a heat flow rate – T_r diagram. In Fig. 4, the two peaks of the heat flow rate were observed at the mass fractions 0.30 and 0.34. The peak observed at the lower temperature would correspond to the ice melting. This ice would be formed with the extra water after forming $TBASO_4$ hydrate. The lower peak started at below 273 K due to the freezing point depression. The higher peak at approximately 286 K would mean hydrate dissociation. At w_{TBASO4} = 0.30, the hydrate dissociation temperature started at approximately 273 K was the lowest of that at the three mass fractions. The peak of the heat flow rate curve due to $TBASO_4$ hydrate dissociation was the widest of that at the three mass fractions. If the sample mass fraction was not the congruent point, the liquid composition changed with forming hydrate. At the congruent point, the composition of the aqueous solution and $TBASO_4$ hydrate were the same. The change rate of the liquid composition would increase with the increase of the difference between the sample mass fraction and congruent point. Therefore, the widest peak would mean that the mass fraction 0.30 was the largest difference from the congruent point of that at the three mass fractions. At w_{TBASO4} = 0.34, the peak of the ice melting was shallower than that at w_{TBASO4} = 0.30. On the contrary, the peak of the hydrate dissociation was deeper. This would mean that the amount of ice was decreased and the amount of hydrate was increased with the increase of the mass fraction. The temperature of the peak end at w_{TBASO4} = 0.34 differed from that at the mass fractions 0.30 and 0.38. The hydrate dissociation would not finish at the equilibrium temperature because the heating rate was fast for the dissociation speed of $TBASO_4$ hydrate. At w_{TBASO4} = 0.38, the observed single peak was the endothermic peak of the heat flow rate by the hydrate dissociation heat. That peak was the deepest and the narrowest of that at the three mass fractions. The endothermic peak of the ice melting was not observed. When the mass fraction was higher than the congruent point, the guest materials remained and host materials ran out. The mass fraction 0.38 would be higher than the congruent point.

Ionic semiclathrate hydrates with the monovalent anions have the metastable hydrate [13], [15]–[17]. At the three mass fractions of $TBASO_4$ hydrate, the metastable hydrate was not observed from the heat flow rate curves measured in this study.

3.2. Dissociation Heat Measurements

To confirm the reliability of the dissociation heat measurements with DSC, the latent heat of water was measured by the experiment method in this study. The latent heat of water was 334 $\mathrm{kJ \cdot kg^{-1}}$. The measured latent heat of water corresponded to the literature data within the uncertainty of DSC [19]. The dissociation heats measured in this study would be reliable.

Table 2. The Dissociation Heat of $TBASO_4$ Hydrate on the Mass Fraction

Mass Fraction	Dissociation Heat ($\mathrm{kJ \cdot kg^{-1}}$)
0.30	150
0.34	190
0.38	165

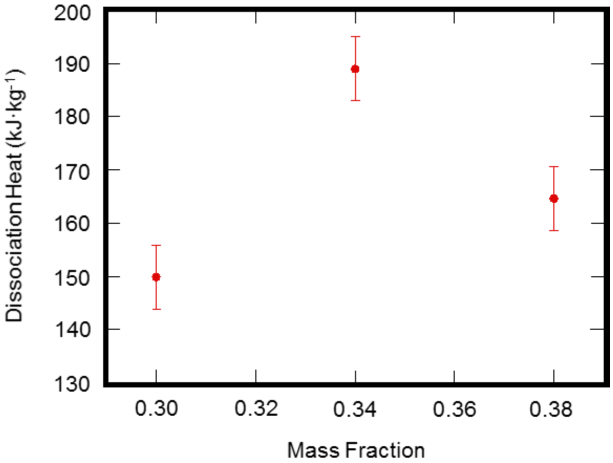

Fig. 5. The dissociation heat of $TBASO_4$ hydrate on the mass fraction.

The dissociation heats of $TBASO_4$ hydrate were obtained by integrating the peak of the heat flow rate during the hydrate dissociation at the mass fractions 0.30, 0.34 and 0.38. The measured dissociation heats are presented in Table 2 and Fig. 5 in the form of a dissociation heat – w_{TBASO4} diagram. The bars on Fig. 5 showed the uncertainty of DSC. At w_{TBASO4} = 0.30, the amount of the guest material would be the least of that at the three mass fractions. The dissociation heat was also the smallest because the minimum amount of formed hydrate. At w_{TBASO4} = 0.38, the extra guest material would exist. The amount of formed hydrate would be less than that at w_{TBASO4} = 0.34. The dissociation heat was also smaller. At w_{TBASO4} = 0.34, the dissociation heat was the largest of that at the three mass fractions. The amount of formed hydrate would be also the greatest. At the congruent point, the amount of hydrate would be the greatest. And the dissociation heat would be the largest [17]. The mass fraction 0.34 would be the closest to the congruent point. The peak of the dissociation heat was observed in ionic semiclathrate hydrate with the bivalent anion. That peak of the dissociation heat was also observed for ionic semiclathrate hydrates with the monovalent anions [13]–[17].

The largest dissociation heat of $TBASO_4$ hydrate was 190 $kJ\cdot kg^{-1}$. This result was close to the dissociation of ionic semiclathrate hydrate with the monovalent anions [13]–[17].

The bars showed the uncertainty of DSC. The uncertainty of DSC was ± 6 $kJ\cdot kg^{-1}$.

4. Conclusion

On $TBASO_4$ hydrate, the heat flow rates and the dissociation heats were measured at the mass fractions 0.30, 0.34 and 0.38. At the mass fractions 0.30 and 0.34, as ice would be formed with the extra water after forming TBASO4 hydrate, the two peaks of the heat flow rate were observed. At w_{TBASO4} = 0.38, the single peak due to the hydrate dissociation was observed. The congruent point of $TBASO_4$ hydrate would be the mass fraction range from 0.34 to 0.38. The metastable hydrates formed with ionic semiclathrate hydrate consisting of the monovalent anions were not observed from the DSC curves at the three mass fractions on $TBASO_4$ hydrate holding the bivalent anion. The largest dissociation of $TBASO_4$ hydrate was 190 $kJ\cdot kg^{-1}$ at w_{TBASO4} = 0.34. Then, the amount of formed hydrate would be the greatest of that at the three mass fractions.

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