The Measurement of Dissociation Heat and Equilibrium Temperature of Tetrabutylammonium Propionate Hydrate

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Abstract

This paper reports the results of an experimental study conducted to measure the thermodynamics properties of ionic semicladrate hydrate formed with tetrabutylammonium propionate (TBAPr). The thermodynamic measurements were performed on the equilibrium temperature and on the dissociation heat of the hydrate in the range of the mass fraction of tetrabutylammonium propionate $w_{\text{TBAPr}}$ from 0.10 to 0.43. The highest equilibrium temperature of the TBAPr system was 17.5 °C at $w_{\text{TBAPr}} = 0.37$. The largest dissociation heat of TBAPr system was 193 kJ/kg at $w_{\text{TBAPr}} = 0.37$. These findings indicate that TBAPr hydrate is promising for application in cool energy storage material.

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1. Introduction

Demand for electric power in the daytime is greater than in the nighttime due to the mass usage of air conditioning. This causes the difference in demand for electric power to be much larger in summer. Imbalance in demand of electric power in a day leads to the rising cost in producing electric power. If the peak of demand for electric power in the daytime can be shifted towards the nighttime, the maximum demand of electric power in a day can be reduced, and the cost for generating electric power would be decreased subsequently. Thermal energy storage is listed as one of the potential technologies to perform this peak shifting of power demand. Thermal energy storage, here, means that electric power produced in the nighttime is converted into thermal energy by a refrigerator and stocked in the thermal energy storage materials, then, during the daytime, cold thermal energy is utilized from the thermal energy storage materials for the air conditioning.

Thermal energy storage systems commonly utilize the liquid-solid phase change, and as a thermal energy storage material, water is widely utilized for air conditioning. Water is advantageous, as it has a large latent heat of the phase change, but it requires the temperature of the refrigerator to be as low as 263-268 K for to form ice. The difference of this temperature and the room temperature is large, hence, the coefficient of performance (COP) of the refrigerator is decreased. Temperature of the air is

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needs to be 278-288 K for a general air conditioner. The temperature may be higher for air conditioners of data centers. The equilibrium temperature of water, 0 °C, is far from the required temperature range, and this decreases the energy efficiency. To improve the COP of the refrigerator of such thermal energy storage systems, it is necessary to select suitable energy storage materials that can change freeze under near room temperature. Therefore, it is proposed that clathrate hydrates will be a more suitable option than water for cool energy storage material.

Clathrate hydrates, or hydrates, are ice-like crystalline compounds consisting of host water molecules hydrogen-bonded to form cages that encloses different guest molecules within. Generally hydrates are stable only under high pressures and low temperatures. When hydrates are formed with ionic guest substances such as tetrabutylammonium bromide however, some of the water molecules which form cages are replaced with the anions of the guest; and hence they are called ionic semiclathrate hydrate.[1,2,3] Ionic semiclathrate hydrates have the property of being thermodynamically stable around room temperature conditions under atmospheric pressure. Ionic semiclathrate hydrate is expected to pave way for useful applications in industry, such as cool energy storage material. [4,5,6] But the number of examples with hydrate as a practical thermal storage material is limited. Tetrabutylammonium bromide (TBAB) hydrate, for example, which is practically utilized as thermal storage material is a type of ionic semiclathrate hydrate. The equilibrium temperature of TBAB hydrate is approximately 10 °C, and the dissociation heat is approximately 200 kJ/kg. But there are several ionic semiclathrate hydrates that may be suitable for thermal storage material, hence finding a more suitable hydrate is necessary.

Nakayama et al.[7] and Dyadin et al.[1] reported that the phase equilibrium temperature of tetrabutylammonium propionate hydrate (TBAPr), one of the semiclathrate hydrate, is approximately 291 K. This phase equilibrium temperature is higher than water by approximately 18 °C. If we use TBAPr hydrate as a cool energy storage material, required temperature of the refrigerator is higher than water’s, and COP of the refrigerator will increase. Therefore, this property suggests TBAPr may be suitable as cool energy storage material. In order to use TBAPr hydrate for cool energy storage material, however, the dissociation heat of the TBAPr hydrate needs to be quantitatively clarified. As the dissociation heat of the TBAPr hydrate have not been measured, and uncertainty of the equilibrium temperature measurement was not clearly reported, in the present study, we have performed measurement of the phase equilibrium temperature and dissociation heat of TBAPr hydrate.

2. Experimental methods

2.1. Materials

The liquid water used in the experiments was laboratory-made distilled liquid water. Sample of TBAPr hydrate for the phase equilibrium and the dissociation heat measurements were formed with tetrabutylammonium propionate aqueous solutions. Tetrabutylammonium propionate aqueous solution was obtained by neutralizing the tetrabutylammonium hydroxide solution (40 mass% solution in water, Aldrich Chemical Co.) with propionic acid (99.5% solution, Aldrich Chemical Co.). The sample compositions were adjusted in the mass fraction range from 0.10 to 0.43 with the aid of an electric balance.

2.2. Equilibrium temperature

Fig. 1 shows a schematic of the experimental apparatus used in the observation of the TBAPr hydrate formed in tetrabutylammonium propionate aqueous solution. The experimental procedure is the same as that performed in the previous studies reported by Sakamoto et al.[4], Suginaka et al.[8] and Sato et al.[9] We confirmed the reliability of the measurement.
performed in our study by measuring the melting point of the ice under atmospheric pressure.

Glass test tubes (external diameter 10 mm, inside diameter 8 mm, height 90 mm) were filled with tetrabutylammonium propionate aqueous solution (approximately 0.5 g) and were set in the bath. The bath was filled with ethylene glycol solution. We observed the hydrate in the test tube with a CMOS digital camera that was attached to the microscope. The temperature was controlled by a chiller (CTP-3000 EYELA). The temperature of surrounding the test tube was measured by a platinum resistance temperature detector (with the uncertainty of ± 0.1 K) inserted in the glass container. These temperature-mass fraction measurements were performed under atmospheric pressure.

The system temperature was first kept constant at 1 °C, and seed crystals of TBAPr hydrate (approximately 5 mg), which was formed in a refrigerator in advance, were dropped in each aqueous solution. This procedure uses artificially induced nucleation to ensure that the hydrate grow in the test tube. The system temperature was kept constant for 24 hours to allow the hydrate to grow completely. The temperature was then increased in steps every 0.1 K. At each temperature step, the temperature was maintained for at least 4 hours. If hydrate crystals started to dissociate within 4 hours, the system temperature was maintained for a longer time. If the crystals did not visually change for 4 hours, we assessed that the hydrate dissociation has stopped, and the temperature of the system was increased by 0.1 K. The stepwise increasing of the system temperature was repeated until all of the TBAPr hydrate dissociated. The equilibrium temperature was determined as the one just before the hydrate completely dissociated. This procedure was repeated with different mass fraction solutions until the hydrate was completely dissociated.

2.3. Dissociation heat

The dissociation heat was measured by a differential scanning calorimetry (DSC-822e METTLER TOLEDO Corporation). The mass of the aluminum test cell (often called as the test pan) was measured by an electronic balance. Then tetrabutylammonium propionate aqueous solution (approximately 30 mg) was injected into the cell by a syringe, and the cell was covered with a round plate. The mass of the cell containing the solution was measured again to accurately measure the mass of the aqueous solution.

The system in the DSC was filled with dry nitrogen with 0.1 MPa. The system temperature was controlled throughout the experiment. First, the system was kept at 10 °C for 10 minutes. Then the system was cooled to −20 °C by 10 K/min, and kept for 15 minutes in order to form hydrate. From −20 °C, the temperature was raised constantly by 1 or 2 K/min until 30 °C. We confirmed that the hydrate was completely formed at the chilled process, and the hydrate is completely dissociated at the heating process by checking the heat flow curve under each different composition.

3. Result

3.1. Equilibrium temperature

The phase equilibrium temperature of TBAPr hydrate was measured in the mass range from 0.10 to 0.43. That mass fraction 0.43 is the highest which we could obtain by neutralizing the tetrabutylammonium hydroxide solution with propionic acid. The results are summarized in Table 1 and Fig. 2 in the form of $T_{eq}$ - $w_{TBAPr}$ diagram. $T_{eq}$ is the equilibrium temperature of the TBAPr hydrate and $w_{TBAPr}$ is the mass fraction of the TBAPr in the aqueous solution. At $w_{TBAPr} = 0.10$, the equilibrium temperature was 8.3 °C. When the mass fraction range was from 0.10 to 0.37, the equilibrium temperature increased with the increase in mass

<table>
<thead>
<tr>
<th>$w_{TBAPr}$</th>
<th>$T_{eq}$ / °C</th>
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<tbody>
<tr>
<td>0.10</td>
<td>8.3</td>
</tr>
<tr>
<td>0.15</td>
<td>11.0</td>
</tr>
<tr>
<td>0.20</td>
<td>13.2</td>
</tr>
<tr>
<td>0.25</td>
<td>15.8</td>
</tr>
<tr>
<td>0.30</td>
<td>17.2</td>
</tr>
<tr>
<td>0.35</td>
<td>17.4</td>
</tr>
<tr>
<td>0.37</td>
<td>17.5</td>
</tr>
<tr>
<td>0.40</td>
<td>17.4</td>
</tr>
<tr>
<td>0.43</td>
<td>17.2</td>
</tr>
</tbody>
</table>

Fig. 2 Relationship between the equilibrium temperature and the mass fraction in TBAPr system
fraction. When the mass range was 0.35 and 0.37, the difference of equilibrium temperature was small. The highest equilibrium temperature of TBAPr hydrate was 17.5 °C at \( w_{\text{TBAPr}} = 0.37 \). From \( w_{\text{TBAPr}} = 0.37 \), the equilibrium temperature decreased with the increase in the mass fraction, and at \( w_{\text{TBAPr}} = 0.43 \), the equilibrium temperature was 17.2 °C.

In this experiment, there were different dissociation behaviors as mass fraction changed. In the mass fraction range of 0.10 to 0.30, the hydrates dissociated gradually before the temperature reached their equilibrium temperature. But in the mass range from 0.35 to 0.40, the hydrate dissociated as soon as they reached their equilibrium temperature.

### 3.2. Dissociation heat

The dissociation heat of TBAPr hydrate was measured in the mass range from 0.30 to 0.43. Obtained results of DSC heating curve are presented in Fig. 3 to Fig. 5, and the results of dissociation heat of TBAPr hydrate at different mass fraction are summarized in Table 2. \( \Delta H_d \) is the dissociation heat of hydrates, which is obtained by integrating heat flow rate of the peak of the DSC heating curve. In the mass fraction range from 0.35 to 0.43, heating rate was set at 2 K/min, and at \( w_{\text{TBAPr}} = 0.30 \), heating rate was 1 K/min to clearly show the shape of each peak of heat flow rate. At \( w_{\text{TBAPr}} = 0.30 \), shown in Fig. 3, there are three peaks in the heat flow rate. The peak at approximately 0 °C should corresponds to ice melting by the frozen surplus water, and the other two peaks are caused by the dissociation of the hydrates. The largest peak at approximately 20 °C is due to the dissociation of stable hydrate phase, and the peak at approximately 15 °C is due to the dissociation of metastable hydrate phase. In the DSC heating curve at \( w_{\text{TBAPr}} = 0.35 \), there were two peaks, and the ice melting peak was not observed. In the DSC heating curve at

![Fig. 3 Heating curve obtained by the DSC in TBAPr system at \( w_{\text{TBAPr}} = 0.30 \)](image1)

![Fig. 4 Heating curve obtained by the DSC in TBAPr system at \( w_{\text{TBAPr}} = 0.37 \)](image2)

![Fig. 5 Heating curve obtained by the DSC in TBAPr system at \( w_{\text{TBAPr}} = 0.43 \)](image3)
Table 2. Dissociation heat of the TBAPr hydrate.

<table>
<thead>
<tr>
<th>$w_{TBAPr}$</th>
<th>$\Delta H_d / \text{kJ/kg}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.30</td>
<td>194</td>
</tr>
<tr>
<td>0.35</td>
<td>183</td>
</tr>
<tr>
<td>0.37</td>
<td>193</td>
</tr>
<tr>
<td>0.40</td>
<td>177</td>
</tr>
<tr>
<td>0.43</td>
<td>153</td>
</tr>
</tbody>
</table>

$w_{TBAPr} = 0.37$ and at $w_{TBAPr} = 0.43$, shown in Fig. 4 and Fig. 5, there was exclusively one peak, and the existence of ice and metastable phase was not identified. Comparing the heat flow rates of peaks in the two TBAPr system, the peak of the hydrate made from mass fraction 0.37 solution was larger.

The largest dissociation heat was 194 kJ/kg at $w_{TBAPr} = 0.30$, but from previous experience, this is due to dissociation of metastable phase, and there might be influence of water, hence, larger value was obtained. And the temperature range of hydration dissociation is large and this means that when we use TBAPr hydrate made from mass fraction 0.30 solution as the thermal storage material, we obtain a large range of temperature and the design of refrigerator would be more difficult. In this paper, the result 194 kJ/kg at $w_{TBAPr} = 0.30$ is not considered as the dissociation heat of TBAPr system. Except this result, the largest dissociation heat was 193 kJ/kg at $w_{TBAPr} = 0.37$.

4. Discussion

For the TBAPr system, the highest equilibrium temperature of TBAPr hydrate was 17.5 °C at $w_{TBAPr} = 0.37$, and the largest dissociation heat was 193 kJ/kg at $w_{TBAPr} = 0.37$. The relationship between equilibrium temperature and dissociation heat is shown in Fig. 6. In this measurement, the mass fraction of the system with the highest equilibrium temperature and the mass fraction of the system with the largest dissociation heat were the same. The mass fraction when the equilibrium temperature being highest, is considered to be the congruent point. In the present study, the congruent point of TBAPr system was 0.37. Congruent point means that the composition of the hydrate is equal to that of the solution. The reason why the dissociation heat was the largest at the congruent point is that at the congruent point, the compositions of solution and hydrate are the same, and thus during the process of the solution becoming hydrate, the composition of solution was kept constant and greater amount of hydrate was produced.

The dissociation heat measurement was performed under that the heating rate 2 K/min. When the dissociation heat measurement was performed under the heating rate 1 K/min several times for the same mass fraction, obtained results of dissociation heat was the same in the uncertainty. From this result, influence of the difference of heating rate is negligible when the heating rate is 1 K/min or 2 K/min.

On the highest equilibrium temperature of TBAPr hydrate, Nakayama et al.[7] reported $T_{eq} = 291.2$ K, and Dyadin et al.[1] reported $T_{eq} = 291.3$ K. In our measurement of equilibrium temperature, the highest equilibrium temperature was 17.5 °C (290.7 K), with the uncertainty of ± 0.1 K. There was not consistency in the result on equilibrium temperatures. In the previous studies, the method of increasing temperature was not stepwise. During our measurements of the equilibrium temperature of the hydrate, there were some steps where the hydrate continued to dissociate through approximately three hours. Therefore the equilibrium temperature might have been measured higher than the true equilibrium temperature.

This phase equilibrium temperature is higher than the water freezing point by approximately 17 °C. When COP of the refrigerator for TBAPr system is calculated by the inverse Carnot cycle, COP will be improved approximately 80 percent than when using water as cool thermal energy storage material.
5. Conclusion

In this study, the highest equilibrium temperature of TBAPr hydrate was 17.5 °C at $w_{TBAPr} = 0.37$, and the largest dissociation heat was 193 kJ/kg at $w_{TBAPr} = 0.37$. For the equilibrium temperature at 17.5 °C, when TBAPr hydrate is utilized as cool thermal energy storage materials, COP will be improved approximately 80 percent compared with the system using ice. TBAPr hydrate is more suitable than water as cool thermal energy storage material.

References