Crystal Growth Observation of Tetrabutylphosphonium Acetate (TBPAce) Hydrate Suitable as Thermal Energy Storage Medium

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Abstract: Formation and growth of tetrabutylphosphonium acetate (TBPAce) hydrate was observed. This study was performed at the mass fraction 0.35 and 0.42. The crystal growth was observed respectively at the subcooling temperature 3 K and 7 K. When the subcooling temperature was 3 K, the skeletal crystals were observed at both mass fractions. When the subcooling temperature was 7 K, the dendrite crystals were observed at both mass fractions.

Keywords: TBPAce, crystal growth, morphology, ionic semiclathrate hydrate, phase change material.

1. Introduction

Ionic semiclathrate hydrate is a crystalline compound consisting of hydrogen-bonded water molecules and ionic guest compounds. The cations of guest compounds are included into the cages formed with hydrogen-bonded water molecules and the anions of guest compounds [1]-[3].

Recently, utilizing naturally occurring gas hydrate as an energy resource has been proposed. Clathrate hydrate can also be applied to energy and environmental technologies [4]-[7]. Clathrate hydrates are nonflammable materials because hydrates are formed with water and guest substances. However, the technologies using clathrate hydrate require high pressure for hydrate formation. Ionic semiclathrate hydrate would become the breakthrough on this problem. Ionic semiclathrate hydrates have large dissociation heat and can be formed under atmospheric pressure around room temperature [8]. For above reasons, utilizing ionic semiclathrate hydrate as a thermal energy storage medium has been proposed [9]-[11].

Actually, tetrabutylammonium bromide (TBAB) hydrate has been commercialized as a thermal energy storage medium [12]. Previous studies reported that the phase equilibrium temperature was 12.7 °C [13] and the dissociation heat was 193.2 kJ/kg [14]. Therefore, TBAB hydrate is suitable to a thermal energy storage medium for general air conditioning system. However TBAB hydrate is a unique commercialized example because the studies on other ionic semiclathrate hydrate have not been reported enough. To develop thermal energy storage system using ionic semiclathrate hydrate, it is required to collect thermophysical properties as well as reveal the crystal growth behavior and the morphology of other ionic semiclathrate hydrate.

Tetrabutylphosphonium acetate (TBPAce) hydrate would be suitable as a new thermal energy storage...
medium. TBPAce hydrate is an eco-friendly material because it has non-halide ion. TBPAce has the simplest carboxylate group. Revealing the thermophysical properties and the crystal growth and morphology of TBPAce hydrate would be the fundamental basis of further understanding of ionic semiclathrate hydrate.

As the previous study on TBPAce hydrate, the phase equilibrium temperature was 11.2 °C and the dissociation heat was 192 kJ/kg [15]. These thermophysical properties are comparable to TBAB hydrate. However, the crystal growth behavior and morphology of TBPAce hydrate has not been reported. It is required to understand them to design thermal energy storage system. Therefore the crystal growth and morphology were observed in this study.

2. Experiment Details

2.1. Materials

Tetrabutylphosphonium acetate (TBPAce) aqueous solution was obtained by neutralizing acetic acid (99%, Sigma-Aldrich Co. LLC) with tetrabutylphosphonium hydroxide (TBPOH) (40%, Sigma-Aldrich Co. LLC) on Table 1. The mass fraction of all sample was adjusted by adding the distilled water to TBPAce aqueous solution. In this study, the mass fraction 0.35 and 0.42 of TBPAce aqueous solution were made. The distilled water was made by the water distillation unit (Yamato Scientific Co., Ltd., WG 222).

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Chemical formula</th>
<th>Mass fraction</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>tetrabutylphosphonium hydroxide</td>
<td>(CH₃CH₂CH₃CH₂)₄POH</td>
<td>0.40</td>
<td>Sigma-Aldrich Co.</td>
</tr>
<tr>
<td>acetic acid</td>
<td>CH₃COOH</td>
<td>0.99</td>
<td>Sigma-Aldrich Co.</td>
</tr>
<tr>
<td>distilled water</td>
<td>H₂O</td>
<td>~</td>
<td>laboratory made</td>
</tr>
</tbody>
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2.2. Crystal Growth Observation

The schematic diagram of the apparatus used in this study is shown on Fig. 1. Approximately 0.2 g of TBPAce aqueous solution was injected into a glass test tube (external diameter 10 mm, internal diameter 8 mm, height 90 mm) as a sample. The sample was set in a water bath and the system temperature was controlled by a chiller (Tokyo Rikakikai Co., CTP-3000). The system temperature around the glass test tube was measured by a platinum resistance temperature detector with the uncertainty of ± 0.1 K (coverage factor k = 2).

The morphology of hydrate crystals depends on the system subcooling temperature ΔT_{sub} [16]. Here the subcooling temperature is defined as ΔT_{sub} ≡ T_{eq} - T_{ex}, where T_{eq} is the phase equilibrium temperature and T_{ex} is the experimental temperature. In this study, crystal growth behavior was observed at the subcooling temperatures 3 K and 7 K. Previous study reported that the phase equilibrium temperature of TBPAce hydrate [15]. The experimental conditions in this study are shown on Table 2, where w_{TBPAce} indicates the mass fraction of TBPAce aqueous solution.

First the system temperature was set at 273.2 K to form hydrate crystal in the glass test tube. After the completion of the hydrate formation, the system temperature was heated to T_{ex}. When the system temperature became stable, the glass test tube was took out and the hydrate crystal was completely dissociated. After the completion of the hydrate dissociation, the glass test tube was set in the water bath again. Through this process, the memory effect could be used to shorten the induction time for the nucleation of hydrate crystals [17]. It was reported that the memory effect has no influence with the growth of the hydrate crystals [18]. The formation and the growth of the hydrate crystal was monitored and recorded with a microscope and a CMOS camera.
3. Results and Discussion

TBPace hydrate crystals growing at $w_{\text{TBPace}}=0.35$ and at $w_{\text{TBPace}}=0.42$ were respectively observed at $\Delta T_{\text{sub}}=3 \text{K}$ and $\Delta T_{\text{sub}}=7 \text{K}$. The observed images are shown on Figs. 2 and 3. Here $w_{\text{TBPace}}$ was defined as the mass fraction of TBPace aqueous solution. The time below each pictures indicates the elapsed time after the first observation of TBPace hydrate crystal.

At the mass fraction 0.35 and the subcooling temperature 3 K or 7 K, the nucleation of the hydrate crystal occurred at the bottom of the glass test tube. At the both subcooling temperature, the columnar crystals grew in the vertical direction. The growth stopped when the crystal reached to the interface between TBPace aqueous solution and air in the glass test tube. At the subcooling temperature 3 K, the skeletal crystals were observed as shown on Fig. 2 (a). The skeletal crystal was cylindrical shape like columnar crystal without the central part. With the growth of the skeletal crystal in the vertical direction, the vacancy of the skeletal crystal was filled with the hydrate grown from the bottom of the skeletal crystal. This results indicate that the crystals also grew into the central of the skeletal crystal. At the subcooling temperature 7 K, the skeletal crystals were not observed.

At the mass fraction 0.42 and the subcooling temperature 3 K and 7 K, the crystal nucleation occurred on the bottom of the glass test tube and the columnar crystals grew in the vertical direction. At the subcooling temperature 3 K, the skeletal crystals similar to that of the mass fraction 0.35 were observed as shown on Fig. 3(a). The dendrite crystals were not observed. At the subcooling temperature 7 K, The columnar crystals radially grew and the dendrite crystals formed immediately after the nucleation. The dendrite crystals kept growing and stopped the growth when the crystals reached at the interface between TBPace aqueous solution and air. The dendrite crystals formed because the subcooling temperature was large similar to that at the mass fraction 0.35 and the subcooling temperature 7 K. However the direction of the
crystal growth was different between the mass fraction 0.35 and 0.42 at the same subcooling temperature 7 K. At the mass fraction 0.35, the crystals grew in the vertical direction. At the mass fraction 0.42, the crystals grew radially. These results indicate that the crystal structure would be different between mass fraction 0.35 and 0.42. It is known that ionic semicladathrate hydrates have polymorphism [8], [14], [20], [21]. The difference of the crystal structure would influence the morphology.

![Sequential images of TBPAce hydrate crystal growth (wtbpa=0.35).](image1)

![Sequential images of TBPAce hydrate crystal growth (wtbpa=0.42).](image2)

From these results, the subcooling temperature has the significant influence on the morphology. When the subcooling temperature was small, the skeletal crystals were observed regardless of the mass fraction. When the subcooling temperature was large, the dendrite crystals were observed regardless of the mass fraction. These difference of the morphology influences the specific surface area of crystals. This indicates
that the difference of the subcooling temperature influences the heat transfer process. For designing the thermal energy storage pool, it should be considered that the efficiency of heat transfer depends on the subcooling temperature and the resulting crystal morphology.

4. Conclusion

TBPAce hydrate crystal was observed at the mass fraction 0.35 and 0.42 and the subcooling temperature 3 K and 7 K. The subcooling temperature has the biggest impact to the morphology. When the subcooling temperature was 3 K, the skeletal crystals were observed at both mass fractions. When the subcooling temperature 7 K, the dendrite crystals were observed at both mass fractions. However, the difference of the mass fraction influenced the growth direction at the subcooling temperature 7 K. The crystals vertically grew at the mass 0.35 and the crystals radially grew at the mass fraction 0.42. When TBPAce hydrate is used as a thermal energy storage medium, the subcooling temperature influences with the efficiency of heat transfer.

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References


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