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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 semiclathrate 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 wTBAPr from 0.10 to 0.43. The highest equilibrium temperature of the TBAPr system was 17.5 °C at wTBAPr = 0.37. The largest dissociation heat of TBAPr system was 193 kJ/kg at wTBAPr = 0.37. These findings indicate that TBAPr hydrate is promising for application in cool energy storage material.

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Keywords: clathrate hydrate; semiclathrate hydrate; tatrabutylammonium propionate

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

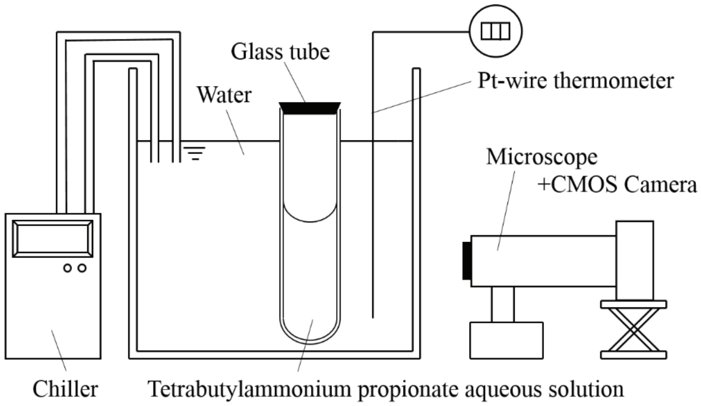

Fig. 1 Diagram of the measurement apparatus for TBAPr hydrate observation