

Thermodynamic properties of tetra-*n*-butylphosphonium dicarboxylate semiclathrate hydrates

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Abstract

Semiclathrate hydrate (SCH) is a crystalline inclusion compound that consists of host water molecules and guest substances. SCH has been investigated for a thermal storage material by using the enthalpy of phase change (about 160-220 J·g⁻¹), since the equilibrium temperatures are located below 300 K. One of the advantages of using SCH is a designability of the thermodynamic properties by selecting the guest substances. Conventional SCHs consist of halide anions, but in recent years, a number of SCHs including monocarboxylate anions from environmental and biocompatible reasons have been reported. In the present study, various tetra-*n*-butylphosphonium dicarboxylate (TBP-DC) SCHs were prepared, where we selected oxalate, malonate, succinate, and glutarate as environmentally friendly dicarboxylate species.

The equilibrium temperatures of TBP-DC SCHs depended on the steric structure of anions, and were located in the range of 282.7-287.7 K. The highest equilibrium temperature and the largest dissociation enthalpy, which were observed in TBP-Glutarate SCH, were 287.7 K and 206 J·g⁻¹, respectively.

Keywords

Phase equilibria, Dissociation enthalpy, Semiclathrate hydrate

1. Introduction

It is essential to develop technologies for efficient utilization of thermal energy. Especially, phase change materials (PCMs) are promising for unused thermal energy storage. Semiclathrate hydrate (SCH), a crystalline inclusion compound consisting of water molecules and quaternary ammonium/phosphonium salts, is a prospective candidate due to their unique thermodynamic properties, such as the equilibrium temperature located below 300 K and the relatively large dissociation enthalpy ($160\text{--}220\text{ J}\cdot\text{g}^{-1}$) at atmospheric pressure [1]. The cations are enclathrated in conjunct polyhedral water cages and the anions participate in the hydrogen-bonded networks with host water molecules.

Thermodynamic properties of SCHs depend on the cation and anion species. Although simple effects of guest substances, such as alkyl size and anion species, have been studied [2], the effects of steric conformation of the guest substances have not been investigated well.

In the present study, how tetra-*n*-butylphosphonium dicarboxylates (TBP-DCs) affect the thermodynamic properties of their SCHs were studied. Oxalate (TBP-Oxa), malonate (TBP-Mal), succinate (TBP-Suc), and glutarate (TBP-Glu) anions were selected as guest dicarboxylate anions.

2. Experimental

Each TBP-DC salt was synthesized by neutralization reaction between tetra-*n*-butylphosphonium hydroxide and the corresponding dicarboxylic acid in the aqueous solvent. The products were confirmed by ^1H , ^{13}C , and ^{31}P nuclear magnetic resonance (NMR) measurements (Bruker, AVANCE500).

TBP-DC SCH samples were formed in a glass vials at 250 K. The vials were put in a propylene glycol bath thermostated with a cooling water circulator at 268 K (Taitec, CL-80R and EYELA, NCB-3100), and the system temperature was elevated with a step of 0.1 K. While the temperature was kept for 5 hours at each temperature, the glass vials were often shaken by hands. The phase equilibrium temperature was determined when the hydrate crystal was dissolved completely. The system temperature was measured by a platinum resistance thermometer (the uncertainty of 0.1 K) calibrated with the thermistor thermometer (Takara, D632, reproducibility: 0.02 K. The probe was calibrated with a Pt resistance thermometer defined by ITS-90).

The dissociation enthalpies of TBP-DC SCHs were measured by a micro differential scanning calorimeter (Setaram, $\mu\text{DSC VII evo}$) at atmospheric pressure. Approximately 20 mg

of the prepared TBP-DC aqueous solution was loaded into a DSC cell. The precise mass of the loaded aqueous solutions was measured with the electric balance (A&D, BM-22) with an uncertainty of 0.02 mg. We calibrated the microDSC with a dedicated Joule heat calibrator (Setaram, EJ3). In addition, water and naphthalene were adopted as references. The uncertainty in the dissociation enthalpy is less than $3 \text{ J}\cdot\text{g}^{-1}$.

3. Results and discussion

The equilibrium temperatures of each TBP-DC SCH are summarized in **Figure 1**. The equilibrium temperatures of TBP-Oxa, -Mal, -Suc, and -Glu SCHs were 283.1 K at $x = 0.0180$ ($n = 55$), 283.4 K at $x = 0.0162$ ($n = 61$), 282.7 K at $x = 0.0157$ ($n = 63$), and 287.7 K at $x = 0.0174$ ($n = 56$), respectively. The symbols x and n represent the mole fraction and the hydration number, respectively. The maximum equilibrium temperature of TBP-Oxa SCH was slightly higher than the value (282.6 K at $w = 0.35$) reported by Miyamoto *et al.* [3], where w represents the mass fraction.

The maximum equilibrium temperatures of TBP-Oxa, -Mal, and -Suc SCHs were similar. On the other hand, TBP-Glu SCH showed the highest equilibrium temperature of SCHs based on four dicarboxylate anions. Similar trend was observed in tetra-*n*-butylammonium dicarboxylate SCH system. Dyadin *et al.* explained that how the oxygen atoms of a carboxylate anion are substituted for water molecules are important to determine the thermodynamic stability [4]. For example, oxalate anion replaces two water molecules with *cis* oxygen atoms. Malonate anion replaces four water molecules, though the distance between these oxygen atoms is much shorter than hydrogen-bond length. The equilibrium temperature of TBP-Glu SCH is the highest because the distance between both carboxyl groups would be the most suitable. In fact, considering dicarboxylate anion having methylene chains longer than glutarate in ammonium SCH systems, the equilibrium temperatures were lowered [4].

The dissociation enthalpies of TBP-Oxa, -Mal, -Suc, and -Glu SCHs were 193, 198, 194, and $206 \text{ J}\cdot\text{g}^{-1}$, respectively.

4. Conclusion

We investigated the effects of steric structures on the thermodynamic properties of TBP-DC SCHs. The equilibrium temperatures of TBP-DC SCHs depended on the methylene length between carboxyl groups. The results showed the highest thermodynamic stability of TBP-Glu SCH, which means that the size and shape of the glutarate anion to hydrate cage was the most appropriate of the four kinds of anions used in the present study. The value of the dissociation enthalpies was suitable for the thermal energy storage. These results will lead to develop the SCHs having desired thermodynamic properties.

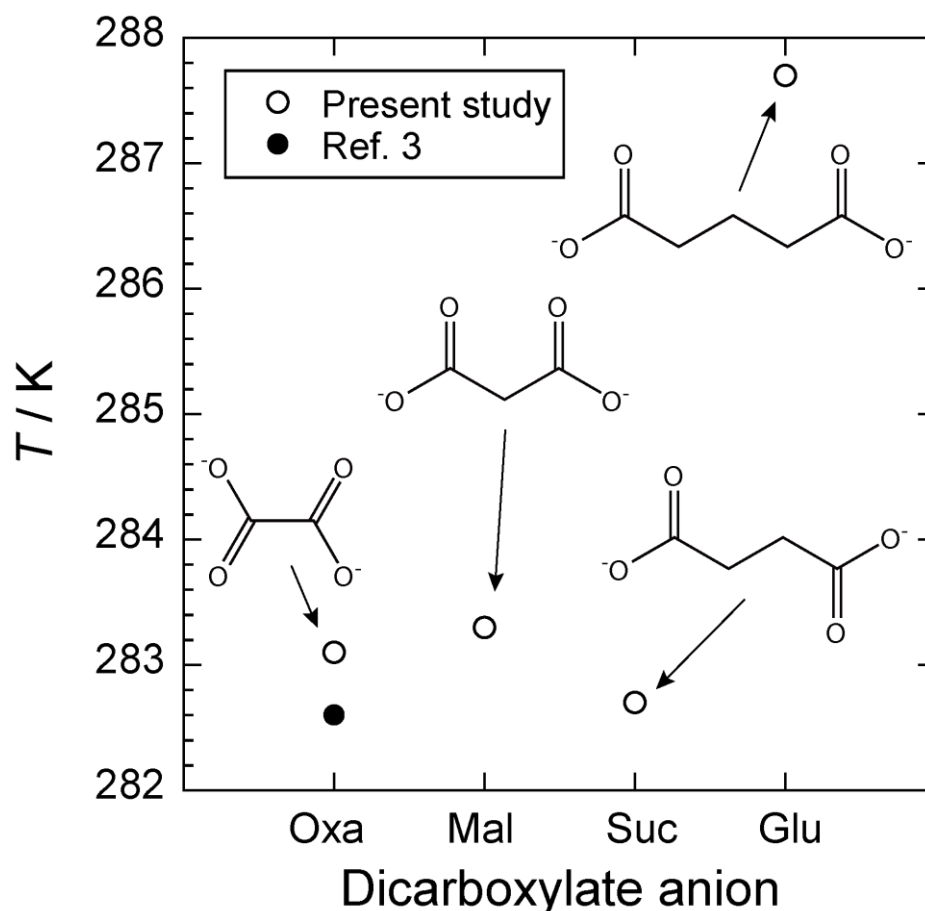


Figure 1. The equilibrium temperatures (T) of TBP-DC SCHs (open circles, present study) and the reported data of TBP-Oxa SCH (closed circle, ref. [3]).

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