

# Thermodynamic Stabilities of Clathrate Hydrates Including Tetrahydrofuran and Quaternary Onium Salts

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## Abstract

Tetrahydrofuran (THF), one of the most popular clathrate hydrate formers, forms the structure-II (sII) hydrate at temperatures below 277.5 K and atmospheric pressure. The sII unit lattice consists of 16 small cages (S-cages) as well as 8 large cages (L-cages). A THF molecule occupies the L-cage, whereas the S-cage remains vacant. The application of vacant S-cages, that is, the enclathration of another guest species into S-cages, has been investigated in the fields of gas separation or storage media. Considering the application of clathrate hydrates as latent heat storage materials, the enclathration of another guest species into vacant S-cages would be essential because it should lead to the increases in decomposition temperature and decomposition enthalpy of clathrate hydrates. It has been reported that, as a guest species other than small gas molecules, tetra-*n*-propylammonium fluoride (N<sub>3333</sub>F) can be enclathrated in the sII clathrate hydrate with THF (Manakov *et al.*, *J. Incl. Phenom. Mol. Recogn. Chem.*, vol. **17** (1994) pp. 99-106). In the present study, we investigated thermodynamic stabilities of (THF + quaternary onium salt) mixed hydrates. The characterization of the (THF + quaternary onium salt) mixed hydrates was done with differential scanning calorimeter and powder X-ray diffractometer.

## Keywords

Clathrate hydrate, Phase change material, Enthalpy

## 1. Introduction

Clathrate hydrate is a crystalline solid that consists of the host framework of hydrogen-bonded water molecules and the guest molecules in the void (called “cage”) of the framework [1]. Thermodynamic stability of clathrate hydrates depends on pressure-temperature-composition relations. The combination of some kinds of cages constructs a hydrate unit cell. Methane ( $\text{CH}_4$ ), carbon dioxide ( $\text{CO}_2$ ), or xenon ( $\text{Xe}$ ) hydrates form the structure-I (sI) unit lattice that consists of two small cages (dodecahedron ( $5^{12}$ ), S-cage) and six middle cages (tetrakaidecahedron ( $5^{12}6^2$ ), M-cage). The  $\text{CH}_4$ ,  $\text{CO}_2$ , and  $\text{Xe}$  molecules are small enough to occupy S-cages as well as M-cages. Propane, tetrahydrofuran (THF), or acetone hydrates form the structure-II (sII) unit lattice that consists of 16 S-cage and 8 large cages (hexakaidecahedron ( $5^{12}6^4$ ), L-cage). The clathrate hydrate formed from quaternary onium salt aqueous solutions has been well known as a semiclathrate hydrate (or an ionic clathrate hydrate). The quaternary onium cation and anion are incorporated with the water molecules to construct the hydrate framework. Semiclathrate hydrate has been well investigated for a cold storage material [2-8].

Here, we focus on THF hydrate, which has the maximum three-phase (THF vapor+THF aqueous solution+THF hydrate) equilibrium temperature of 277.5 K at 4.9 kPa [9]. Thus, THF hydrate can be a useful cold storage material because it forms at atmospheric pressure. The THF molecule is too large to occupy the S-cages of sII unit lattice; that is, all the S-cages of sII THF hydrate remain vacant. Considering the sII THF hydrate as a cold storage material, the existence of vacant S-cages is energetically disfavored. If a suitable guest species occupied the S-cages of THF hydrate, the decomposition temperature could be raised dependent on the S-cage occupancy ratio, which means that decomposition enthalpy could be increased. When small gas molecules, such as  $\text{CH}_4$  or  $\text{CO}_2$ , were used, however, THF binary hydrate formation should require a high pressure and the advantage of THF hydrate is lost ( $\text{Xe}$  is good for the S-cage occupancy at low pressures but too expensive). Therefore, a cheap guest species, generating hydrates at low pressures, is necessary to be developed. Manakov *et al.* [10] have reported tetra-*n*-propylammonium fluoride ( $\text{N}_{3333}\text{F}$ ) can be enclathrated in the S-cages of the sII THF clathrate hydrate. The literature does not include calorimetric data of the THF+ $\text{N}_{3333}\text{F}$  semiclathrate hydrate. In the present study, we measured the thermodynamic stability, decomposition enthalpy, and crystal structure of THF+ $\text{N}_{3333}\text{F}$  and THF+other onium salt semiclathrate hydrates.

## 2. Experimental

### 2.1. Calorimetric measurement

The microDSC (Setaram,  $\mu\text{DSC VII evo}$ ) with the high-pressure batch cells was used to investigate the equilibrium temperature-composition relations and decomposition enthalpy of THF binary semiclathrate hydrates at the atmospheric pressure. Approximately 20 mg of an

aqueous solution with given compositions of THF and onium salts was loaded in a DSC cell. The precise mass of the loaded sample was measured with the electric balance (A&D, BM-22) with an uncertainty of 0.02 mg. The furnace temperature was decreased to 248 K at the cooling rate of 0.5 K/min. After held at 258.2 K for 10 min, the temperature was increased to 289.2 K at the heating rates of 0.1 K/min. We calibrate the microDSC with a dedicated Joule heat calibrator (Setaram, EJ3). The uncertainty of the dissociation enthalpy is less than 2 J/g. In addition, the water and naphthalene were adopted as references. The uncertainty of the temperature based on the melting temperatures of water and naphthalene is  $\pm 0.06$  K.

## 2.2. Powder X-ray diffraction

The single crystals of THF+N<sub>3333</sub>F and THF+other onium salt semiclathrate hydrates were prepared from an aqueous solution with the reported stoichiometric composition [10]. The crystal structure of the ground single crystals was analyzed by powder X-ray diffraction (PXRD). The PXRD patterns were measured at 150 K and atmospheric pressure by use of a diffractometer (PANalytical, X'Pert-MPD) with a cold stage (Anton Paar, TTK450) and Cu K $\alpha$  X-ray (45 kV, 40 mA). The PXRD measurements were performed in the stepscan mode with a scan rate of 2.7 deg/min and a step size of approximately 0.02 deg.

## 3. Experimental results

The decomposition temperature of THF+N<sub>3333</sub>F semiclathrate hydrate obtained in the present study agrees well with the literature value [10]. PXRD pattern of THF+N<sub>3333</sub>F semiclathrate hydrate showed the similarity to sII unit cell. The lattice constant of THF+N<sub>3333</sub>F semiclathrate hydrate was slightly larger than that of sII THF hydrate at the same temperature. In case of tetra-*n*-propylphosphonium fluoride (P<sub>3333</sub>F) instead of N<sub>3333</sub>F, THF+P<sub>3333</sub>F semiclathrate hydrate was formed and its decomposition temperature was slightly higher than that of THF+N<sub>3333</sub>F semiclathrate hydrate. The decomposition enthalpies of THF+N<sub>3333</sub>F and THF+P<sub>3333</sub>F semiclathrate hydrates were smaller than that of THF hydrate on a unit-mass basis of the aqueous solution. This is because the mass of N<sub>3333</sub>F or P<sub>3333</sub>F is added. Considering the decomposition enthalpy on a volume basis, the diminution by the addition of N<sub>3333</sub>F was not so large. The addition of N<sub>3333</sub>F to THF aqueous solution might be preferable to only THF one in this case because the decomposition temperature can be raised by a couple of degrees from 277.5 K.

## 4. Conclusion

The enclathration of N<sub>3333</sub>F (also other onium salts) into S-cages of THF hydrate did not bring benefits that more than compensate for the mass increase of aqueous solution. If THF+N<sub>3333</sub>F semiclathrate hydrate was used as a cold storage material in a stationary device

(when we can consider the decomposition enthalpy on a volume basis), the addition of N<sub>3333</sub>F to THF aqueous solution might work better from the viewpoint of the decomposition temperature.

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