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| Note | |

# Phase equilibrium relations of tetra-*n*-butylphosphonium propionate and butyrate semiclathrate hydrates

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## Abstract

This paper reports phase equilibrium (temperature–composition) relations of semiclathrate hydrates formed from tetra-*n*-butylphosphonium propionate (TBP-Pro) and butyrate (TBP-But) + water systems. Their maximum solid–liquid phase equilibrium temperatures at atmospheric pressure were located at (288.75±0.06) K and the mole fraction $x_1$ = 0.035±0.001 and (287.01±0.06) K and $x_1$ = 0.028±0.001, respectively. They showed equilibrium temperatures higher than those of tetra-*n*-butylphosphonium formate, acetate, and lactate semiclathrate hydrates. The dissociation enthalpies of TBP-Pro and TBP-But semiclathrate hydrates were (190±5) J·g$^{-1}$ and (204±5) J·g$^{-1}$, respectively. The temperature difference between formation and dissociation, that is, the maximum allowable degree of supercooling, was (17.7±1.5) K for TBP-Pro semiclathrate hydrate and (15.4±1.4) K for TBP-But one.

**Keywords**

Semiclathrate hydrate, Phase equilibria, Differential scanning calorimetry, Enthalpy, Supercooling

## 1. Introduction

Clathrate hydrates are ice-like crystalline inclusion-compounds that consist of the hydrogen-bonded water (host) and hydrophobic substance (guest). Clathrate hydrates form several cages having various size and shapes, which depends on the chemical structures of the guest substances. Under suitable pressure and temperature conditions, the hydrate structures are stabilized by the van der Waals interactions between guest molecules and water host cavities.

When the ionic guest substances, *e.g.*, tetra-*n*-butylammonium (TBA) and tetra-*n*-butylphosphonium (TBP) salts are enclosed, such cations can be enclathrated in several hydrate cages, and counter anions replace water molecules in the hydrate framework. These crystalline compounds are called semiclathrate hydrates [1, 2], showing unique properties, such as thermodynamic stability even around 300 K at the atmospheric pressure, large formation/dissociation enthalpy, gas trapping, etc. As a consequence, semiclathrate hydrates have been regarded as potential candidates for cold storage materials of air conditioning [3–8], gas absorption media [9–14], and gas separation media, etc. [9–14]

Semiclathrate hydrates are also well known to exhibit similar physical properties to typical clathrate hydrates with the exception of low-temperature and high-pressure conditions necessary for clathrate hydrate formation. Besides, the properties of semiclathrate hydrates are dependent on the shape, size, and character of guest substances. In particular, the dependence of the anion species on the equilibrium temperatures has been frequently studied in semiclathrate hydrate systems based on TBA cations with halide anions. In these cases, the equilibrium temperatures were decreased with increasing anion size. [2, 15–17].

Recently, halogen-free salts based semiclathrate hydrates have attracted much attention because major semiclathrate hydrates contain halide anions. The presence of the halide anions may cause the chemical corrosion and/or give high impact to the environment, which would restrict the industrial applications of the semiclathrate hydrates. As an alternative to halide anions-based semiclathrate hydrates, carboxylate-based semiclathrate hydrates are expected [18–24]. Recently, we have reported the phase equilibrium relations regarding semiclathrate hydrates based on tetra-*n*-butylphosphonium formate (TBP-For), acetate (TBP-Ace), and lactate (TBP-Lac) [25].

Generally, phosphonium cations-based semiclathrate hydrates provide the equilibrium temperatures lower than those of ammonium based semiclathrate hydrates [6, 18, 25–27]. However, quaternary phosphonium salts significantly offered relatively high chemical and thermal stabilities when compared to the corresponding ammonium counterparts [28–32]. In this work, we present phase equilibrium relations of TBP cation combined with carboxylate anions larger than acetate anion by using a differential scanning calorimetry (DSC).

## 2. Experimental

### *2.1. Materials*

The chemicals used in the present study were listed in **Table 1**. Tetra-*n*-butylphosphonium propionate (TBP-Pro) and butyrate (TBP-But) were synthesized by aqueous neutralization of tetra-*n*-butylphosphonium hydroxide with the corresponding propanoic and butanoic acids. The aqueous solutions were completely evaporated to isolate the salts, and then the products thus obtained were dried in vacuo at 313 K for 72 h. The products were assigned by $^{1}$H, $^{13}$C, $^{31}$P NMRs. In order to confirm the purity of the obtained salts, the residual halogen content was measured by a silver nitrate titration using an automatic potentiometric titrator (Kyoto Electronics Manufacturing Co., Ltd, AT-710) with an uncertainty of ±0.01 mL, which was found to be less than 500 ppm or less. From both measurements, the purities of the synthesized TBP-Pro and TBP-But were higher than those of tetra-*n*-butylphosphonium hydroxide (on a water free basis) and propanoic acid or butanoic acid. Majority of the impurity was tributylphosphine oxide derivatives. The impurity effect on the mass fraction purity of TBP-Pro or TBP-But was less than 0.01.

**Table 1** Information on chemicals used in the present study.

| Chemical name | Source | Mass fraction purity |
|---|---|---|
| tetra-*n*-butylphosphonium hydroxide | Tokyo Chemical Industry Co., Ltd. | 0.402 mass fraction in aqueous solution |
| propanoic acid | Wako Pure Chemical Industries | > 0.98 |
| butanoic acid | Tokyo Chemical Industry Co., Ltd. | > 0.99 |
| water | homemade (distilled and deionized) | resistivity is 0.46 MΩ cm |

### *2.2. Apparatus and procedure*

A micro differential scanning calorimeter (Setaram, *μ*DSC VII evo) was used to investigate the thermodynamic stability and dissociation enthalpy of TBP-Pro and TBP-But semiclathrate hydrates at atmospheric pressure. The aqueous solutions were prepared at different compositions from $x_1$ = 0.006–0.059 ($w_1$ = 0.103–0.538) for TBP-Pro and $x_1$ = 0.006–0.039 ($w_1$ = 0.097–0.438) for TBP-But with the electric balance (A&D, GF-300) with an uncertainty ($u$) of $u(x)$ = 0.001 and $u(w)$ = 0.002. The symbols $w_1$ and $x_1$ represent the mass and mole fractions of TBP-carboxylate, respectively. Approximately 20 mg of the prepared TBP-Pro and TBP-But aqueous solutions were loaded into the DSC cell. The precise sample mass of the loaded aqueous solutions 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 a cooling rate of 0.5 K/min and then increased to a desired temperature at the heating rate of 0.05, 0.1 and 0.2 K/min for measuring the dependence of the heating rate. We calibrated the microDSC with a dedicated Joule heat calibrator (Setaram, EJ3). In addition, water and naphthalene were adopted as references. The uncertainty of the dissociation enthalpy is less than 2 $J\cdot g^{-1}$. The uncertainty of the temperature based on the melting temperatures of water and naphthalene is 0.06 K.

Generally, a DSC melting peak of a pure material is sharp and the onset temperature is identical to the equilibrium phase transition temperature. For a semiclathrate hydrate, a single peak should be detected only at either eutectic or stoichiometric composition. In the case of the sample prepared from the aqueous solution with a composition between eutectic and stoichiometric ones, the hydrate starts to dissociate and ice completely melts at the eutectic temperature ($T_{\mathrm{eutect.}}$). Further increasing temperature, the relative amount of the hydrate gradually decreases. Finally, at the equilibrium temperature, the amount of the hydrate is negligible. In the DSC measurement, the equilibrium temperature of a semiclathrate hydrate should be defined by the end of dissociation ($T_{\mathrm{end}}$) [33, 34]. There are three possible points in a DSC peak as an equilibrium point of the end of dissociation): peak top, offset, and inflection point between peak top and offset. The last one has been already reported on the validation in the NaCl-water binary system where the onset and inflection temperatures correspond to the eutectic and dissociation temperatures, respectively [33]. In the present study, we adopted the same determination method, that is, $T_{\mathrm{eutect.}}$ from the onset of the eutectic peak and $T_{\mathrm{end}}$ from the inflection of the dissociation peak of a semiclathrate hydrate.

## 3. Results and discussion

**Fig. 1** presents the DSC curves of TBP-Pro semiclathrate hydrate dissociations at $x_1$ = 0.006–0.040. In the range of $x_1$ = 0.006–0.035, the DSC curves exhibited two endothermic peaks. **Fig. 2** exhibits the DSC curves of TBP-But semiclathrate hydrate dissociations at $x_1$ = 0.006–0.039. Also in this case, the DSC curves exhibited two endothermic peaks at low concentrations. The first endothermic peaks observed around 272 K were attributed to the eutectic mixtures of ice and semiclathrate hydrates since the peaks were independent of TBP salt concentrations. On the contrariwise, the second peaks depended on the concentrations of TBP salts, therefore the peaks were determined to be derived from semiclathrate hydrates.

In the case of TBP-Pro semiclathrate hydrate, the higher inflection temperatures of semiclathrate hydrate peak at the heating rate of 0.1 K/min were in good agreement with the equilibrium temperatures determined by direct observation (the method is the same as the one previously reported [25]). The dependence of the heating rate was quite small and within the uncertainty of temperature determination by DSC. This behavior was the same as those in the literature [33, 34], where it has been reported that the equilibrium liquidus temperature is close to the higher inflection temperature of DSC peak at enough slow heating rate. However, in the TBP-But semiclathrate hydrate system, neither inflection temperature nor offset one at the heating rate of 0.1 K/min was in good agreement with equilibrium temperature determined by direct observation. Therefore, equilibrium temperatures in the TBP-But semiclathrate hydrate were measured at three different of heating rates: 0.05 K/min, 0.1 K/min, and 0.2 K/min. **Fig. 3** shows the heating rate dependences of the peak top, inflection, and offset temperatures. The inflection temperatures extrapolated to 0 K/min showed very good agreements with the equilibrium temperatures obtained by visual observation.

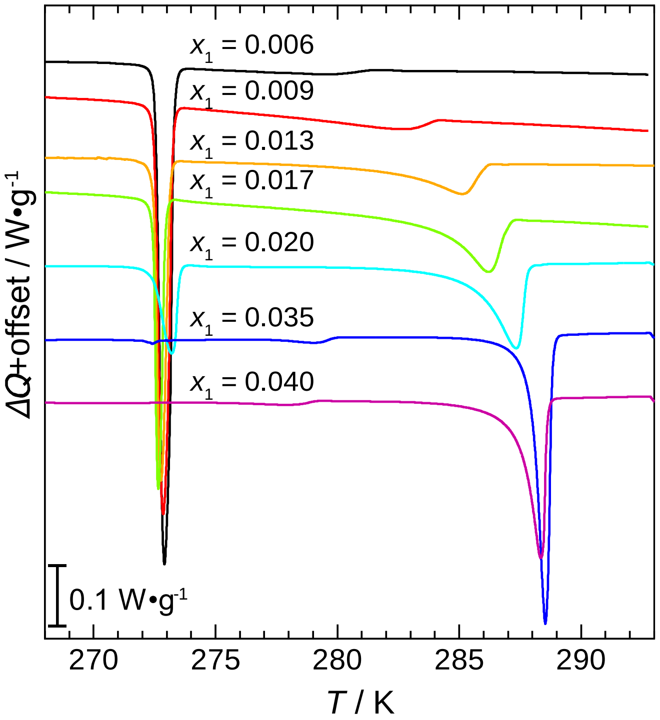

**Fig. 1**. DSC curves at a heating rate of 0.1 K/min in the TBP-Pro(1) + water(2) system at atmospheric pressure.

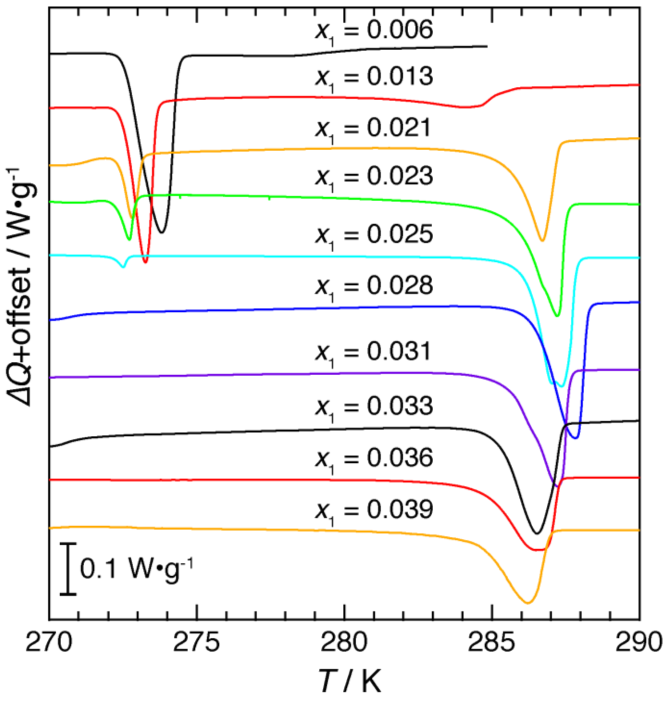

**Fig. 2**. DSC curves at a heating rate of 0.1 K/min in the TBP-But(1)+ water(2) system at atmospheric pressure.

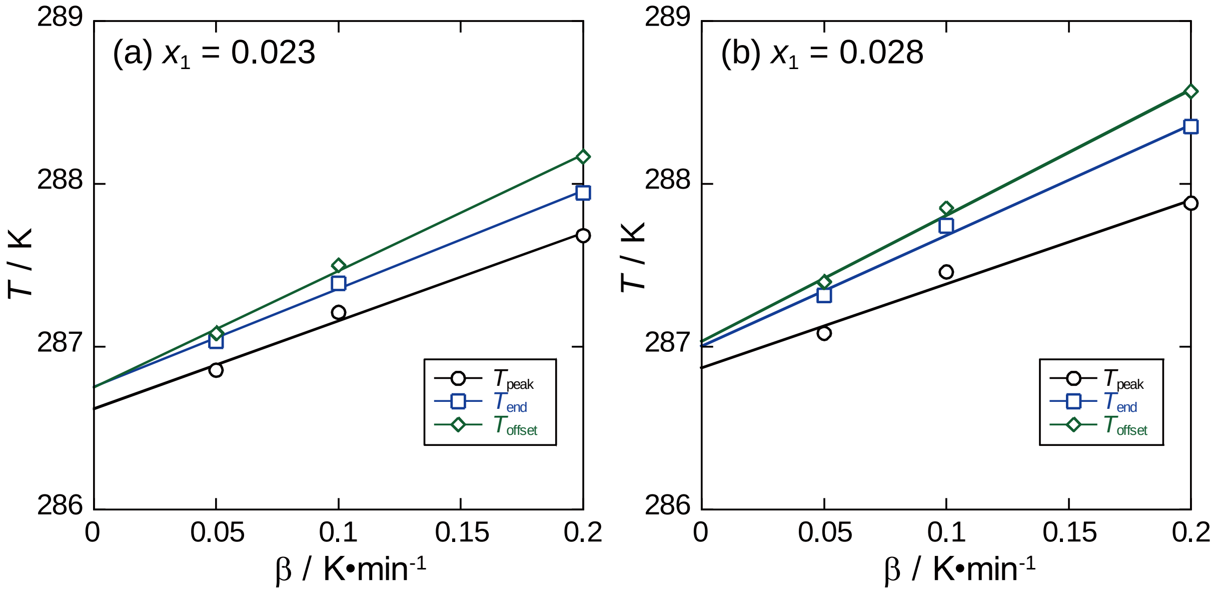

**Fig. 3**. Rate dependence of DSC peak in the TBP-But(1) + water(2) system at atmospheric pressure.

The equilibrium temperature–composition relations in the TBP-Pro semiclathrate hydrate system are summarized in **Table 2** and shown in **Fig. 4**. In the composition range from 0.006 to 0.035, the equilibrium temperatures were increased with increasing in mole fraction. Conversely, in the composition range from 0.035 to 0.059, the equilibrium temperatures were decreased with increasing in mole fraction. Additionally, a metastable phase appeared in this range. The highest equilibrium temperature in TBP-Pro semiclathrate hydrate system was located at (288.75±0.06) K and $x_1$ = 0.035±0.001. Similarly, the equilibrium temperature–composition relations in the TBP-But semiclathrate hydrate system are summarized in **Table 3** and shown in **Fig. 5**. The equilibrium temperature was increased in the composition range from 0.006 to 0.028, while the equilibrium temperature was decreased in the composition range from 0.028 to 0.039. The highest equilibrium temperature in TBP-But semiclathrate hydrate system was determined as (287.01±0.06) K at $x_1$ = 0.028±0.001.

**Table 2** Equilibrium temperature (inflection temperature $T_{\mathrm{end}}$, eutectic temperature $T_{\mathrm{eutect.}}$) – composition (mass fraction $w$, mole fraction $x$) relation of TBP-Pro semiclathrate hydrate (TBP-Pro, 1; water, 2).[a]

| $w_1$ | $x_1$ | $T_{\mathrm{end}}$ / K | $T_{\mathrm{eutect.}}$ / K |
|---|---|---|---|
| 0.103 | 0.006 | 280.99 | 272.52 |
| 0.103 | 0.006 | 281.25 | 272.54 |
| 0.149 | 0.009 | 283.84 | 272.50 |
| 0.201 | 0.013 | 285.66 | 272.47 |
| 0.243 | 0.017 | 286.67 | 272.44 |
| 0.243 | 0.017 | 286.76 | 272.54 |
| 0.275 | 0.020 | 287.64 | 272.42 |
| 0.302 | 0.023 | 287.41 | 272.29 |
| 0.399 | 0.035 | 288.69 | - |
| 0.399 | 0.035 | 288.70 | - |
| 0.399 | 0.035 | 288.78 | - |
| 0.399 | 0.035 | 288.81 | - |
| 0.400 | 0.035 | 288.73 | - |
| 0.437 | 0.040 | 288.52 | - |
| 0.493 | 0.051 | 287.89 | - |
| 0.503 | 0.052 | 287.40 | - |
| 0.538 | 0.059 | 286.22 | - |
| 0.538 | 0.059 | 286.37 | - |

[a] Standard uncertainties $u$ are $u(w) = 0.002$, $u(x) = 0.001$, and $u(T) = 0.06$ K.

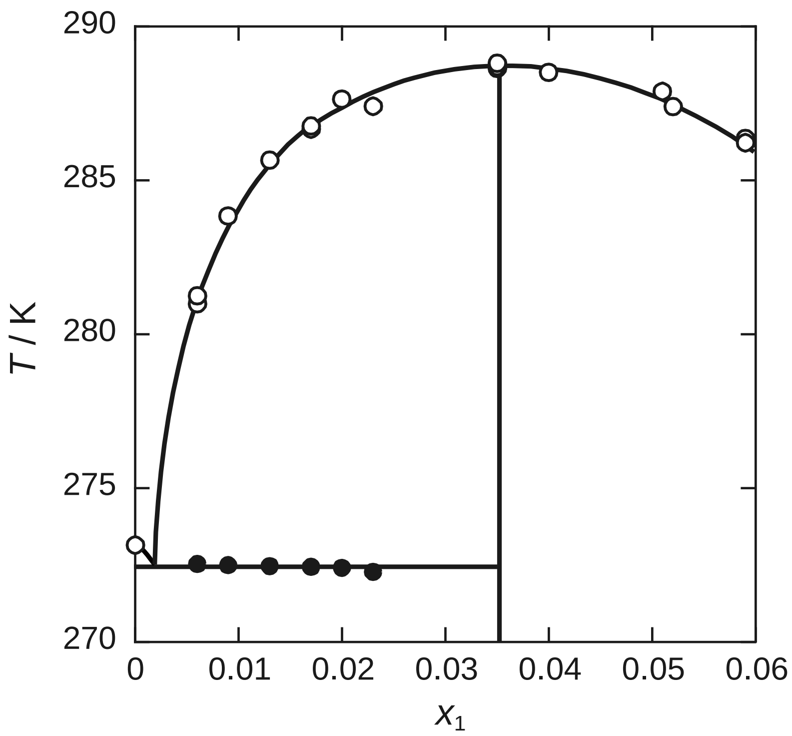

**Fig. 4**. Equilibrium temperature–composition diagram of TBP-Pro(1) + water(2) system. Equilibrium temperature of semiclathrate hydrate, open circles; eutectic temperatures, closed circles.

**Table 3** Equilibrium temperature (inflection temperature $T_{\mathrm{end}}$, eutectic temperature $T_{\mathrm{eutect.}}$) – composition (mass fraction $w$, mole fraction $x$) relation of TBP-But semiclathrate hydrate (TBP-But, 1; water, 2).[a]

| $w_1$ | $x_1$ | $T_{\mathrm{end}}$ / K | $T_{\mathrm{eutect.}}$ / K |
|---|---|---|---|
| 0.097 | 0.006 | 278.75 | 272.55 |
| 0.198 | 0.013 | 284.60 | 272.52 |
| 0.295 | 0.021 | 286.47 | 272.38 |
| 0.311 | 0.023 | 286.75 | 272.15 |
| 0.332 | 0.025 | 286.98 | 272.10 |
| 0.356 | 0.028 | 287.01 | - |
| 0.379 | 0.031 | 286.90 | - |
| 0.398 | 0.033 | 286.70 | - |
| 0.398 | 0.033 | 286.64 | - |
| 0.417 | 0.036 | 286.56 | - |
| 0.438 | 0.039 | 286.28 | - |

[a] Standard uncertainties $u$ are $u(w) = 0.002$, $u(x) = 0.001$, and $u(T) = 0.06$ K.

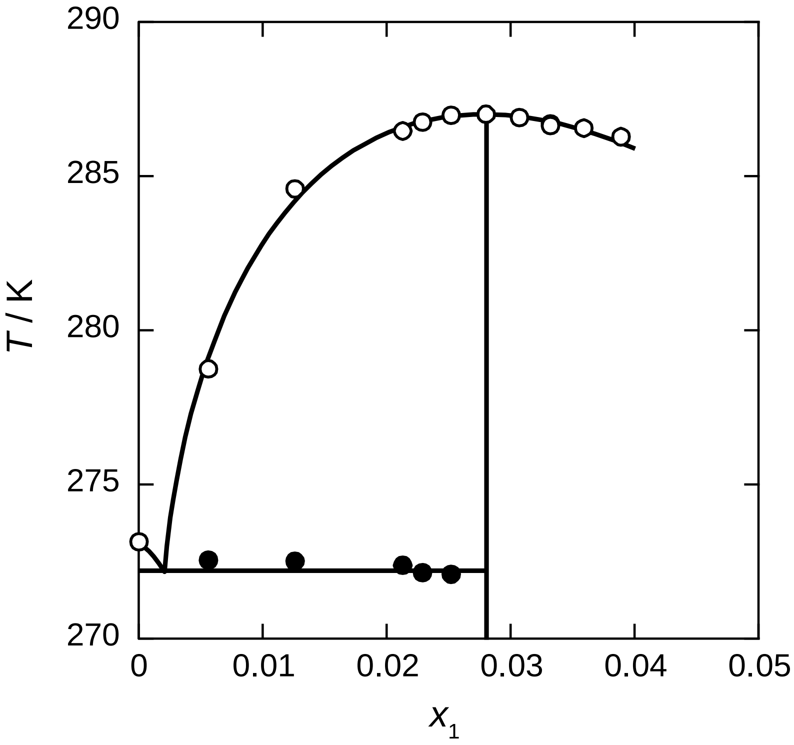

**Fig. 5**. Equilibrium temperature–composition diagram of TBP-But(1) + water(2) system. Equilibrium temperature of semiclathrate hydrate, open circles; eutectic temperatures, closed circles.

We have reported the phase equilibrium relations in the TBP-For, TBP-Ace, and TBP-Lac semiclathrate hydrate systems [25]. The highest equilibrium temperatures of TBP-For and TBP-Ace semiclathrate hydrates were 280.9 K and 284.6 K at the atmospheric pressure, respectively, where the stoichiometric composition was $x_1 = 0.035\pm0.001$ in every system. The TBP-Pro and TBP-But semiclathrate hydrates showed higher equilibrium temperatures in comparison with those of TBP-For and TBP-Ace semiclathrate hydrates, as shown in **Fig. 6**. Particularly in the TBP-For, TBP-Ace, and TBP-Pro semiclathrate hydrates, the longer the alkyl head of the carboxylate anion becomes, the higher the equilibrium temperature is. On the other hand, the TBP-But semiclathrate hydrate showed an equilibrium temperature lower than that of TBP-Pro semiclathrate hydrate. This trend is similar to that of the TBA-carboxylate semiclathrate hydrate systems [22, 35, 36], although Dyadin et al. [37] reported different behavior in the TBA-carboxylate semiclathrate hydrate systems. These results implied that the suitable alkyl chain of carboxylate anions stabilized the hydrate cages, and propionate anion is the most suitable size for stabilizing cages. The butyrate anion is a little too large for the hydrate cage in which the propyl head of butyrate anion is originally included, thereby resulting in the decreased equilibrium temperature. The stoichiometric composition of TBP-But semiclathrate hydrate ($x_1$ = 0.028±0.001) was greatly smaller than those of the other TBP carboxylate semiclathrate hydrates, *i.e.*, $x_1$ = 0.035±0.001. Generally, in the case of TBA-formate, -acetate, and -propionate semiclathrate hydrates, the hydrophobic alkyl head is accommodated in the $5^{12}$ cage, where $5^{12}$ denotes a 12-hedron composed of 12 pentagonal faces [21, 23, 24], and the hydration number is 30±1 [22]. Similarly, TBP-Pro semiclathrate hydrate showed that hydration number is 28±1. Therefore, TBP-Pro semiclathrate hydrate forms the same crystal structure with TBA-propionate one. Meanwhile, TBP-But semiclathrate hydrate (hydration number is approximately 35±1) forms a crystal structure different from that of TBP-For, TBP-Ace, and TBP-Pro ones.

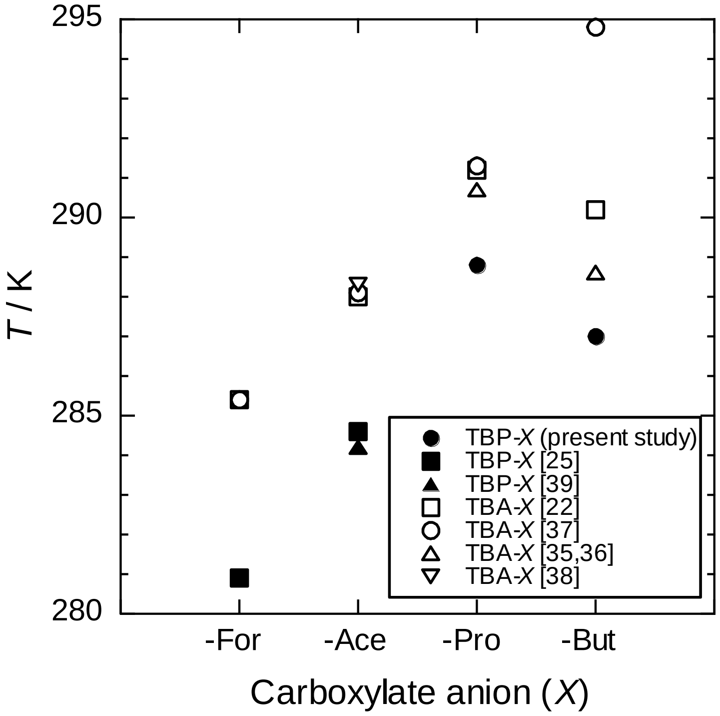

**Fig. 6**. Highest equilibrium temperatures of semiclathrate hydrates based on formate, acetate, propionate, and butyrate anions. Opened and closed keys represent the highest equilibrium temperatures of TBA and TBP carboxylate semiclathrate hydrates, respectively.

The dissociation enthalpies of TBP-Pro and TBP-But semiclathrate hydrates were (190±5) $J\cdot g^{-1}$ and (204±5) $J\cdot g^{-1}$, respectively. In the previous study, the dissociation enthalpies of TBP-For and TBP-Ace semiclathrate hydrates were (187±3) $J\cdot g^{-1}$ and (193±3) $J\cdot g^{-1}$, respectively. [25] The reason why the dissociation enthalpy of TBP-But semiclathrate hydrate was slightly larger than those of TBP-Ace and TBP-Pro ones, although they have similar equilibrium temperature, is the larger hydration number of TBP-But semiclathrate hydrate.

The DSC curves of the TBP-Pro and TBP-But semiclathrate hydrate nucleation are also recorded (not shown). We focused only on the onset temperature of the spontaneous nucleation. The spontaneous nucleation temperature also depends on the TBP-carboxylate composition. The temperature difference between dissociation and spontaneous nucleation, corresponding to the maximum allowable degree of supercooling ($\Delta T_{\mathrm{sup.}}$), is shown in **Fig. 7**. The $\Delta T_{\mathrm{sup.}}$ of (17.7±1.5) K for TBP-Pro semiclathrate hydrate is very similar to that (17.7±0.7) of tetra-*n*-butylammonium bromide (TBAB) one [40] at the TBAB mole fraction of 0.0356, whereas the $\Delta T_{\mathrm{sup.}}$ of (15.4±1.4) K for TBP-But one is slightly smaller.

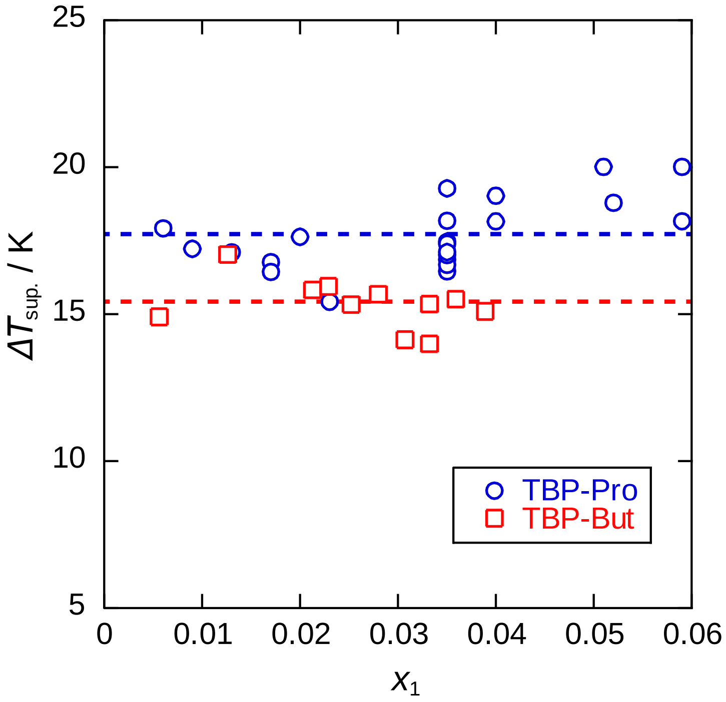

**Fig. 7**. The maximum allowable degree of supercooling ($\Delta T_{\mathrm{sup.}}$) in TBP-Pro and TBP-But semiclathrate hydrate nucleation at atmospheric pressure.

## 4. Conclusion

The phase equilibrium relations (temperature $T$–composition $x_1$ relations) in the TBP-Pro and TBP-But semiclathrate hydrate systems were investigated with DSC. The highest equilibrium temperature and the dissociation enthalpy of TBP-Pro semiclathrate hydrate were (288.75±0.06) K and (190±5) $\mathrm{J \cdot g^{-1}}$, respectively. In the TBP-But semiclathrate hydrate, they were (287.01±0.06) K and (204±5) $\mathrm{J \cdot g^{-1}}$, respectively. The stoichiometric composition of TBP-Pro and TBP-But semiclathrate hydrates was different; the former was $x_1 = 0.035 \pm 0.001$ (hydration number $n = 28 \pm 1$) and the latter was $x_1 = 0.028 \pm 0.001$ ($n = 35 \pm 1$). TBP-But semiclathrate hydrate showed larger dissociation enthalpy in comparison with other TBP carboxylate semiclathrate hydrate systems, because TBP-But semiclathrate hydrate has large hydration number.

The maximum allowable degree of supercooling, necessary for the spontaneous nucleation of TBP-Pro and TBP-But semiclathrate hydrates, was similar to and slightly smaller than that of TBAB semiclathrate hydrate, respectively.

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## List of Symbols

| | |
|---|---|
| $n$ | hydration number [-] |
| $p$ | pressure [Pa] |
| $Q$ | heat flow [W·g$^{-1}$] |
| $T$ | temperature [K] |
| $\Delta T_{\mathrm{sup.}}$ | maximum allowable degree of supercooling [K] |
| $w$ | mass fraction [-] |
| $x$ | mole fraction [-] |
| $X$ | carboxylate anion (formate, acetate, propionate, or butyrate) [-] |

Greek letter

| | |
|---|---|
| $\beta$ | heating rate [K·min$^{-1}$] |

Subscripts

| | |
|---|---|
| 1 | tetra-*n*-butylphosphoium carboxylate |
| 2 | water |

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## Graphical Abstract