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Note	

Phase equilibrium temperature and dissociation enthalpy in the tri-*n*-butylalkylphosphonium bromide semiclathrate hydrate systems

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Highlights

1. Tri-*n*-butylalkylphosphonium bromide semiclathrate hydrates (SCHs) were studied.

2. The maximum equilibrium temperature of SCHs depends on an alkyl group of cations.

3. Most of the tri-*n*-butylalkylphosphonium SCHs have an orthorhombic structure.

4. The size and shape of phosphonium cations affect dissociation enthalpy of SCHs.

ABSTRACT

Semiclathrate hydrate (SCH) is one of the phase change materials suitable for cold storage. The thermodynamic properties of SCHs, such as an equilibrium temperature and a dissociation enthalpy, depend on the size and shape of guest substances. In this study, to reveal the effect of cation size and shape on the thermodynamic properties, tri-*n*-butylalkylphosphonium bromide (P444R-Br) SCHs, where the alkyl group was *n*-propyl (R = 3), *n*-butyl (R = 4), *n*-pentyl (R = 5), *i*-butyl (R = i-4), *i*-pentyl (R = i-5), or allyl (R = Al)), were investigated. The branched alkyl groups (R = i-4 or i-5) raised the equilibrium temperature, whereas the shorter alkyl groups (R = 3 or Al) lowered one. Except for P4445-Br and P444(Al)-Br SCHs, the other P444R-Br SCHs had the same orthorhombic structure. Among the orthorhombic systems in the present study, the semiclathrate hydrate with a higher equilibrium temperature had a larger dissociation enthalpy.

1. Introduction

Clathrate hydrates are crystalline inclusion compounds that consist of host water molecules and appropriate guest substances (Sloan and Koh, 2008). The host water molecules construct polyhedral

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cages which depend on the size and shape of enclosed guest substances. Among clathrate hydrates, the hydrates formed from specific quaternary alkyl onium salts, such as tetra-*n*-butylammonium (TBA, N4444) and tetra-*n*-butylphosphonium (TBP, P4444) salts, have been well known as "semiclathrate hydrates" (Jeffrey, 1997; Dyadin and Udachin, 1987). The cations are enclathrated in multiple polyhedral cages and the anions participate in the hydrogen-bonded network with host water molecules. Each alkyl group of the cation is incorporated in a compartment hydrate cage. The vertex shared by all four cavities is occupied by the nitrogen or phosphorus atoms of the cation (Shimada et al., 2005).

Semiclathrate hydrates are promising for phase change materials (PCMs) and gas separation media due to their unique thermal properties, such as equilibrium temperature located at 273–300 K and large dissociation enthalpy (160–200 J·g^{-1}) at atmospheric pressure (Rodionova et al., 2013; Oyama et al., 2005; Sun et al., 2008, Sato et al., 2013). For example, TBA bromide (TBAB, N4444-Br) semiclathrate hydrate has been already commercialized as PCMs for air conditioning in a building (Ogoshi and Takao, 2004). The maximum solid-liquid phase equilibrium temperature is around 285 K, and the dissociation enthalpy is about (185 to 195) J·g^{-1} on the TBAB·26H$_2$O (Oyama et al., 2005; Oshima et al., 2015; Sugahara and Machida, 2017). As other applications of PCMs, the role of cold insulators for the distribution of fresh foods or pharmaceutical products has been expected. One of the most advantages in the semiclathrate hydrate utilization is designability of the thermal properties resulting from chemical structure of guest substances. The combination of ammonium cations with a variety of

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anions produces ammonium-based semiclathrate hydrates working at various temperatures, because

the substitution of the anion is relatively easy. A number of semiclathrate hydrates modified with

various anions have been investigated to reveal the thermal properties and crystal structures (Shimada

et al., 2018, 2019; Arai et al., 2019; Muromachi and Takeya, 2019; Arai et al., 2019; Koyama et al.,

2020). TBA 2-ethylbutyrate (TBA-2EB) and TBP acetate (TBP-Ace) semiclathrate hydrates have been

recently reported as one of the suitable PCMs because their equilibrium temperatures are close to 285

K which is a desirable temperature for air conditioning (Sugahara et al., 2019; Arai et al., 2018). In

contrast to anion substitution, the effects of cation size and shape on the thermal properties have been

slightly investigated. The substitution of the central atom of cations, *i.e.* ammonium or phosphonium,

has been well known as the typical cation change and the difference has been discussed in several

papers (Kobori et al., 2015; Muromachi et al., 2014). Besides, binary systems of water + salts of

quaternary ammonium cation composed of the same sort of alkyl group, such as

tetramethylammonium, tetraethylammonium, tetra-*n*-propylammonium, tetra-*n*-pentylammonium

(tetra-*n*-amylammonium), and tetraisopentylammonium (tetraisoamylammonium), have been also

demonstrated (Su et al., 2016, 2017). From the literature, the butyl and isopentyl groups are preferable

for clathrate hydrate formation. However, binary systems of water + salts of quaternary onium cations

composed of the combination of different alkyl groups like tri-*n*-butylalkylammonium have been

rarely investigated. Phase diagrams have been reported in a series of tri-*n*-butylalkylammonium

fluoride (Nakayama and Watanabe, 1976) and tri-*n*-butylalkylammonium bromide (Dyadin and

Udachin, 1987) semiclathrate hydrates. Nevertheless, insufficient information is available to

understand the effects of an alkyl group on dissociation enthalpies and crystal structures even in the

tri-*n*-butylalkylammonium salt systems. In addition, it has been reported that the equilibrium

temperature of TBP bromide (TBPB, P4444-Br) semiclathrate hydrate is slightly lower than that of

TBAB one (Suginaka et al., 2012). In other words, the substitution of the central atom in an onium

cation is also an effective method for designing the equilibrium temperature of semiclathrate hydrates.

In this study, we revealed how the size and shape of phosphonium cations affected the phase

equilibrium condition, dissociation enthalpy, and crystal structure of the semiclathrate hydrates. We

compared the thermal properties of tri-*n*-butylalkylphosphonium bromide (P444R-Br) semiclathrate

hydrates with those of tri-*n*-butylalkylammonium bromide (N444R-Br) ones.

2. Experimental

2.1 Materials

The chemicals used in the present study were listed in Table 1, and the schematic structures of the

P444R-Br salts were shown in Figure 1. P4444-Br (Hishicolin PX-4B) and tri-*n*-

butylallylphosphonium bromide (P444(Al)-Br, Hishicolin PX-4ALB) were obtained from Nippon

Chemical Industrial Co., Ltd. The other P444R-Br salts were prepared according to the procedure

described in the literature (Yoshii et al., 2013), at 373 K in a nitrogen atmosphere by a quaternization reaction in toluene solvent, which is also known as Menschutkin reaction between tri-*n*-butylphosphine and alkyl bromide. The obtained P444R-Br salts were rinsed with *n*-hexane to remove unreacted tri-*n*-butylphosphine and alkyl bromide at least six times. The P444R-Br was completely dried *in vacuo* at 353 K for 24 h, and stored in an argon-gas-filled glovebox prior to their characterization and combination with water. The products were assigned by ^{1}H, ^{13}C, and ^{31}P NMR (Bruker, AVANCE500). The results were shown in the Supporting Information. From NMR measurements, there were no impurity-derived signals or aberrant integration ratio. The impurities of the synthesized P444R-Br salts were lower than or equal to those originally included in the synthetic reagents. Majority of the impurity, considering the synthetic pathway, would be tri-*n*-butylphosphine oxide derivatives.

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

Chemical name	Source	Mass fraction purity
Tri-*n*-butylphosphine	Nippon Chemical Industrial Co., Ltd.	> 0.995
1-Bromopropane	Kanto Chemical Co., Inc.	> 0.98
1-Bromo-2-methylpropane	Tokyo Chemical Industry Co., Ltd.	> 0.97
1-Bromopentane	Kanto Chemical Co., Ltd.	> 0.97
1-Bromo-3-methylbutane	Tokyo Chemical Industry Co., Ltd.	> 0.96
Tetra-*n*-butylphosphonium bromide	Nippon Chemical Industrial Co., Ltd.	> 0.98
Tri-*n*-butylallylphosphonium bromide	Nippon Chemical Industrial Co., Ltd.	> 0.99
water	Distilled and deionized	Resistivity is 0.46 MΩ cm
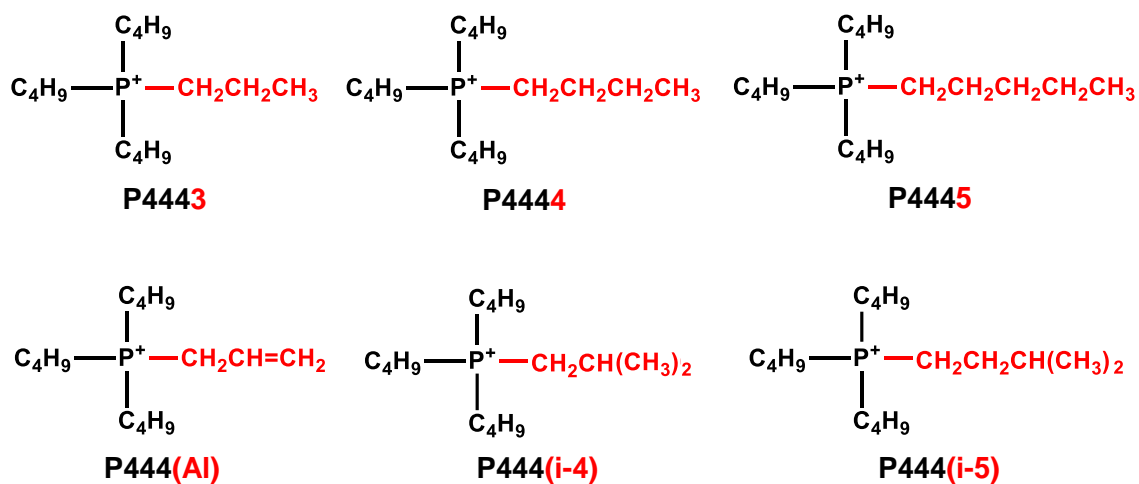
Figure 1. Schematic structures for the P444R cations used in the present study.

2.2 Apparatus and procedures

The aqueous solutions were prepared at different compositions from $x = 0.003–0.053$ ($w = 0.056–0.501$) for P4443-Br, $x = 0.003–0.051$ ($w = 0.050–0.501$) for P444(i-4)-Br, $x = 0.003–0.053$ ($w = 0.051–0.499$) for P444(Al)-Br, $x = 0.003–0.039$ ($w = 0.047–0.440$) for P4445-Br, $x = 0.003–0.049$ ($w = 0.053–0.501$) for P444(i-5)-Br with the electric balance (A&D, GF-300) with an uncertainty of 1 mg. In addition, the aqueous solution based on P4444-Br were also prepared at compositions from $x = 0.024–0.028$ ($w = 0.320–0.350$). The symbols x and w represent the mole and mass fractions, respectively. Approximately 1 cm³ of the aqueous solutions were injected into glass vials. The vials were set in a freezer kept at 250 K to crystallize the samples. The samples were set in an ethylene glycol bath thermostated with a cooling water circulator at 270 K (Taitec, CL-80R), 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 hydration number of each P444R-Br semiclathrate hydrate was estimated from the composition at the highest equilibrium temperature. The equilibrium temperatures

around the maximum equilibrium temperature were independent of the composition within the uncertainty (±0.1 K) of temperature. It is difficult, therefore, to precisely determine the maximum equilibrium temperature and the hydration number based on the results of direct phase equilibrium measurements. To determine them, apparent dissociation enthalpies per unit mass of aqueous solution, were measured with differential scanning calorimetry (Koyama et al., 2020; Sugahara et al., 2019). The value of apparent dissociation enthalpy reaches to the maximum at the stoichiometric composition, because the excess amount of water or phosphonium salt remains at a composition except for the stoichiometric composition.

The crystal structure of the prepared samples 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^{-1} and a step size of approximately 0.02 deg.

The dissociation enthalpy of semiclathrate hydrates was measured by a micro differential scanning calorimeter (Setaram, μDSC VII evo) at atmospheric pressure. Approximately 20 mg of the prepared P444R-Br 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. The furnace temperature was decreased to 248 K at the cooling rate of 0.5 K·min^{-1} and then increased to a

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desired temperature at the different heating rates, 0.02, 0.05, and 0.1 K·min^{-1}. It has been reported that

extrapolating the higher inflection temperatures to 0 K·min^{-1} gave us the equilibrium temperatures

which was equal to the results of visual observation experiments (Lin et al., 2013; Kousksou et al.,

2007). 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 J·g^{-1}.

3. Results

3.1. Phase equilibrium measurements

The phase equilibrium (temperature T – composition x) relations of P444R-Br semiclathrate hydrates

were presented in Figure 2 and summarized in Tables 2–6. The maximum equilibrium temperatures of

P4443-Br, P4445-Br, P444(i-4)-Br, P444(Al)-Br, and P444(i-5)-Br semiclathrate hydrates, determined

based on the phase equilibrium measurement as well as DSC, were 274.1 K at x = 0.026 (n = 38),

276.8 K at x = 0.025 (n = 39), 275.4 K at x = 0.028 (n = 35), 275.4 K at x = 0.034 (n = 28), and 288.8

K at x = 0.027 (n = 36), respectively, where n represents the hydration number. For the phase

equilibrium relation of P4444-Br semiclathrate hydrate, the data reported by Suginaka et al. (2012)

were plotted. The equilibrium relation between temperature and composition of P4444-Br

semiclathrate hydrate have been reported by many researchers (Dyadin and Udachin, 1987; Mayoufi

et al., 2010, 2011; Suginaka et al., 2012; Lin et al., 2013; Zhang et al., 2013; Sales Silva et al., 2016).

However, there are slight differences in maximum equilibrium temperature and stoichiometric composition. In the present study, the maximum equilibrium temperature, stoichiometric concentration, and dissociation enthalpy of P4444-Br were determined in advance. The results (as shown in Table S1 of the Supporting Information, the maximum equilibrium temperature and the dissociation enthalpy were 282.4 K at $x = 0.024$ and 214 J·g^{-1}, respectively) were very close to those of Suginaka et al. (2012). The maximum equilibrium temperature of P444(i-5)-Br semiclathrate hydrate measured in the present study shows good agreement with the reported result (Dyadin and Udachin, 1987). In the P444R-Br semiclathrate hydrate systems, the maximum equilibrium temperatures depended on the size and shape of an alkyl group in the phosphonium cations.
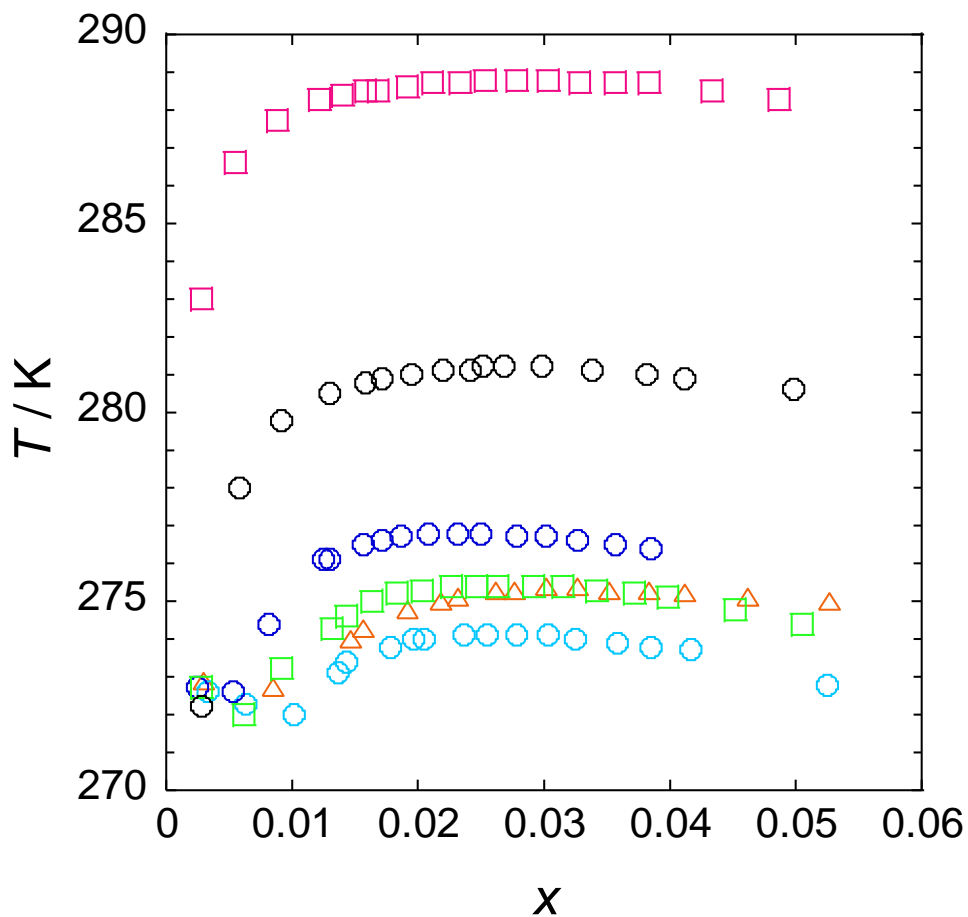
Figure 2. Equilibrium temperature (*T*)–composition (*x*) diagrams in the P444R-Br. Open circles represent the results in normal-alkyl groups of P444R-Br semiclathrate hydrate system (R = 3 in light blue (present study), and R = 5 in blue (present study), together with R = 4 in black (Suginaka et al., 2012)). Open squares represent that in the branched groups (R = i-4 in light green (present study), and R= i-5 in pink (present study)). Open triangles represent that in the unsaturated group (R = Al in orange (present study)). (For interpretation of the references to color in this figure legend, please see the web version of this article.)

Table 2. Equilibrium temperature (T) – composition (mole fraction x, mass fraction w) relation of P4443-Br semiclathrate hydrate (P4443-Br, 1; Water, 2).[a]

x_1	w_1	T / K	x_1	w_1	T / K
0.003	0.056	272.6	0.026	0.321	274.1
0.006	0.103	272.3	0.028	0.340	274.1
0.010	0.157	272.0	0.030	0.361	274.1
0.014	0.201	273.1	0.033	0.378	274.0
0.014	0.209	273.4	0.036	0.401	273.9
0.018	0.246	273.8	0.038	0.419	273.8
0.020	0.265	274.0	0.042	0.439	273.7
0.021	0.274	274.0	0.053	0.501	272.8
0.024	0.304	274.1			

[a]Standard uncertainties u are $u(x) = 0.001$, $u(w) = 0.002$, and $u(T) = 0.1$ K.

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Table 3. Equilibrium temperature (T) – composition (mole fraction x, mass fraction w) relation of P4445-Br semiclathrate hydrate (P4445-Br, 1; Water, 2).[a]

x_1	w_1	T / K	x_1	w_1	T / K
0.003	0.047	272.7	0.021	0.295	276.8
0.005	0.097	272.6	0.023	0.318	276.8
0.008	0.138	274.4	0.025	0.334	276.8
0.012	0.199	276.1	0.028	0.360	276.7
0.013	0.205	276.1	0.030	0.378	276.7
0.016	0.239	276.5	0.033	0.399	276.6
0.017	0.255	276.6	0.036	0.420	276.5
0.019	0.272	276.7	0.039	0.440	276.4

[a]Standard uncertainties u are $u(x) = 0.001$, $u(w) = 0.002$, and $u(T) = 0.1$ K.

Table 4. Equilibrium temperature (T) – composition (mole fraction x, mass fraction w) relation of P444(i-4)-Br semiclathrate hydrate (P444(i-4)-Br, 1; Water, 2).[a]

x_1	w_1	T / K	x_1	w_1	T / K
0.003	0.050	272.7	0.025	0.323	275.4
0.006	0.104	272.0	0.026	0.338	275.4
0.009	0.148	273.2	0.029	0.361	275.4
0.013	0.200	274.3	0.031	0.380	275.4
0.014	0.215	274.6	0.034	0.399	275.3
0.016	0.239	275.0	0.037	0.421	275.2
0.018	0.260	275.2	0.040	0.438	275.1
0.020	0.281	275.3	0.045	0.471	274.8
0.023	0.303	275.4	0.051	0.501	274.4

[a]Standard uncertainties u are $u(x) = 0.001$, $u(w) = 0.002$, and $u(T) = 0.1$ K.

Table 5. Equilibrium temperature (T) – composition (mole fraction x, mass fraction w) relation of P444(i-5)-Br semiclathrate hydrate (P444(i-5)-Br, 1; Water 2).[a]

x_1	w_1	T / K	x_1	w_1	T / K
0.003	0.053	283.0	0.023	0.319	288.7
0.006	0.098	286.6	0.025	0.339	288.8
0.009	0.150	287.7	0.028	0.359	288.8
0.012	0.196	288.3	0.030	0.381	288.8
0.014	0.218	288.4	0.033	0.399	288.7
0.016	0.240	288.5	0.036	0.420	288.7
0.017	0.253	288.5	0.038	0.439	288.7
0.019	0.277	288.6	0.043	0.470	288.5
0.021	0.298	288.7	0.049	0.501	288.3

[a]Standard uncertainties u are $u(x) = 0.001$, $u(w) = 0.002$, and $u(T) = 0.1$ K.

Table 6. Equilibrium temperature (T) – composition (mole fraction x, mass fraction w) relation of P444(Al)-Br semiclathrate hydrate (P444(Al)-Br, 1; Water, 2).[a]

x_1	w_1	T / K	x_1	w_1	T / K
0.003	0.051	272.9	0.028	0.337	275.3
0.009	0.134	272.7	0.030	0.358	275.4
0.015	0.211	274.0	0.033	0.377	275.4
0.016	0.222	274.3	0.035	0.396	275.3
0.019	0.259	274.8	0.038	0.417	275.3
0.022	0.285	275.0	0.041	0.435	275.2
0.023	0.298	275.1	0.046	0.465	275.1
0.026	0.325	275.3	0.053	0.499	275.0

[a]Standard uncertainties u are $u(x) = 0.001$, $u(w) = 0.002$, and $u(T) = 0.1$ K.

3.2. Crystal structure analysis

The PXRD patterns of the P444R-Br semiclathrate hydrates were shown in Figure 3. The unit cell of the P4444-Br semiclathrate hydrate was determined as an orthorhombic structure with the space group *Pmma* and unit cell parameters of a = 21.0813 Å, b = 12.6119 Å, and c = 12.0040 Å, which were in good agreement with a = 21.065(5) Å, b = 12.657(3) Å, and c = 11.992(3) Å (Muromachi et al., 2014). As shown in the Figure 3, the crystal structures of P4443-Br, P444(i-4)-Br, and P444(i-5)-

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Br semiclathrate hydrates were almost the same as P4444-Br one, whereas the crystal structures of

P4445-Br and P444(Al)-Br semiclathrate hydrates were different from that of P4444-Br one.
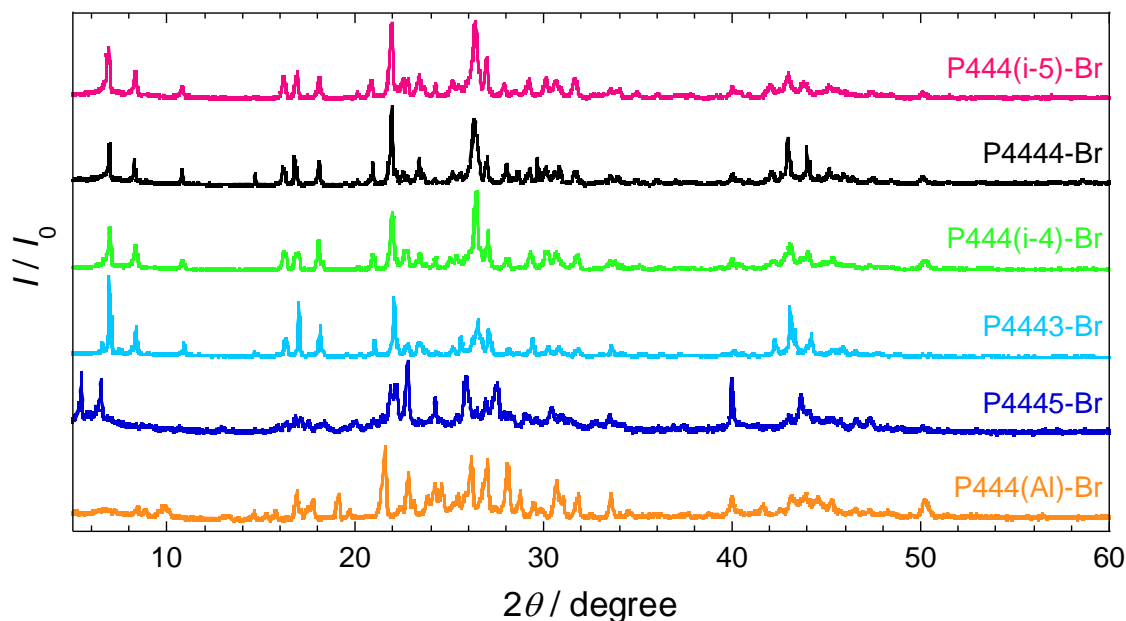

Figure 3. PXRD patterns of P444R-Br semiclathrate hydrates. All the patterns were recorded at 150

K and atmospheric pressure.

3.3. Dissociation enthalpy

The dissociation enthalpies ($\Delta_d H$) of P444R-Br semiclathrate hydrates were measured with DSC.

Typical DSC thermograms at the heating rate of 0.1 K·min^{-1} are shown in Figure 4, and dissociation

enthalpies are listed in Table 7. To measure the equilibrium temperature with DSC precisely, we need

to figure out how the DSC thermograms depend on the heating rates. In the DSC measurement, the

equilibrium temperature of a semiclathrate hydrate should be defined by the end of dissociation (Lin et al., 2013; Kousksou et al., 2007). The higher inflection temperatures of the dissociation peak correspond to the end of dissociation. The higher inflection temperature extrapolated to the heating rate of 0 was in good agreement with the equilibrium temperature obtained by visual observation method.
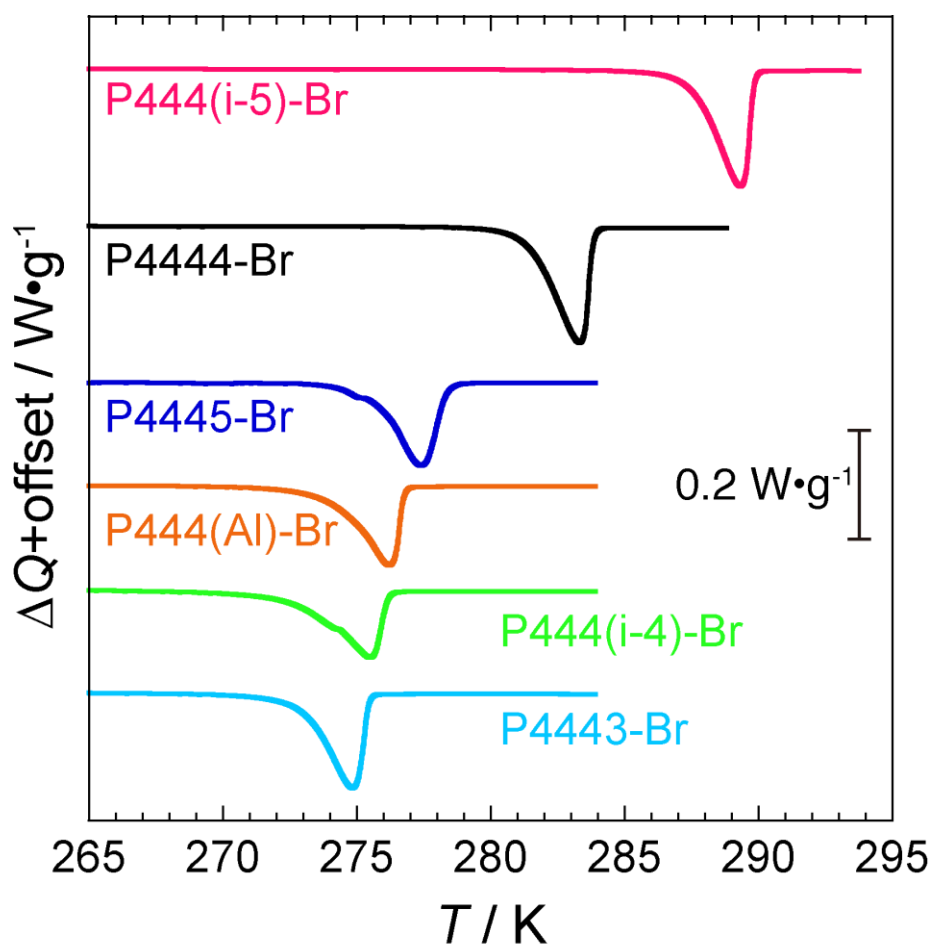

Figure 4. Typical DSC thermograms (heat flow ΔQ, temperature T) of the P444R-Br (1) + water (2) systems at a heating rate of 0.1 K·min⁻¹.

Table 7. Dissociation enthalpy $\Delta_d H$ of the P444R-Br (1) + water (2) systems.[b]

Compound	x_1	w_1	n	$\Delta_d H$ / J·g⁻¹	$\Delta_d H$ / kJ·mol⁻¹
P4443-Br	0.026	0.321	38	190	192
P4444-Br	0.026	0.339	37	214	215
P4445-Br	0.025	0.335	39	185	195
P444(i-4)-Br	0.028	0.351	35	181	175
P444(i-5)-Br	0.027	0.351	36	225	225
P444(Al)-Br	0.034	0.387	28	175	145

[b]Standard uncertainties u are $u(x) = 0.001$, $u(w) = 0.002$, and $u(H) = 3$ J·g⁻¹ or 3 kJ·mol⁻¹.

4. Discussion

4.1. Effect of size and shape of a substituted alkyl group

The maximum equilibrium temperatures of P444R-Br semiclathrate hydrates were plotted in Figure

5. The data of tri-*n*-butylalkylammonium bromide (N444R-Br) (Dyadin and Udachin, 1987) shown in

Figure 5 are discussed later. The size and shape of a substituted alkyl group in the phosphonium cations

affect the equilibrium temperature of semiclathrate hydrates. Here, we would like to summarize the

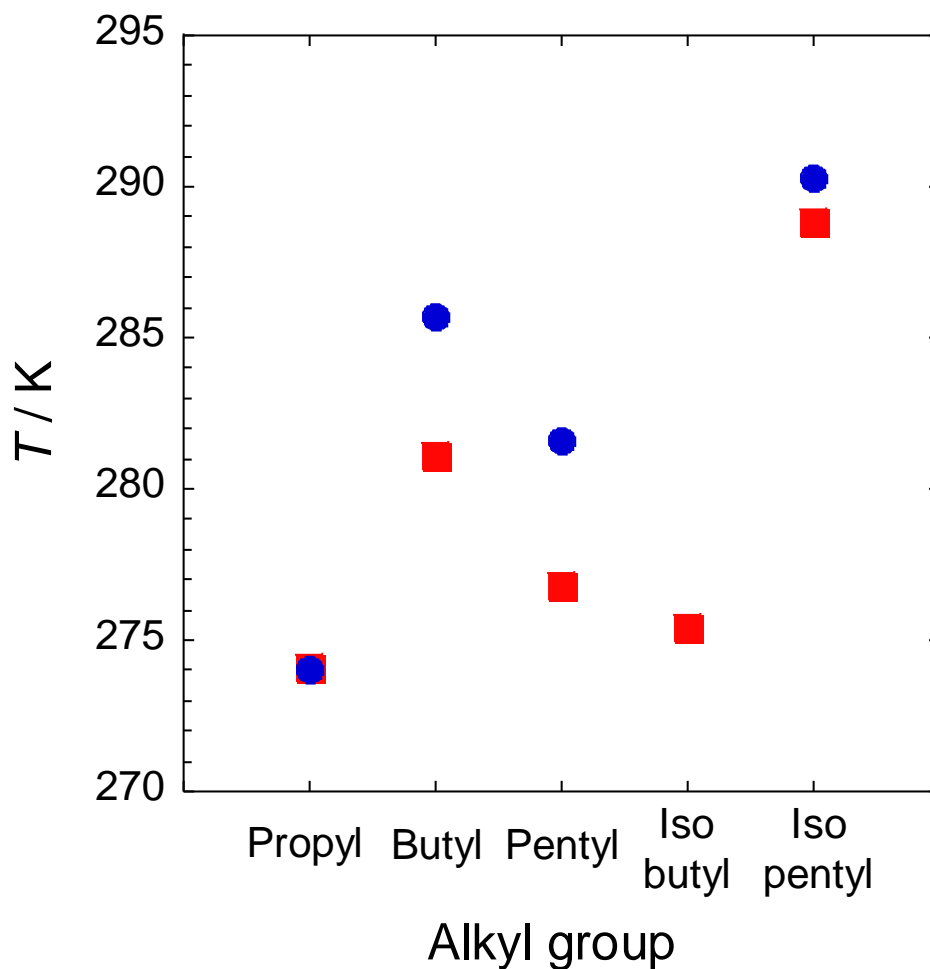effects of a substituted alkyl group: alkyl length, branch, and unsaturated bond.

Figure 5. The maximum equilibrium temperatures (*T*) – alkyl groups relations of P444R-Br (red squares) and N444R-Br (blue circles) semiclathrate hydrates. The equilibrium data of N444R-Br semiclathrate hydrates (the result of N444(i-4)-Br semiclathrate hydrate was not available) were cited from ref (Dyadin and Udachin, 1987).

4.1.1. Effect of normal-alkyl length

P4444-Br semiclathrate hydrate had an equilibrium temperature higher than the other P4443-Br and P4445-Br semiclathrate hydrates. It suggests that the length of butyl group fits well to hydrate cages.

In the case of P4443-Br semiclathrate hydrate, whose crystal structure was identified as orthorhombic structure with the space group *Pmma* (the same as that of P4444-Br semiclathrate hydrate), the equilibrium temperature was drastically lower than that of P4444-Br semiclathrate hydrate. It was attributed to the propyl group much shorter than the hydrate cage. According to the literature (Dyadin and Udachin, 1987), N444R-Br (R: proton, methyl, and ethyl groups) semiclathrate hydrates were not formed. This suggests that the normal-alkyl groups shorter than butyl group make semiclathrate hydrates unstable. The single substitution to normal propyl group, that is P4443-Br or N4443-Br, would be a border of P444R-Br or N444R-Br semiclathrate hydrate formation.

P4445-Br semiclathrate hydrate had a crystal structure different from that of P4444-Br one. The maximum equilibrium temperature is 276.8 K, which is lower than that of P4444-Br semiclathrate hydrate. This implies that the size of the pentyl group is over the usual size of the hydrate cage occupied by alkyl groups of cations. The pentyl group may be included in a cage larger or more distorted than the cage occupied by butyl or propyl group. This trend is similar to the same ammonium bromide systems (Dyadin and Udachin, 1987). The equilibrium temperature of N4445-Br semiclathrate hydrate is lower than that of N4444-Br one.

4.1.2. Effect of the branched alkyl groups

Comparing the equilibrium temperature between normal alkyl groups and branched alkyl groups, *i.e.*

P4443-Br and P444(i-4)-Br, or P4444-Br and P444(i-5)-Br semiclathrate hydrates, the equilibrium temperature of semiclathrate hydrate with the branched alkyl group was higher than that of the normal-alkyl group. As the branched alkyl group is bulkier, the branched group may occupy the hydrate cage more spatially, resulting in high thermodynamic stability of the semiclathrate hydrate. Our results are concordant with those in semiclathrate hydrates of ammonium salts (Nakayama and Watanabe, 1976; Dyadin and Udachin, 1987). The maximum equilibrium temperature of N444(i-5)-Br semiclathrate hydrate is 290.3 K at $x = 0.0254$, which is 5.2 K higher than that of N4444-Br one. Semiclathrate hydrates further substituted with branched alkyl group, tri-isopentylbutylphosphonium bromide and tetra-isopentylphosphonium bromide semiclathrate hydrates have been reported (Dyadin and Udachin, 1987). The maximum equilibrium temperatures were 297.2 K at $x = 0.0256$ and 303.2 K at $x = 0.0298$, respectively. These data indicate that the larger the number of isopentyl groups was, the higher the equilibrium temperature was.

The equilibrium temperature of P444(i-4)-Br semiclathrate hydrate was 1.3 K higher than that of P4443-Br one. The methyl substitution to the preterminal carbon of propyl group also led to high thermodynamic stability, similar to the case of P4444-Br and P444(i-5)-Br semiclathrate hydrates.

4.1.3. Effect of unsaturated bond in the alkyl group

P444(Al)-Br semiclathrate hydrate had a different crystal structure and a smaller hydration number

in comparison with those of P4443-Br semiclathrate hydrate. The P444(Al)-Br semiclathrate hydrate

showed 1.3 K higher equilibrium temperature than P4443-Br one. Due to the more restricted rotation

of Al group than propyl one, the apparent length of Al group would be larger than that of propyl one.

4.2. Difference of equilibrium temperatures between the phosphonium and ammonium semiclathrate hydrates

As shown in Figure 5, the size and shape of substituted alkyl groups in the phosphonium and

ammonium cations apparently affect the equilibrium temperature of semiclathrate hydrates. The

equilibrium temperature of P444R-Br semiclathrate hydrates was generally lower than that of the

N444R-Br semiclathrate hydrates with the same alkyl group as P444R-Br. It means that, when the

phosphonium cations are compared with the ammonium cations composed of the same alkyl groups

as the phosphonium ones, the phosphonium cations make the semiclathrate hydrates less stable than

the ammonium ones. This may be attributed to the difference of the size of the alkyl cations as well as

the surface charge distribution (Muromachi et al., 2014; Shimada et al., 2018). As an exception, the

equilibrium temperature of P4443-Br semiclathrate hydrate was slightly higher than or equal to that

of the N4443-Br semiclathrate hydrate. This is maybe caused by a bond length between carbon and

phosphorus atoms slightly longer than that between carbon and nitrogen atoms (Muromachi et al.,

2014) since the propyl group is much smaller than the hydrate cages.

4.3. Relation between dissociation enthalpy and equilibrium temperature

The relation between the dissociation enthalpies and the equilibrium temperatures in P444R-Br semiclathrate hydrates at each stoichiometric composition was shown in Figure 6A. In the semiclathrate hydrate systems with orthorhombic structure (space group, *Pmma*), the higher equilibrium temperatures were, the larger dissociation enthalpies became. It is mainly caused by the heat capacity difference between the semiclathrate hydrate and the aqueous phases as shown in Figure 6B. Except for P444(Al)-Br, the hydration numbers of the semiclathrate hydrates studied in the present study are similar. In this case, the heat capacities of these semiclathrate hydrates ($C_{p,\text{hydrate}}$) are not widely different. Also, the heat capacities of their aqueous solutions ($C_{p,\text{solution}}$) in every semiclathrate hydrate system are not so different. Therefore, it appears that there is a correlation between the enthalpy dissociation ($\Delta_d H$) and the equilibrium temperature because the value of $C_{p,\text{hydrate}}$ is different from that of $C_{p,\text{solution}}$.
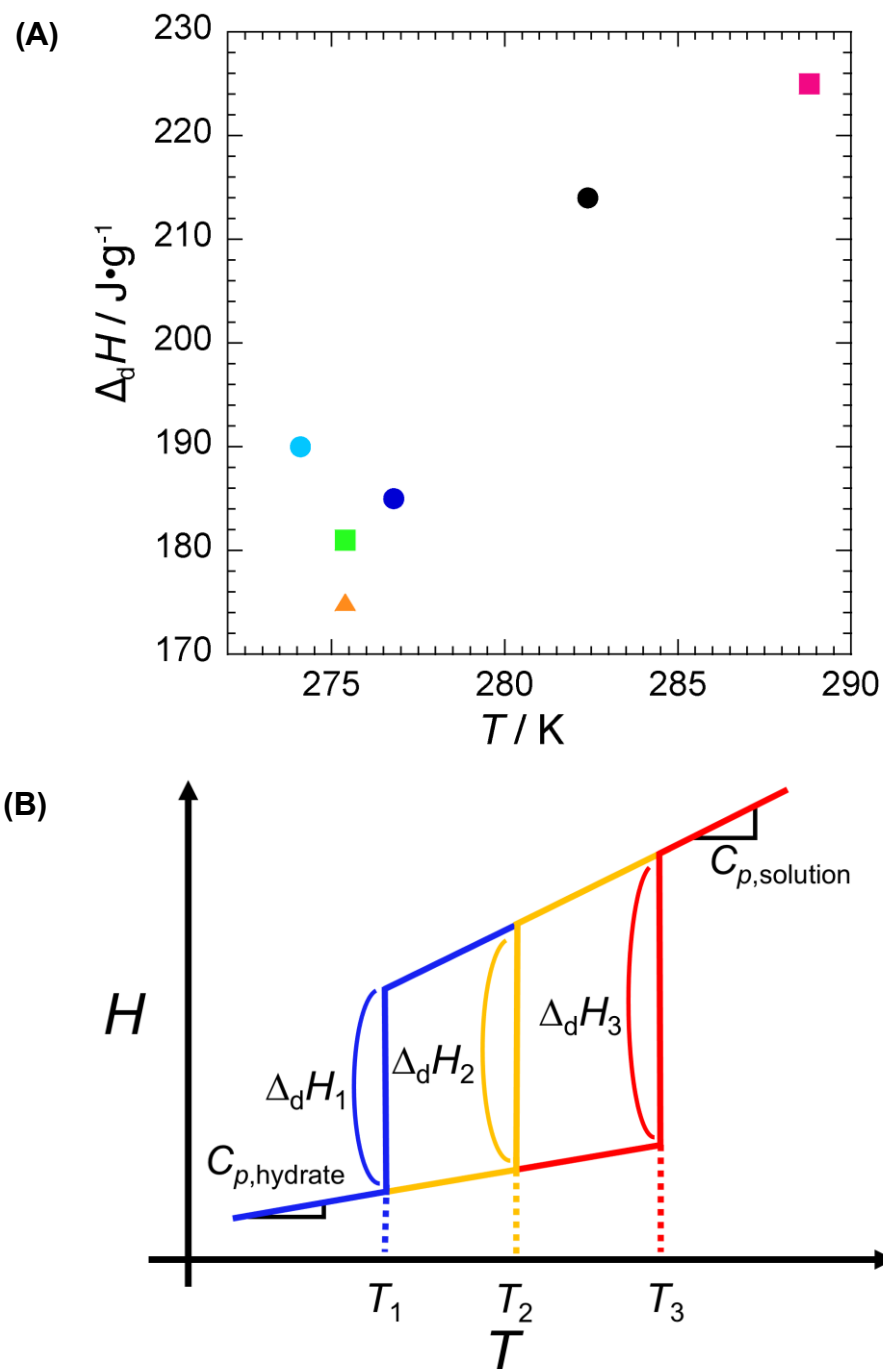
Figure 6. (A) The relationship between the dissociation enthalpy ($\Delta_{\mathrm{d}}H$) and the equilibrium temperature (T) in P444(i-5)-Br (pink square), P4444-Br (black circle), P4445-Br (blue circle), P444(Al)-Br (orange triangle), P444(i-4)-Br (light green square), P4443-Br (light blue circle) semiclathrate hydrates at each stoichiometric composition. (B) Schematic enthalpy-temperature diagram.

Conclusion

In the present study, we investigated how the size and shape of P444R cations affect phase equilibrium temperature, crystal structure, and dissociation enthalpy. The maximum equilibrium temperatures of the tri-*n*-butylalkylphosphonium bromide semiclathrate hydrates and the mole fraction at these temperatures were (274.1 K and 0.026 for P4443-Br semiclathrate hydrate), (276.8 K and 0.025 for P4445-Br one), (275.4 K and 0.028 for P444(i-4)-Br one), (288.8 K and 0.027 for P444(i-5)-Br one), and (275.4 K and 0.034 for P444(Al)-Br one), respectively. The maximum equilibrium temperature of P4444-Br was 282.4 K at x = 0.024. Branched alkyl groups largely raised the equilibrium temperature. The maximum temperature change may be caused by interaction of water cages with the phosphonium cations. Powder X-ray diffraction of the samples showed the same orthorhombic structure except the semiclathrate hydrates based on pentyl and allyl chains. The dissociation enthalpies of P4443-Br, P4444-Br, P4445-Br, P444(i-4)-Br, P444(i-5)-Br, and P444(Al)-Br semiclathrate hydrates were 190, 214, 185, 181, 225, and 175 J·g^{-1}, respectively. Among the orthorhombic semiclathrate hydrates with the space group *Pmma*, the higher the equilibrium temperatures are, the larger the dissociation enthalpies are. These findings indicate that the design of phosphonium cation can be an additional approach to control the thermal properties of semiclathrate hydrate. For PCMs, an equilibrium temperature suitable for each application are required. The

combination of cations and anions makes it possible to design semiclathrate hydrates with desired thermal properties.

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