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Effect of introducing a cyclobutylmethyl group to an onium cation on the thermodynamic properties of ionic clathrate hydrate

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Ionic clathrate hydrates (ICHs) have been applied to thermal storage materials, which can be utilized as unusual thermal energy sources. In the present study, we developed a novel ICH including tri-*n*-butyl(cyclobutylmethyl)phosphonium bromide (P444(1c4)-Br) as an unprecedented guest species. The highest equilibrium temperature and the dissociation enthalpy of P444(1c4)-Br ICH were 279.5±0.1 K and 202±2 J/g at the mole fraction of 0.0255±0.0008, respectively. The highest equilibrium temperature of P444(1c4)-Br ICH was slightly lower than that of tetra-*n*-butylphosphonium bromide (P4444-Br) ICH. The dissociation enthalpy of P444(1c4)-Br ICH was relatively larger than that of other ICHs having similar highest equilibrium temperatures. Cyclic hydrocarbon groups as well as normal, branched, saturated, and unsaturated hydrocarbon chains can be one of the options for tuning the equilibrium temperature of ICHs.

Introduction

In order to achieve the efficient utilization of thermal energy, the development of a latent heat storage technology is absolutely essential. The latent heat storage technology is a method of thermal storage using the enthalpy of phase transition of the latent heat storage materials.^{1–3} For the latent heat storage materials, water,^{1–3} paraffin,^{3,4} and molten salt^{4,5} have been well known. Ionic clathrate hydrate (ICH) is also one of the promising thermal storage materials, especially, suitable for being utilized as thermal energy in a temperature range of 273 – 300 K.^{6–9}

ICH is a crystalline inclusion compound composed of hydrogen-bonded water molecules and quaternary alkylammonium or alkylphosphonium salts.^{8–12} ICHs have the equilibrium temperatures around 270 – 300 K with the dissociation enthalpies around 200 J·g^{–1}.^{6–10,13–22} The thermodynamic properties including the equilibrium temperature and the dissociation enthalpy can be adjusted by choosing the appropriate guest species. For example, tetra-*n*-butylammonium bromide (TBAB, N4444-Br) ICH has the

equilibrium temperatures located at 284.8–286.1 K with the dissociation enthalpies of 188.8–197.3 J·g^{–1}.^{10,12,23–25} On the other hand, tetra-*n*-butylphosphonium bromide (TBPB, P4444-Br) ICH has the equilibrium temperature located at 281.2–282.6 K^{17,22,26–29} with the dissociation enthalpy of 214 J·g^{–1}.^{17,22} The development of ICHs having desirable thermodynamic properties should realize the efficient utilization of thermal energy. Especially, ICH is applicable to the cooling applications, such as shipping boxes for medicine or fresh foods. Also, they could be used in the air-conditioning systems, instead of ice or chilled water.^{8,30}

To develop ICHs suitable for each application, it is essential to understand the relations between chemical structure of guest ions and thermodynamic properties of ICHs. The effects of anion replacement, such as halide anions,^{31–35} carboxylate anions,^{6,7,10,14–16,18,36,37} and inorganic anions,^{38–40} on the thermodynamic properties have been often investigated. In addition, several researchers have focused on the differences in the center atoms of the cations, that is, the differences between tetra-*n*-butylammonium and tetra-*n*-butylphosphonium cations.^{15,16,22,39–41} Recently, we reported the effects of the alkyl and alkenyl groups in tri-*n*-butylalkylphosphonium bromide (P444R-Br)¹⁷ and tri-*n*-butylalkenylphosphonium bromide (P444(R₁=R₂)-Br)¹⁹ on the thermodynamic stabilities of ICHs. The size and shape of alkyl and alkenyl groups significantly affect the thermodynamic properties of ICHs.

In the case of P444R-Br (R is a normal-alkyl group) ICHs,¹⁷ the equilibrium temperature of P4444-Br (R = 4) is the highest among them. The equilibrium temperatures of P4443-Br (R = 3) and P4445-Br (R = 5) are 8.2 K and 5.5 K lower than that of P4444-Br (R = 4), respectively. The branched-alkyl groups, such as isobutyl and isopentyl groups, increased the equilibrium temperatures of ICHs compared with the normal-alkyl groups,

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because the branched-alkyl groups filled the inner spaces of the hydrate cages more spatial than the corresponding normal-alkyl groups. These results revealed how important the space filling of hydrocarbon group in hydrate cage is. In the present study, we investigated the thermodynamic properties of novel ICH composed of a hydrocarbon group bulkier than normal-alkyl group, that is, the cycloalkylmethyl groups. Here, we synthesized the tri-*n*-butyl(cyclobutylmethyl)phosphonium bromide (P444(1c4)-Br, shown in Figure 1). There is no report that onium salts with a cyclic hydrocarbon group in their onium cation form ICH. How such a bulky cyclic hydrocarbon group in the cation affects the properties of ICH is scientifically interesting. The equilibrium phase relation, dissociation enthalpy, and crystal structure of P444(1c4)-Br ICH were investigated to reveal the effects of the cyclobutylmethyl group on the thermodynamic properties of ICH.

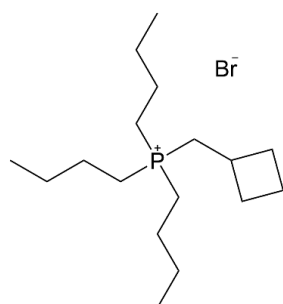


Figure 1. Chemical structure of tri-*n*-butyl(cyclobutylmethyl)phosphonium bromide (P444(1c4)-Br).

Experimental

The chemicals used in the present study are listed in Table 1. P444(1c4)-Br was synthesized by nucleophilic substitution reaction in toluene solvent at nitrogen atmosphere according to the procedures described in the literature.⁴² The crude product was rinsed with *n*-hexane to remove unreacted tri-*n*-butylphosphine and (bromomethyl)cyclobutane. The crystalline product thus obtained was dried *in vacuo* at 393 K for 24 h and was stored in a glovebox filled with argon gas. P444(1c4)-Br was confirmed by ¹H, ¹³C, and ³¹P NMR (Bruker, AVANCE400). The NMR results were summarized in the supplementary information. From NMR results, there were no impurity-derived signals or aberrant integration ratios. The majority of the impurities, considering the synthetic pathway, would be tri-*n*-butylphosphine oxide derivatives. The mass fraction purities of the P444(1c4)-Br measured by silver nitrate titration (Kyoto Electronics Manufacturing, AT-710, uncertainty: 0.004 mass fraction) was higher than 0.98.

The aqueous solutions were prepared at different compositions from $x_1 = 0.0029$ – 0.0487 ($w_1 = 0.053$ – 0.500) with an electric balance (A&D, GF-200, uncertainty: 2 mg and A&D, GR-300, uncertainty: 0.3 mg). The symbols x and w represent the mole and mass fractions, respectively. Approximately 1 cm³ of the aqueous solutions were introduced into glass vials. The vials were set into a refrigerator kept at 258 K to form the ICH. After that, the vials containing ICH were immersed into an

ethylene glycol bath thermostated at 270 K with a cooling antifreeze solution circulator (Taitec, CL-80R). The system temperature was elevated from 270 K with a step of 0.1 K. While the temperature was kept for at least 6 h at each temperature, the glass vials were often shaken by hands. The equilibrium temperature was determined when the hydrate crystal was completely dissolved. Temperature in the thermostated bath was measured by a platinum resistance thermometer (the uncertainty of 0.1 K) calibrated with a thermistor thermometer (Takara, D632, reproducibility: 0.02 K). The probe was calibrated with a Pt resistance thermometer defined by ITS90). The maximum uncertainty of equilibrium temperature was 0.1 K.

The dissociation enthalpy of the P444(1c4)-Br ICH was investigated by a micro differential scanning calorimeter (Setaram, μ DSC VII evo) at atmospheric pressure. Approximately 20 mg of the prepared P444(1c4)-Br aqueous solution was loaded into a 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⁻¹ and then increased to a desired temperature at the heating rate of 0.1 K·min⁻¹. We calibrated the μ DSC 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 2 J·g⁻¹.

The stoichiometric composition and the hydration number were estimated from the composition at the highest equilibrium temperature. The equilibrium temperatures around the stoichiometric composition were independent of the composition within the uncertainty (± 0.1 K) of temperature. To precisely determine the stoichiometric composition and the hydration number, the apparent dissociation enthalpies, $\Delta_d H^{app}$, per unit mass of aqueous solution were measured with μ DSC. The value of the $\Delta_d H^{app}$ 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.^{6,19,43}

The crystal structure of P444(1c4)-Br ICH was analysed 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 α X-ray (45 kV, 40 mA). The PXRD measurements were performed in a step-scan mode with a scan rate of 2.7 °·min⁻¹ and a step size of approximately 0.02°. The PXRD pattern indexing and cell refinement were obtained with use of the Chekcell⁴⁴ and PowderX⁴⁵ programs and the initial lattice parameters⁴¹ for the refinement.

A laser Raman microprobe spectrometer with a multichannel CCD detector (Jasco, NRS-1000) was used. A diode pumped solid state (DPSS) laser (Cobolt, Fandango) was used to irradiate the samples at 77 K. The wavelength of the DPSS laser was 514.5 nm, and the output power was adjusted to 100 mW. The spectral resolution of the obtained Raman spectra was approximately 1 cm⁻¹.

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

chemical name	chemical formula	molecular weight	CAS reg. no	source	mass fraction purity
tri- <i>n</i> -butylphosphine	P(C ₄ H ₉) ₃	202.32	998-40-3	Nippon Chemical Industrial Co., Ltd.	>0.995
(Bromomethyl) cyclobutane	C ₄ H ₇ CH ₂ Br	149.03	17247-58-4	Tokyo Chemical Industry Co., Ltd.	>0.98
water	H ₂ O	18.02	7732-18-5	distilled	resistivity is 0.60 MΩ·cm

Results and discussion

Equilibrium phase relation (temperature T – composition x) obtained by direct observation is summarized in Table 2 and shown in Figure 2. The equilibrium temperatures in a composition range from $x_1 = 0.0219$ to 0.0286 were located at 279.5 K and independent of the composition within the uncertainty of 0.1 K. To precisely determine the stoichiometric composition of P444(1c4)-Br ICH, apparent dissociation enthalpies per unit mass of aqueous solution, $\Delta_d H^{app}$, were measured with μ DSC. The $\Delta_d H^{app}$ at each composition is shown in Figure 3, where the quadratic curve in the lower figure is for visualization of trend. From the vertex of the curve, we determined that the stoichiometric composition of P444(1c4)-Br ICH was $x_1 = 0.0255 \pm 0.0008$ ($w_1 = 0.338 \pm 0.005$, $n = 38 \pm 1$). The eutectic temperature of P444(1c4)-Br ICH was also determined from the onset of the eutectic peak of DSC thermograms at low compositions. The eutectic temperature of P444(1c4)-Br ICH was 272.1 ± 0.1 K.

The highest equilibrium temperature of P444(1c4)-Br ICH was 2.8 K lower than that of P4444-Br ICH¹⁷ (the highest equilibrium temperature was 282.32 K at $x_1 = 0.026$). On the other hand, the highest equilibrium temperature of tri-*n*-butylpropylphosphonium bromide (P4443-Br) ICH was reported to be 274.1 K at $x_1 = 0.026$,¹⁷ which is 5.4 K lower than that of P444(1c4)-Br ICH. The largest diameter of cyclobutylmethyl group is shorter than that of *n*-butyl group because the angle of C-C-C in the cyclobutyl group is 90°, whereas the angle of C-C-C in the *n*-butyl group is almost 113°. Generally, it is well known that the thermodynamic stability of ICH is mainly determined by interactions between the guest ions and water molecules.^{10,15,41} The guest ions, which fill the inner-space of hydrate cages efficiently (which size is similar to that of inner-space of hydrate cages), increase the thermodynamic stability of ICHs. In comparison with cyclobutylmethyl group, the butyl group could stabilize the hydrate cages more efficient. The largest diameter of cyclobutylmethyl group is relatively close to that of the *n*-butyl group rather than that of the *n*-propyl group. Therefore, the equilibrium temperature of P444(1c4)-Br ICH was close to that of P4444-Br ICH. In comparison with P444(i-5)-Br ICH,¹⁷ which has the branched alkyl group, the equilibrium temperature of

P444(1c4)-Br ICH was 9.3 K lower than that of P444(i-5)-Br ICH. The space-filling of cyclobutylmethyl group may not be as efficient as that of isopentyl group, although both alkyl groups have similar largest-diameter. It would suffer from the planar configuration of the cyclobutylmethyl group.

Table 2. Equilibrium temperature (T)–composition (mole fraction x , mass fraction w) relation of P444(1c4)-Br ICH (P444(1c4)-Br, 1; Water, 2)^a.

x_1	w_1	T / K
0.0029	0.053	273.1
0.0056	0.099	275.6
0.0087	0.146	277.6
0.0126	0.199	278.9
0.0142	0.219	279.0
0.0158	0.239	279.1
0.0179	0.262	279.3
0.0198	0.283	279.4
0.0219	0.304	279.5
0.0238	0.322	279.5
0.0255 ^b	0.338 ^b	279.5 ^b
0.0256	0.339	279.5
0.0286	0.365	279.5
0.0300	0.377	279.4
0.0329	0.399	279.4
0.0358	0.420	279.4
0.0388	0.441	279.3
0.0436	0.471	279.0
0.0487	0.500	279.0

^aStandard uncertainties u are $u(x) = 0.0008$, $u(w) = 0.005$, and $u(T) = 0.1$ K. ^bStoichiometric composition, which was estimated from the apparent dissociation enthalpies by DSC measurements. The highest equilibrium temperature was measured from the visual observation.

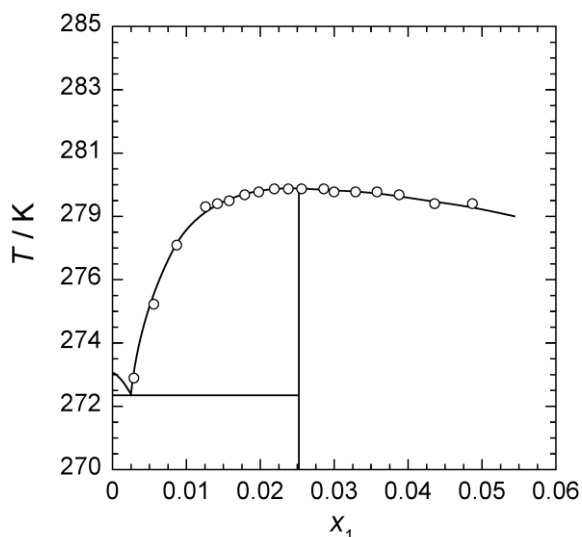


Figure 2. Equilibrium temperature (T)–composition (x) diagram of P444(1c4)-Br (1) + water (2) system.

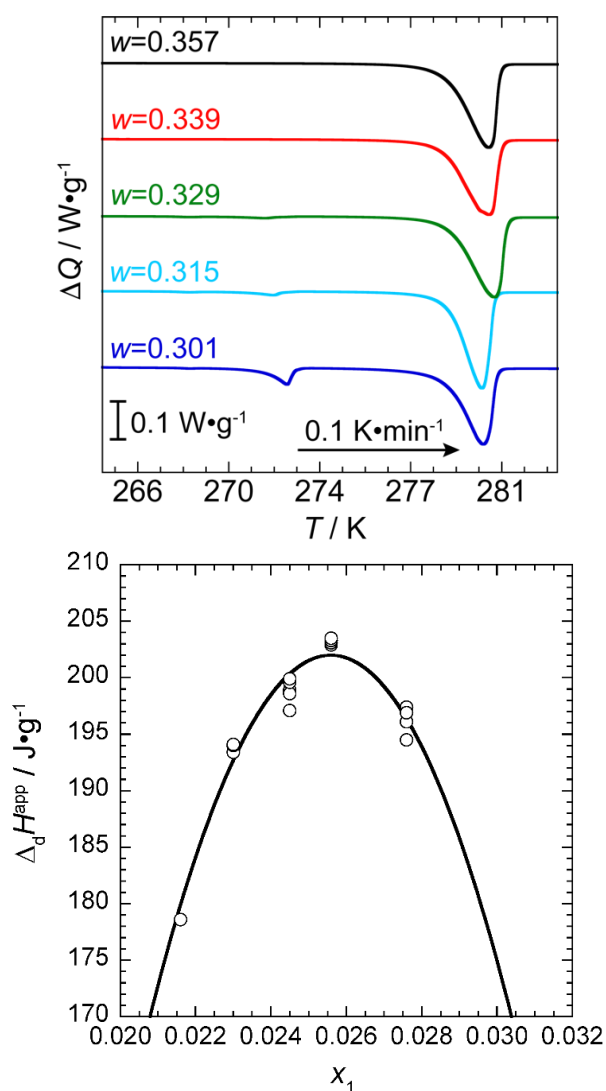


Figure 3. DSC thermograms (upper) and apparent dissociation enthalpy, $\Delta_d H^{\text{app}}$, (lower) of P444(1c4)-Br (1) + water (2) system. The curve in lower figure is for visualization of the trend.

The dissociation enthalpy of P444(1c4)-Br ICH, as shown in Figure 3, was determined to be $202 \pm 2 \text{ J} \cdot \text{g}^{-1}$, which is relatively larger than the other ICHs, such as P4444-Br, tetra-*n*-butylphosphonium formate, and tetra-*n*-butylphosphonium succinate ICHs. Those dissociation enthalpies were reported to be 214 ± 3 ,^{17,22} 187 ± 3 ,¹⁵ and $192 \pm 3 \text{ J} \cdot \text{g}^{-1}$,¹⁸ respectively. The large dissociation enthalpy of P444(1c4)-Br ICH is attributed to the large hydration number of 38, since ICHs containing a large number of water molecules (hydrogen bonds) have larger enthalpy.

We conducted the PXRD measurements at 150 K. The obtained PXRD pattern of P444(1c4)-Br ICH is shown in Figure 4 accompanied with the PXRD pattern of P4444-Br ICH. The crystal structure of P4444-Br ICH has been reported as the orthorhombic structure with the space group of *Pmma*.⁴¹ The PXRD patterns of P4444-Br ICH obtained in the present study agrees well (91 % matched) with the reported ones.⁴¹ The PXRD pattern of P444(1c4)-Br ICH, very similar to that of P4444-Br ICH, can be mostly described (94 % matched) as reflections (shown by tickmarks) from the orthorhombic structure with the space group of *Pmma*. Assuming that the crystal structure of P444(1c4)-Br ICH is the same as that of P4444-Br one, the lattice parameters of P444(1c4)-Br and P4444-Br ICHs were summarized in Table 3. The lattice parameters resemble each other closely.

The hydration number, which is the number of water molecules coordinated to a guest ion pair, was calculated from stoichiometric composition. The hydration number of P444(1c4)-Br ICH was $n = 38$, which also support the similarity to P4444-Br ICH, because the hydration number of P4444-Br ICH is reported to be around 38 from the results of single crystal structural analysis and others.^{17,41}

Raman spectra of P444(1c4)-Br and P4444-Br ICHs measured at 77 K were shown in Figure 5. Significant differences between them exist at 944, 966, 1016, and 2917 cm^{-1} , which correspond to the ring-breathing, ring-deformation, and C-H stretching vibration modes of the cyclobutyl group.⁴⁶ Almost of the other peaks were similar to those of the P4444-Br ICH. Figure 6 shows the Raman spectra of P444(1c4)-Br ICH and salt. The peak at 673 cm^{-1} in P444(1c4)-Br ICH, which is derived from the symmetric C–P stretching mode,⁴⁷ was shifted to a wavenumber lower than that (685 cm^{-1}) in P444(1c4)-Br salt. In a high-wavenumber region, the peaks corresponding to the C–H stretching vibration modes became sharp. Such behavior has been seen in typical ICHs.^{48,49}

Table 3. Optimized lattice parameters of P444(1c4)-Br and P4444-Br ICHs measured at T / K .

ICH	a / nm	b / nm	c / nm	T / K
P444(1c4)-Br	2.107	1.264	1.199	150
P4444-Br ¹⁷	2.108	1.261	1.200	150
P4444-Br ⁴¹	2.1065	1.2657	1.1992	100

^aStandard uncertainties u are $u(a) = 0.001 \text{ nm}$, $u(b) = 0.001 \text{ nm}$, and $u(c) = 0.001 \text{ nm}$.

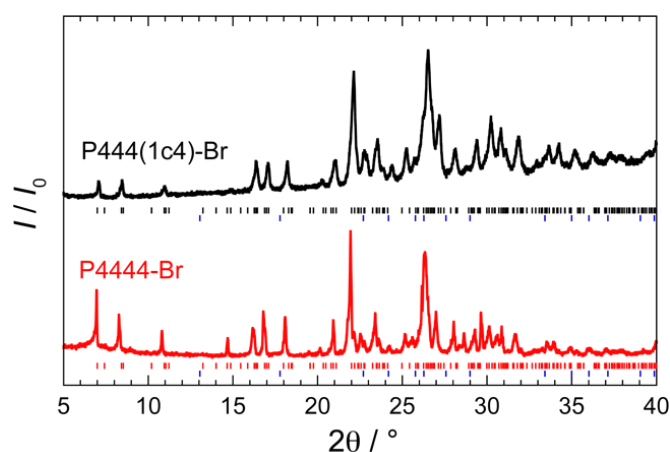


Figure 4. PXRD patterns of P444(1c4)-Br ICH (black line) and P4444-Br ICH (red line) measured at 150 K and atmospheric pressure. For each pattern, the upper tickmarks (black and red) indicate reflections from the orthorhombic structure (*Pmma*) and the lower tickmarks (blue) indicate reflections from the hexagonal ice (Ih).

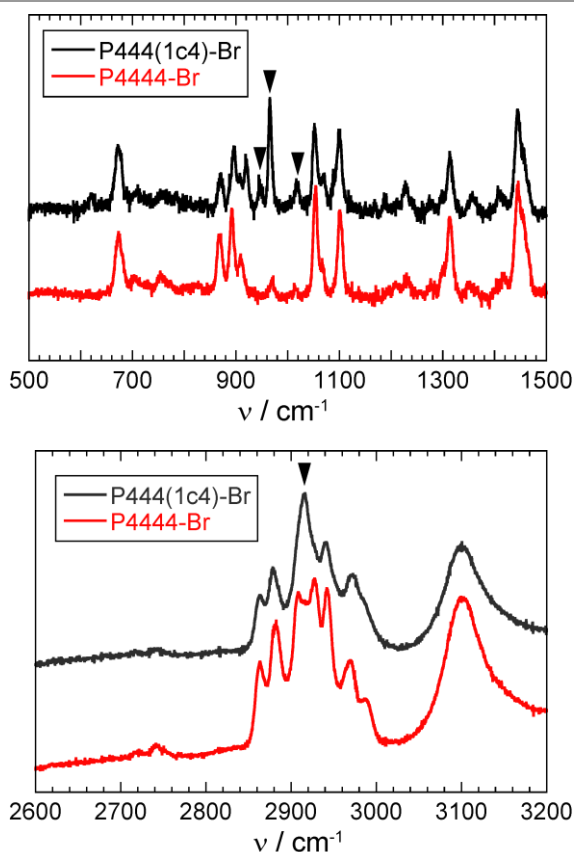


Figure 5. Raman spectra of P444(1c4)-Br and P4444-Br ICHs recorded at 77 K. The marked peaks correspond to the vibration modes of the cyclobutyl group.

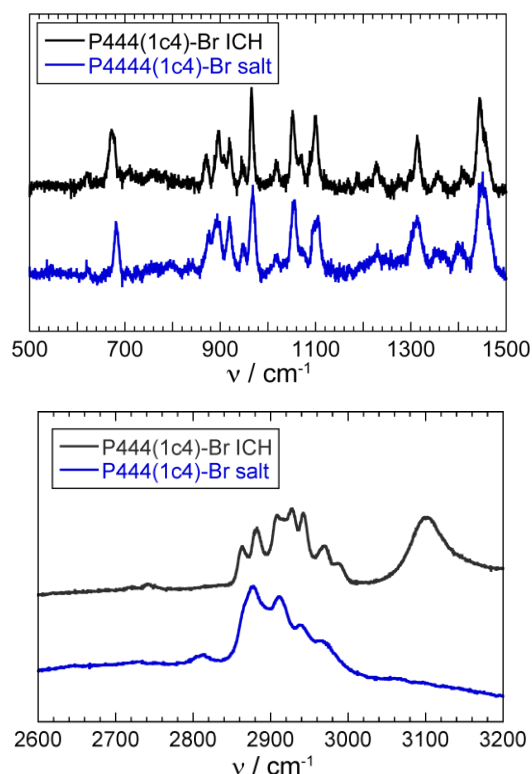


Figure 6. Raman spectra of P444(1c4)-Br ICH and salt recorded at 77 K.

Conclusions

We established a novel guest species with a cyclobutylmethyl group for the ICH formation. The equilibrium phase relation and dissociation enthalpy of P444(1c4)-Br ICH were investigated. The highest equilibrium temperature and the dissociation enthalpy of P444(1c4)-Br ICH were 279.5 ± 0.1 K and 202 ± 2 J·g⁻¹, respectively. The equilibrium temperature of P444(1c4)-Br ICH was lower than that of P4444-Br ICH, because the largest diameter of cyclobutylmethyl group was shorter than a diameter best fitted for the cage. In comparison with branched alkyl groups, the equilibrium temperature of P444(1c4)-Br ICH was also lower than that of P444(i-5)-Br ICH. The space-filling of cyclobutylmethyl group may not be as efficient as that of isopentyl group. The hydration number of P444(1c4)-Br ICH was determined as 38 ± 1 . They are the same as those of P4444-Br ICH. The introduction of cyclobutylmethyl group instead of normal butyl one decreases the equilibrium temperature of ICH slightly, while the crystal structure would not be changed. Cyclic hydrocarbon groups join in the options for tuning the equilibrium temperature of ICHs. The finding of P444(1c4)-Br ICH should help us understand the ICH science, how such a bulky group in onium cation affects the properties of ICHs.

Author Contributions

Sakura Azuma: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing – original draft,

Writing – review & editing, Visualization. **Jin Shimada**: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization, Funding acquisition. **Katsuhiko Tsunashima**: Conceptualization, Methodology, Validation, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Takeshi Sugahara**: Conceptualization, Methodology, Validation, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Takayuki Hirai**: Writing – review & editing, Supervision.

Conflicts of interest

There are no conflicts to declare.

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