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Note	

Equilibrium Phase Relations and Dissociation Enthalpies of Tri-*n*-butylalkenylphosphonium Bromide Semiclathrate Hydrates

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KEYWORDS

semiclathrate hydrate, phase equilibria, alkenyl chain, thermal storage material, enthalpy

ABSTRACT

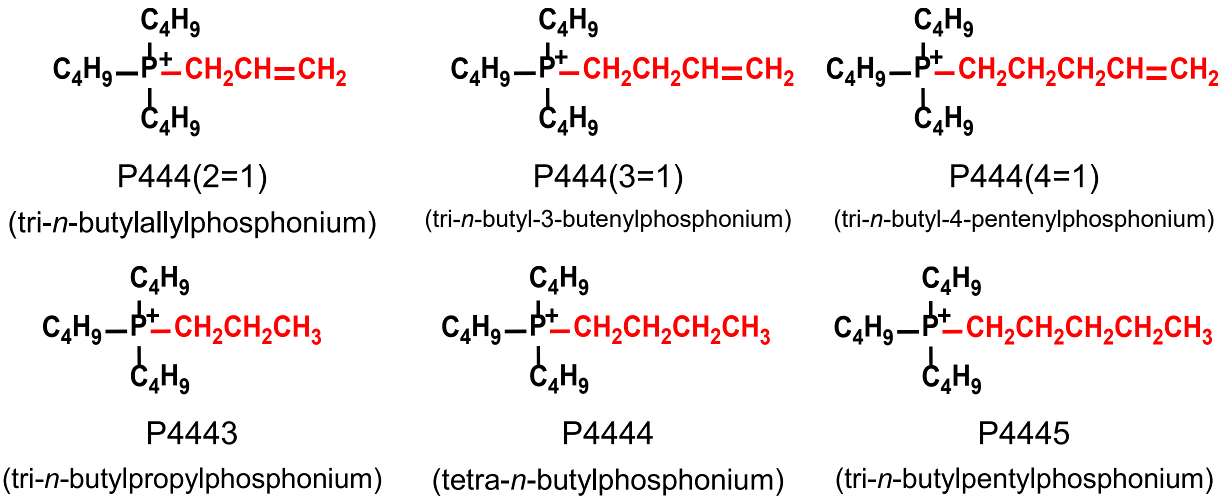
Semiclathrate hydrate (SCH) has received attention as a thermal storage material because of its equilibrium temperature and relatively large dissociation enthalpy. The alkyl length of quaternary onium cations significantly affects the equilibrium temperature and dissociation enthalpy of quaternary onium salt SCHs. To investigate the effects of double bond introduced in onium cation, in the present study, thermodynamic stability of tri-*n*-butylalkenylphosphonium bromide (P444(alkenyl)-Br: alkenyl = 3-butenyl (3=1) or 4-pentenyl (4=1)) SCH was investigated. The equilibrium temperatures and the dissociation enthalpies were determined to be (277.5±0.1) K and (199±2) $J \cdot g^{-1}$ for P444(3=1)-Br SCH, and (274.8±0.1) K and (188±2) $J \cdot g^{-1}$ for P444(4=1)-Br SCH. The equilibrium temperatures of P444(3=1)-Br SCH and P444(4=1)-Br SCH were lower than those of the corresponding normal alkyl SCHs (P4444-Br and P4445-Br), although the equilibrium temperature of tri-*n*-butylallylphosphonium bromide SCH was higher than that of the P4443-Br SCH.

1. INTRODUCTION

Semiclathrate hydrate (SCH) is a crystalline inclusion compound composed of hydrogen-bonded water molecules and quaternary alkylammonium or alkylphosphonium salts.[1,2] SCH is one of the promising candidates of thermal storage materials, because of the equilibrium temperatures (located at a temperature of 273–300 K) and the large dissociation enthalpies around 170–220 $J\cdot g^{-1}$.[3-7] For efficient utilization of thermal energy, the development of SCHs having different thermodynamic stabilities is absolutely essential. Different SCHs have to be used depending on the intended use. For example, the usage of SCHs in the air conditioning system, shipping boxes for medicine and/or fresh foods, and cooling systems of data centers and lithium-ion batteries for electric vehicle are expected.[8-10] As a way of tuning the equilibrium temperature of SCH, the replacement of anion has been well known and widely used.[1,3,11] Carboxylate anions with the different size of alkyl heads have been actively investigated.[1,11-24] As the other way for tuning, the modification of quaternary onium cation as well as anion replacement has been investigated.[1,25-27] We recently reported the thermodynamic properties of tri-*n*-butylalkylphosphonium bromide (P444R-Br) SCHs, which has the different size and shape of alkyl groups in phosphonium cations.[28] In the ref. 28, propyl (R = 3), butyl (R = 4), and pentyl (R = 5) groups were adopted for the normal alkyl groups of the P444R-Br SCHs (the cation structures are shown in **Figure 1**). Among them, P4444-Br SCH had the highest equilibrium temperature of (282.3±0.1) K. The equilibrium temperatures of P4443-Br SCH and P4445-Br SCH were (8.2±0.1) K and (5.5±0.1) K lower than that of P4444-Br SCH, respectively. The results suggested that the alkyl groups smaller and larger than the butyl group decreased the equilibrium temperature of SCHs. In addition, the equilibrium temperature of tri-*n*-butylallylphosphonium bromide (P444(2=1)-Br) SCH was reported, where the size of allyl group (hereafter, R = (2=1)) is similar to that of propyl group (R

= 3)[28]. The equilibrium temperature of P444(2=1)-Br SCH was higher than that of P4443-Br SCH, that is, introducing the double bond to one of alkyl chains in onium cations could increase the equilibrium temperature of SCH. However, the detailed effects of the double bond introduction on the thermodynamic stability of the SCHs have been not yet clear.

In the present study, to reveal the effects of the double bond introduced in the quaternary phosphonium cation on the thermodynamic properties of SCHs, the equilibrium temperatures, crystal structures, and dissociation enthalpies of tri-*n*-butylalkenylphosphonium bromide (P444(R_1=R_2)-Br) SCHs were investigated, where alkenyl group was butenyl ((R_1=R_2) = (3=1)) or pentenyl ((R_1=R_2) = (4=1)). The cation structures of P444(R_1=R_2)-Br used in the present study are summarized in **Figure 1**. The equilibrium temperature, dissociation enthalpy, and powder X-ray diffraction (PXRD) pattern of P444(2=1)-Br SCH have been already reported in the ref. 28.



P444(2=1) (tri-*n*-butylallylphosphonium)

P444(3=1) (tri-*n*-butyl-3-butenylphosphonium)

P444(4=1) (tri-*n*-butyl-4-pentenylphosphonium)

P4443 (tri-*n*-butylpropylphosphonium)

P4444 (tetra-*n*-butylphosphonium)

P4445 (tri-*n*-butylpentylphosphonium)

Figure 1. Chemical structures of tri-*n*-butylalkenylphosphonium cations (P444(R_1=R_2)) and tri-*n*-butylalkylphosphonium cations (P444R). P444(3=1)-Br and P444(4=1)-Br were used in the present study. The results on the other cations[28] were cited for comparison purposes.

2. EXPERIMENTAL SECTION

2.1 Materials.

The chemicals used in the present study are listed in **Table 1**. P444(3=1)-Br and P444(4=1)-Br salts were synthesized, according to the procedures described in the literatures,[28,29] at 353 K in a nitrogen atmosphere by a quaternization reaction in toluene solvent. The products were rinsed with *n*-hexane to remove unreacted tri-*n*-butylphosphine and alkenyl bromide. Subsequently, the salts were dried *in vacuo* at 353 K for 24 hours. The obtained salts were stored in a glove box filled with argon gas and were confirmed by ^{1}H, ^{13}C, and ^{31}P NMR (Bruker, AVANCE400). The NMR results are summarized in the supporting information. From the NMR results, there were no impurity-derived signals or aberrant integration ratios. The purities of the synthesized P444(R_1=R_2)-Br salts were higher than or equal to those originally included in the synthetic reagents. The majority of the impurities, considering the synthetic pathway, would be tri-*n*-butylphosphine oxide derivatives. The mass fraction purities of the P444(R_1=R_2)-Br salts measured by silver nitrate titration was higher than 0.99.

Table 1. Information on Chemicals Used in the Present Study.

chemical name	CAS reg. no	source	mass fraction purity
tri-*n*-butylphosphine	998-40-3	Nippon Chemical Industrial Co., Ltd.	> 0.995
4-bromo-1-butene	5162-44-7	Tokyo chemical industry Co., Ltd.	> 0.97
5-bromo-1-pentene	1119-51-3	Kanto Chemical Co., Inc.	> 0.95
water	7732-18-5	Distilled	resistivity is 0.60 MΩ·cm

2.2 Apparatus and procedures.

Approximately 1 cm^3 of aqueous solutions were prepared at different compositions from x_1 = (0.0029–0.0507) (w_1 = (0.052–0.500)) for P444(3=1)-Br and x_1 = (0.0028–0.0489) (w_1 = (0.052–0.501)) for P444(4=1)-Br with an electronic 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. P444(R$_1$=R$_2$)-Br SCHs were formed in glass vials at 258 K. After that, the glass vials containing SCHs were immersed into an ethylene glycol bath thermostated with a cooling water circulator at 268 K (Taitec, CL-80R). The temperature of thermostatic bath was increased by a step of 0.1 K. While the temperature was maintained at least for 5 hours at each temperature. The glass vials were often shaken by hand. The equilibrium temperatures of SCH were determined when the SCH crystal was dissociated completely. The 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 P444(R_1=R_2)-Br SCH was estimated from the composition at the highest equilibrium temperature. The equilibrium temperatures around the highest equilibrium temperature 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 per unit mass of aqueous solution were measured with differential scanning calorimetry (DSC). The value of the 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 P444(R_1=R_2)-Br SCH 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 Kα X-ray (45 kV, 40 mA). The PXRD measurements were performed in a stepscan mode with a scan rate of 2.7 $°\cdot\text{min}^{-1}$ and a step size of approximately 0.02°.

The dissociation enthalpy of P444(R_1=R_2)-Br SCH was measured by a micro differential scanning calorimeter (Setaram, μDSC VII evo) at atmospheric pressure. About 20 mg of P444(R_1=R_2)-Br aqueous solution was sealed in a glass cell and set in the DSC. The mass of the P444(R_1=R_2)-Br aqueous solution was weighed with an electronic balance (A&D, BM-22, uncertainty: 0.02 mg). The furnace temperature was cooled down to 248 K at a rate of 0.5 $\text{K}\cdot\text{min}^{-1}$ to form the P444(R_1=R_2)-Br SCH. Then, the heating rates for SCH dissociation were 0.02, 0.04, 0.05, and 0.1 $\text{K}\cdot\text{min}^{-1}$ to confirm the heating-rate dependency. The μDSC was calibrated with a Joule heat calibrator (Setaram, EJ3). Water and naphthalene were used as references. The uncertainty of the dissociation enthalpy is less than 2 $\text{J}\cdot\text{g}^{-1}$.

3. RESULTS AND DISCUSSION

Equilibrium phase relations between temperature (T) and composition (x_1) of P444(3=1)-Br and P444(4=1)-Br obtained by direct observation are shown in **Figure 2** and summarized in **Tables 2** and **3**. Both the phase relations of P444(3=1)-Br and P444(4=1)-Br SCHs exhibited the typical phase behavior of SCH. The maximum equilibrium temperatures should be located in a range of x_1 = (0.0202–0.0316) for P444(3=1)-Br and x_1 = (0.0225–0.0302) for P444(4=1)-Br, where the equilibrium temperatures obtained by direct observation were constant within the uncertainty (±0.1 K) of the temperature measurement. To determine the stoichiometric composition and the hydration number, the apparent dissociation enthalpy per unit mass of the aqueous solution, $\Delta_d H^{app}$, (not unit mass of SCH) was measured by DSC.[13,24] The apparent dissociation enthalpy at each composition is shown in **Figure 3**. From the vertex of the fitting quadratic curve, we determined that the stoichiometric compositions were x_1 = (0.0269±0.0007) for P444(3=1)-Br SCH and x_1 = (0.0264±0.0006) for P444(4=1)-Br SCH. The eutectic temperatures of P444(3=1)-Br and P444(4=1)-Br SCHs were also determined from the onset of the eutectic peak of DSC thermograms at low P444(R_1=R_2)-Br compositions. The eutectic temperatures of P444(3=1)-Br and P444(4=1)-Br SCHs were (272.2±0.1) K and (271.4±0.1) K, respectively.

The equilibrium temperatures of P444(2=1)-Br, P444(3=1)-Br, and P444(4=1)-Br SCHs were (275.4±0.1) K,[22] (277.5±0.1) K, and (274.8±0.1) K, respectively, that is, the thermodynamic stability of P444(4=1)-Br SCH is the highest of them. The trend also has been observed in the P4443-Br SCH ((274.1±0.1) K), P4444-Br SCH ((282.3±0.1) K), and P4445-Br SCH ((276.8±0.1) K) systems.[28] The equilibrium temperatures of P444(3=1)-Br and P444(4=1)-Br SCHs were lower than those of the corresponding P4444-Br and P4445-Br SCHs. On the other hands, the equilibrium temperature of P444(2=1)-Br SCH was higher than that of the P4443-Br SCH. It has been considered that the thermodynamic stability of SCH depends on the fittingness of the alkyl chains to the hydrate cages.[28] The volume of butyl group to the void of hydrate cages would be the most appropriate among those of normal alkyl groups because P4444-Br SCH has the highest equilibrium temperature in the normal alkyl system.[28] The results reveal that introducing the double bond to one of alkyl chains in onium cations would make the effective volume of alkyl groups larger, although the bond length of C=C double bond is generally shorter than that of C-C single bond. Only allyl (R= (2=1)) group smaller than *n*-butyl group, in other words, stabilizes the SCH more than *n*-propyl (R = 3) one because the effective volume of the allyl group gets close to that of *n*-butyl one, compared to the *n*-propyl one.

PXRD patterns of P444(R_1=R_2)-Br SCH measured at 150 K are shown in **Figure 4**. In an angle range lower than 2θ=12°, three characteristic diffraction peaks were observed in the P444(3=1)-Br and P444(4=1)-Br SCHs. Such patterns have been observed in P4444-Br SCH as shown at the bottom of **Figure 4**. Crystal structure and lattice constants of P4444-Br SCH have been reported as an orthorhombic structure with the space group *Pmma* and the unit cell parameters of a = 2.11 nm, b = 1.26 nm, and c = 1.20 nm at 150 K.[28] It is suggested that the crystal structure of P444(3=1)-Br and P444(4=1)-Br SCHs were the orthorhombic structure with the space group *Pmma* as in the case of P4444-Br SCH. The lattice constants were estimated to be a = (2.11±0.01) nm, b = (1.27±0.01) nm, and c = (1.20±0.01) nm for P444(3=1)-Br SCH and a = (2.14±0.02) nm, b = (1.26±0.01) nm, and c = (1.20±0.02) nm for P444(4=1)-Br SCH at 150 K. The crystal structure of P444(2=1)-Br SCH has not yet been estimated.[28]

The dissociation enthalpy ($\Delta_d H$) of P444(R_1=R_2)-Br SCH was measured by DSC. Typical DSC thermograms at a heating rate of 0.1 K·min^{-1} are shown in **Figure 5**. The dissociation enthalpies of P444(3=1)-Br SCH and P444(4=1)-Br SCH were (199±2) J·g^{-1} at x = (0.0269±0.0007) and (188±2) J·g^{-1} at x = (0.0264±0.0006). The dissociation enthalpies of P444(2=1)-Br SCH is reported to be (175±3) J·g^{-1}.[28] The dissociation enthalpies of P4443-Br, P4444-Br, and P4445-Br SCHs, which have corresponding normal alkyl groups, are (190±3) J·g^{-1}, (214±3) J·g^{-1}, (185±3) J·g^{-1}, respectively.[28] The introduction of the C=C double bonds in phosphonium cations leads to the effective volume change of each hydrocarbon chain, which affects the dissociation enthalpies as well as the equilibrium temperatures.

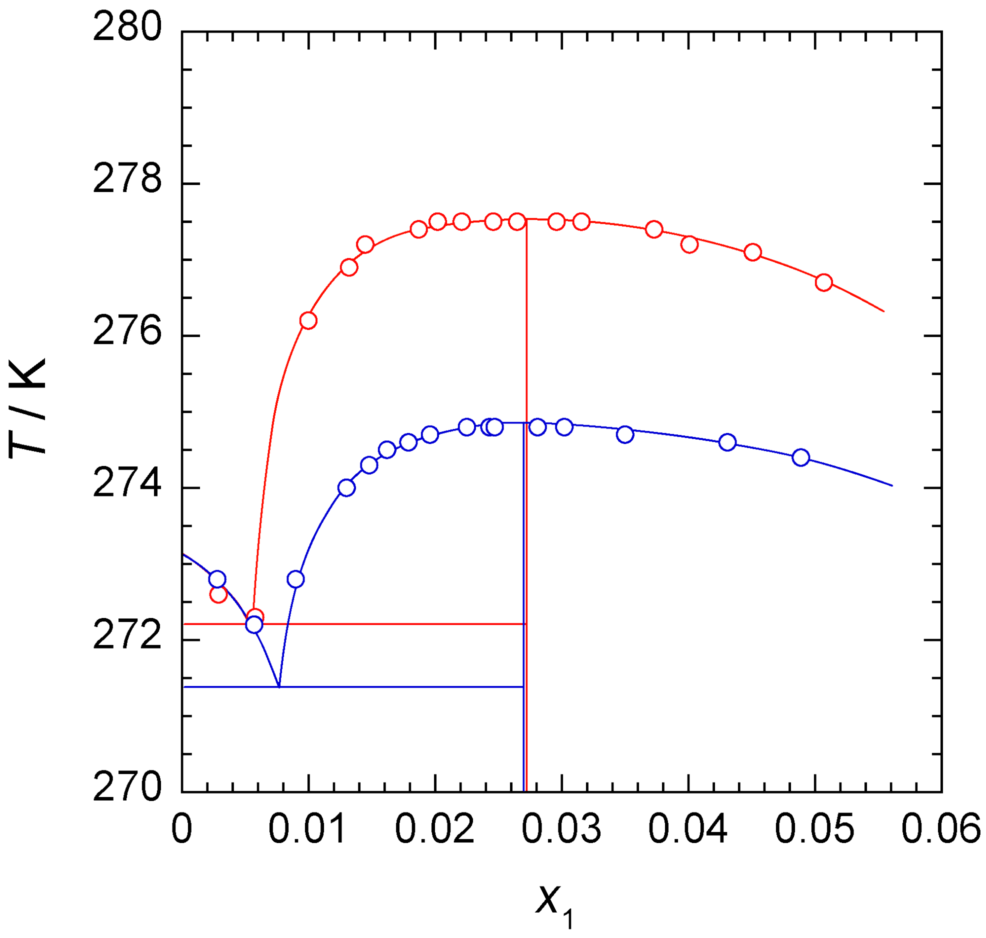


Figure 2. Equilibrium temperature (*T*)-composition (*x*) relations of P444(3=1)-Br (1) + water (2) system (red circles), and P444(4=1)-Br (1) + water (2) system (blue circles). (For interpretation of the references to colors in this figure legend, see the web version of this article.)

Table 2. Relations between Equilibrium Temperature (*T*) and Composition (Mole Fraction *x* and Mass Fraction *w*) of P444(3=1)-Br (1) + Water (2) System.[a]

x_1	w_1	T/K	x_1	w_1	T/K
0.0029	0.052	272.6	0.0265	0.338	277.5
0.0058	0.098	272.3	0.0269[b]	0.341[b]	277.5[b]
0.0100	0.159	276.2	0.0296	0.364	277.5
0.0132	0.200	276.9	0.0316	0.379	277.5
0.0145	0.216	277.2	0.0373	0.421	277.4
0.0187	0.263	277.4	0.0401	0.439	277.2
0.0202	0.279	277.5	0.0451	0.470	277.1
0.0221	0.297	277.5	0.0507	0.500	276.7
0.0246	0.321	277.5			

[a] Standard uncertainties u are $u(x) = 0.0007$, $u(w) = 0.004$, and $u(T) = 0.1$ K. [b] The maximum equilibrium temperature at the stoichiometric composition that was estimated from the apparent dissociation enthalpies obtained by DSC measurements. The maximum equilibrium temperature was measured from the visual observation.

Table 3. Relations between Equilibrium Temperature (*T*) and Composition (Mole Fraction *x* and Mass Fraction *w*) of P444(4=1)-Br (1) + Water (2) System.[a]

x_1	w_1	T/K	x_1	w_1	T/K
0.0028	0.052	272.8	0.0243	0.327	274.8
0.0057	0.100	272.2	0.0247	0.331	274.8
0.0090	0.151	272.8	0.0264[b]	0.346[b]	274.8[b]
0.0130	0.204	274.0	0.0281	0.361	274.8
0.0148	0.227	274.3	0.0302	0.378	274.8
0.0162	0.244	274.5	0.0350	0.414	274.7
0.0179	0.263	274.6	0.0431	0.468	274.6
0.0196	0.280	274.7	0.0489	0.501	274.4
0.0225	0.310	274.8			

[a] Standard uncertainties *u* are $u(x) = 0.0006$, $u(w) = 0.004$, and $u(T) = 0.1$ K. [b] The maximum equilibrium temperature at the stoichiometric composition that was estimated from the apparent dissociation enthalpies obtained by DSC measurements. The maximum equilibrium temperature was measured from the visual observation.

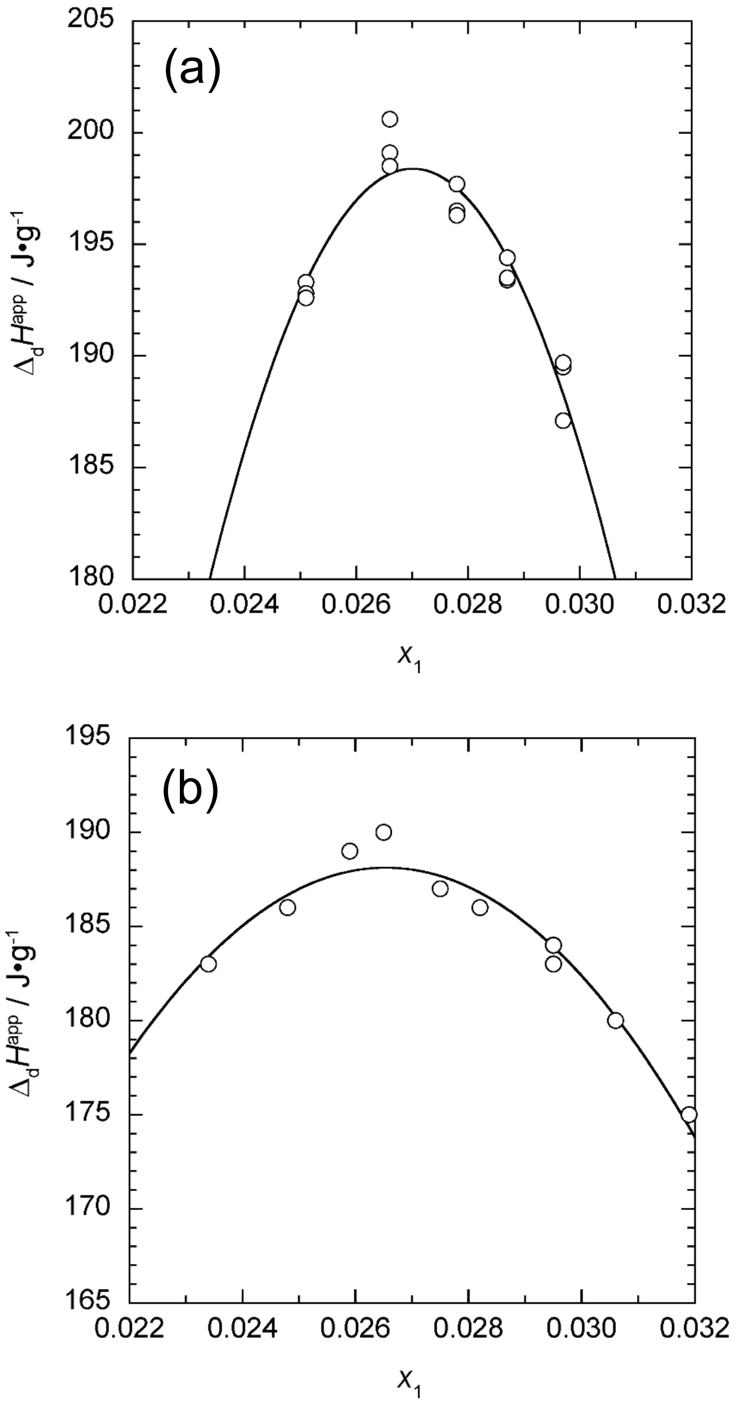


Figure 3. Apparent dissociation enthalpies of (a) P444(3=1)-Br (1) + water (2) system and (b) P444(4=1)-Br (1) + water (2) system.

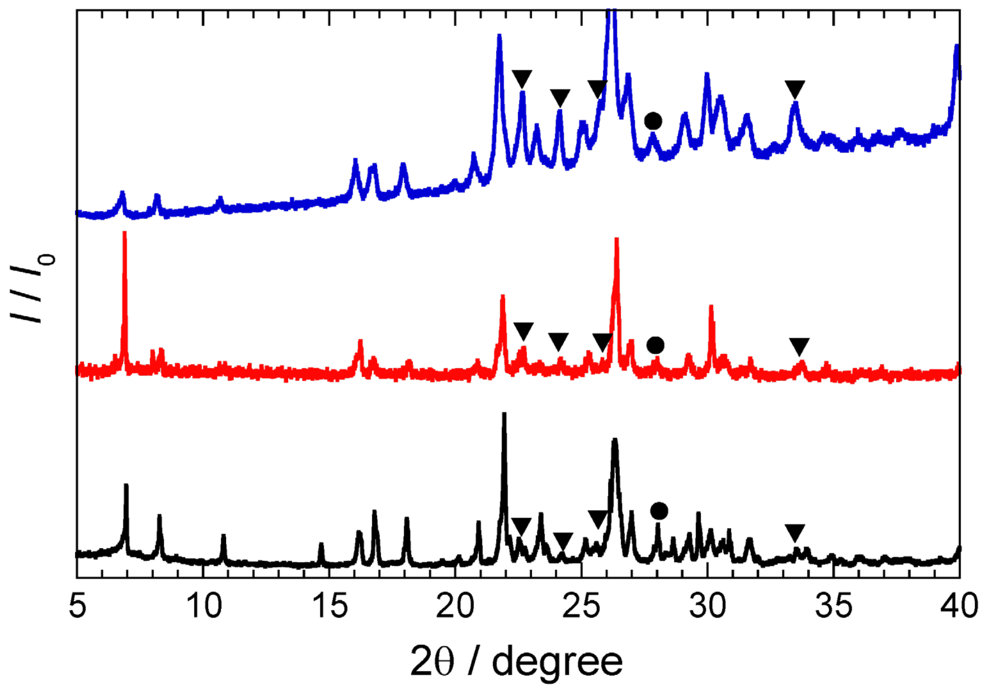


Figure 4. Powder X-ray diffraction (PXRD) patterns of P444(3=1)-Br SCH (red line, middle), P444(4=1)-Br SCH (blue line, top) and P4444-Br SCH (black line, bottom) measured at 150 K and atmospheric pressure. The peaks marked by triangles and circles include the contributions originated from hexagonal ice (Ih) and the stage, respectively. All PXRD patterns suggested that the crystal structure is an orthorhombic structure with the space group *Pmma*.

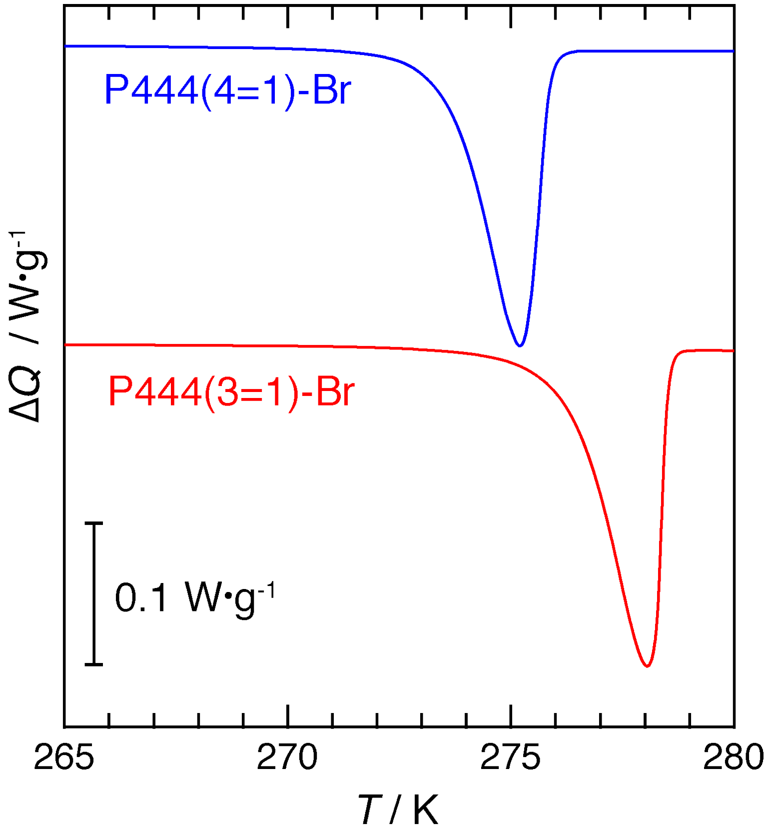


Figure 5. DSC thermograms (heat flow ΔQ, temperature T) of the P444(3=1)-Br (1) + water (2) system (blue line, top) and P444(4=1)-Br (1) + water (2) system (red line, bottom) at a heating rate of 0.1 K·min^{-1}.

4. CONCLUSIONS

Thermodynamic stability, dissociation enthalpy, and crystal structure of P444(3=1)-Br SCH and P444(4=1)-Br SCH were investigated. The maximum equilibrium temperature and the dissociation enthalpy of P444(3=1)-Br SCH and P444(4=1)-Br SCH were (277.5±0.1) K and (199±2) $J \cdot g^{-1}$ at x = (0.0269±0.0007) (w = (0.341±0.004)), and (274.8±0.1) K and (188±2) $J \cdot g^{-1}$ at x = (0.0264±0.0006) (w = (0.346±0.004)), respectively. Both the crystal structures of P444(3=1)-Br SCH and P444(4=1)-Br SCH were an orthorhombic structure with *Pmma*. The maximum equilibrium temperatures of P444(3=1)-Br SCH and P444(4=1)-Br SCH were lower than those of P4444-Br SCH and P4445-Br SCH, although the equilibrium temperature of P444(2=1)-Br SCH was higher than that of P4443-Br SCH.

The obtained SCHs are promising for cooling applications, such as shipping boxes for medicine and/or fresh foods, because of their equilibrium temperatures and dissociation enthalpies. The development of thermal storage materials working at various temperatures has been much anticipated. These results allowed us to figure out how the double bond introduced to phosphonium cations affects the thermodynamic stability of SCHs. The findings obtained in the present study bring an additional method for tuning the working temperature of SCH as a thermal storage material.

ASSOCIATED CONTENT

Supporting Information

The ^{1}H, ^{13}C, and ^{31}P NMR results of the salts prepared in the present study are summarized in the supporting information. This material is available free of charge on the ACS Publications website at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

1. Dyadin, Y.A.; Udachin, K.A. Clathrate polydyhydrates of peralkylonium salts and their analogs. *J. Struct. Chem.* **1987**, 28, 394−432.
2. Shimada, W.; Shiro, M.; Kondo, H.; Takeya, S.; Oyama, H.; Ebinuma, T.; Narita, H. Tetra-*n*-butylammonium bromide-water (1/38). *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2005**. C61, o65−o66.
3. Nakayama, H. Hydrates of Organic Compounds. VI. Heats of Fusion and of Solution of Quaternary Ammonium Halide Clathrate Hydrates. *Bull. Chem. Soc. Jpn.*, **1982**, 55, 389−393.
4. Oshima, M.; Kida, M.; Jin, Y.; Nagao, J. Dissociation behaviour of (tetra-*n*-butylammonium bromide + tetra-*n*-butylammonium chloride) mixed semiclathrate hydrate systems. *J. Chem. Thermodyn.* **2015**, 90, 277−281.
5. Rodionova, T.; Komarov, V.; Villevald, G.; Aladko, L.; Karpova, T.; Manakov, A. Calorimetric and Structural Studies of Tetrabutylammonium Chloride Ionic Clathrate Hydrates. *J. Phys. Chem. B* **2010**, 114, 11838–11846.
6. Rodionova, T. V.; Komarov, V. Y.; Villevald, G. V.; Karpova, T. D.; Kuratieva, N. V.; Manakov, A. Y. Calorimetric and Structural Studies of Tetrabutylammonium Bromide Ionic Clathrate Hydrates. *J. Phys. Chem. B* **2013**, 117, 10677−10685.
7. Sugahara, T.; Machida, H. Dissociation and nucleation of tetra-*n*-butyl ammonium bromide semi-clathrate hydrates at high pressures. *J. Chem. Eng. Data* **2017**, 62, 2721−2725.

8. Ogoshi, H.; Takao, S. Air-Conditioning System Using Clathrate Hydrate Slurry. *JFE Technical Report* 2004, **3**, 1-5.
9. Kiyokawa, H.; Tokutomi, H.; Ishida, S.; Nishi, H.; Ohmura, R. Thermal Energy Storage Performance of Tetrabutylammonium Acrylate Hydrate as Phase Change Materials. *Appl. Sci.* 2021, **11**, 4848, 1−16.
10. Koyama, R.; Arai, Y.; Yamauchi, Y.; Takeya, S.; Endo, F.; Hotta, A.; Ohmura, R. Thermophysical properties of trimethylolethane (TME) hydrate as phase change material for cooling lithium-ion battery in electric vehicle. *J. Power Sources* 2019, **427**, 70−76.
11. Sakamoto, H.; Sato, K.; Shiraiwa, K.; Takeya, S.; Nakajima, M.; Ohmura, R. Synthesis, characterization and thermal-property measurements of ionic semi-clathrate hydrates formed with tetrabutylphosphonium chloride and tetrabutylammonium acrylate. *RSC Adv.*, **2011**, 1, 315−322.
12. Komarov, V. Y.; Rodionova, T. V.; Suwinska, K. Single Crystal X-ray Diffraction Study of the Cubic Ionic Clathrate Hydrate of Tetrabutyl Ammonium Propionate $(C_4H_9)_4NC_2H_5COO\cdot27.0H_2O$. *J. Struct. Chem*. **2012**, 53, 768−775.
13. Koyama, R.; Hotta, A.; Ohmura, R. Equilibrium temperature and dissociation heat of tetrabutylphosphonium acrylate (TBPAc) ionic semi-clathrate hydrate as a medium for the hydrate-based thermal energy storage system. *J. Chem. Thermodyn.* **2020**, 144, 106088, 1−8.
14. Muromachi, S.; Kida, M.; Takeya, S.; Yamamoto, Y.; Ohmura, R. Characterization of the ionic clathrate hydrate of tetra-*n*-butylammonium acrylate. *Can. J. Chem.* **2015**, 93, 954−959.
15. Muromachi, S.; Abe, T.; Yamamoto, Y.; Takeya, S. Hydration structures of lactic acid: characterization of the ionic clathrate hydrate formed with a biological organic acid anion. *Phys.Chem.Chem.Phys*., **2014**, 16, 21467−21472.

16. Muromachi, S.; Kamo, R.; Abe, T.; Hiaki, T.; Takeya, S. Thermodynamic stabilization of semiclathrate hydrates by hydrophilic group. *RSC Adv.*, **2017**, 7, 13590−13594.
17. Muromachi, S.; Takeya, S. Thermodynamic Properties and Crystallographic Characterization of Semiclathrate Hydrates Formed with Tetra-*n*-butylammonium Glycolate. *ACS Omega* **2019**, 4, 7317−7322.
18. Miyamoto, T.; Koyama, R.; Kurokawa, N.; Hotta, A.; Alavi, S.; Ohmura, R. Thermophysical Property Measurements of Tetrabutylphosphonium Oxalate (TBPOx) Ionic Semiclathrate Hydrate as a Media for the Thermal Energy Storage *System. Front. Chem.* **2020**, 8, 1−10.
19. Nakayama, H.; Usui, H. The effect of carboxylate anions on the formation of clathrate hydrates of tetrabutylammonium carboxylates. *J. Inclusion Phenom.* **1984**, 2, 249−257.
20. Nakayama, H.; Watanabe, K. Hydrates of Organic Compounds. III. The formation of Clathrate-like Hydrates of Tetrabutylammonium Dicarboxylates. *Bull. Chem. Soc. Jpn* **1978**, 51, 2518−2522.
21. Rodionova, T.; Komarov, V.; Lipkowski, J.; Kuratieva, N. The structure of the ionic clathrate hydrate of tetrabutylammonium valerate $(C_4H_9)_4NC_4H_9CO_2 \cdot 39.8H_2O$. *New J. Chem.* **2010**, 34, 432−438.
22. Shimada, J.; Shimada, M.; Sugahara, T.; Tsunashima, K.; Tani, A.; Tsuchida, Y.; Matsumiya, M. Phase Equilibrium Relations of Semiclathrate hydrates Based on Tetra-*n*-butylphosphonium Formate, Acetate, and Lactate. *J. Chem. Eng. Data* **2018**, 63, 3615−3620.
23. Shimada, J.; Shimada, M.; Sugahara, T.; Tsunashima, K.; Tani, A.; Tsuchida, Y.; Matsumiya, M. Phase equilibrium relations of tetra-*n*-butylphosphonium propionate and butyrate semiclathrate hydrates. *Fluid Phase Equilibria* **2019**, 485, 61−66.
24. Sugahara, T.; Machida, H.; Muromachi, S.; Tenma, N. Thermodynamic properties of tetra-*n*-

butylammonium 2-ethylbutyrate semiclathrate hydrate for latent heat storage. *Int. J. Refrig*. **2019**, 106, 113−119.

25. Nakayama, H.; Watanabe, K. Hydrates of Organic Compounds. II. The Effect of Alkyl Groups on the Formation of Quaternary Ammonium Fluoride Hydrates. *Bull. Chem. Soc. Jpn* **1976**, 49, 1254−1256.
26. Su, Y.; Bernardi, S.; Searles, D.J.; Wang, L. Effect of Carbon Chain Length of Organic Salts on the Thermodynamic Stability of Methane Hydrate. *J. Chem. Eng. Data* **2016**, 61, 1952−1960.
27. Su, Y.; Searles, D.J.; Wang, L. Semiclathrate hydrates of methane + tetraalkylammonium hydroxides. *Fuel* **2017**, 203, 618−626.
28. Shimada, J.; Shimada, M.; Sugahara, T.; Tsunashima, K.; Takaoka, Y.; Tani, A. Phase equilibrium temperature and dissociation enthalpy in the tri-*n*-butylphosphonium bromide semiclathrate hydrate systems. *Chem. Eng. Sci.* **2021**, 236, 116514, 1−8.
29. Yoshii, K., Yamaji, K., Tsuda, T., Tsunashima, K., Yoshida, H., Ozaki, M., Kuwabata, S., Physicochemical Properties of Tri-*n*-butylalkylphosphonium Cation-Based Room-Temperature Ionic Liquids. *J. Phys. Chem. B* **2013**, 117, 15051−15059.

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