Title	Phase Equilibrium Relations of Semiclathrate Hydrates Based on Tetra- n-butylphosphonium Formate, Acetate, and Lactate
Author(s)	Shimada, Jin; Shimada, Masami; Sugahara, Takeshi et al.
Citation	Journal of Chemical and Engineering Data. 2018, 63(9), p. 3615-3620
Version Type	AM
URL	https://hdl.handle.net/11094/91294
rights	This document is the Accepted Manuscript version of a Published Work that appeared in final form in Journal of Chemical and Engineering Data, © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see https://doi.org/10.1021/acs.jced.8b00481.
Note	

Phase Equilibrium Relations of Semiclathrate Hydrates Based on Tetra-*n*-butylphosphonium Formate, Acetate, and Lactate

Jin Shimada[1], Masami Shimada[1], Takeshi Sugahara[2,], Katsuhiko Tsunashima[3,*] Atsushi Tani[4], Yusuke Tsuchida[5], Masahiko Matsumiya[5]*

[1]Advanced Engineering Faculty, National Institute of Technology, Wakayama College, 77 Noshima, Noda-cho, Gobo, Wakayama 644-0023, Japan.

[2]Division of Chemical Engineering, Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan.

[3]Department of Applied Chemistry and Biochemistry, National Institute of Technology, Wakayama College, 77 Noshima, Noda-cho, Gobo, Wakayama 644-0023, Japan.

[4]Department of Human Environmental Science, Graduate School of Human Development and Environment, Kobe University, 3-11 Tsurukabuto, Nada, Kobe, Hyogo 657-8501, Japan.

[5]Graduate School of Environment and Information Sciences, Yokohama National University, 79-2 Tokiwadai, Hodogaya-ku, Yokohama, Kanagawa 240-8501, Japan.

ABSTRACT

Phase equilibrium (temperature-composition) relations of tetra-*n*-butylphosphonium formate (TBP-For), acetate (TBP-Ace), and lactate (TBP-Lac) semiclathrate hydrate systems have been measured. The highest equilibrium temperatures of TBP-For, TBP-Ace, and TBP-Lac semiclathrate hydrates were 280.9 K, 284.6 K, and 283.8 K at the atmospheric pressure, respectively, where the composition of tetra-*n*-butylphosphonium carboxylate was approximately 0.035±0.001 (mole fraction) in every system. The dissociation enthalpies of tetra-*n*-butylphosphonium carboxylate semiclathrate hydrates were measured by differential scanning calorimetry. The dissociation enthalpies of TBP-For, TBP-Ace, and TBP-Lac semiclathrate hydrates were (187±3) $J \cdot g^{-1}$, (193±3) $J \cdot g^{-1}$, and (177±3) $J \cdot g^{-1}$, respectively.

1. INTRODUCTION

Semiclathrate hydrates (or ionic clathrate hydrates) are crystalline compounds which consist of a guest substance and host water cages. The quaternary onium salts have been typically employed as the guest substances in semiclathrate hydrates. The guest onium cations are incorporated with the water molecules to construct the hydrate framework whereas the counter anions replace water molecules in the hydrate framework, forming the hydrate cages together with neighboring water molecules.[1,2] Since the semiclathrate hydrates have relatively large dissociation enthalpy at atmospheric pressures, semiclathrate hydrates have been recently regarded as potential candidates for heat storage materials.[3,4] For example, the quaternary ammonium salts based on tetra-*n*-butylammonium (TBA, N_{4444}) cation are well known as one of the semiclathrate hydrate formers.[5] In particular, tetra-*n*-butylammonium bromide (TBAB, N_{4444}-Br) has been studied because of its commercial availability.[6-10] In fact, the TBA-based semiclathrate hydrate has been applied to a cooling medium for air conditioners as proposed by Ogoshi et al.[11]

Typical quaternary ammonium salts, like TBAB well investigated as a guest species for semiclathrate hydrate formation, contain halide anions such as fluoride, chloride and bromide anions. However, 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. On the other hand, unlike halide anions, carboxylate anions have been of great interest from the environmental aspects. For instance, the high biocompatibility of various onium salts based on several carboxylate anions has been demonstrated for an application to the microscope observation of diverse biomaterials.[12] This advantage of using carboxylate anions has also attracted attention to the semiclathrate hydrate application. Udachin et al.[2] and McMullan et al.[13] summarized the basic physicochemical data of halogen-free carboxylate-based semiclathrate hydrates. Nakayama et al.[14] systematically evaluated the phase equilibrium relations of various carboxylate-based semiclathrate hydrates. Muromachi et al.[15] determined the crystallographic structure of the carboxylate-based hydrates using a XRD measurement. The major quaternary onium salts proposed as a guest species for the environment-friendly semiclathrate hydrates include quaternary ammonium cations. The semiclathrate hydrates including a quaternary phosphonium salt have been reported.[16-19] Quaternary phosphonium salts significantly offered relatively high chemical and thermal stabilities when compared to the corresponding ammonium counterparts.[20-24] However, to our knowledge, carboxylate-based semiclathrate hydrates containing phosphonium cations have been rarely investigated, except a report published by Arai et al.[25] In the present study, we characterized the thermodynamic properties of the semiclathrate hydrates based on tetra-*n*-butylphosphonium (TBP, P_{4444}) cation in combination with several carboxylate anions (**Figure 1**), investigating the relationship between equilibrium temperature and the composition in the aqueous solutions.

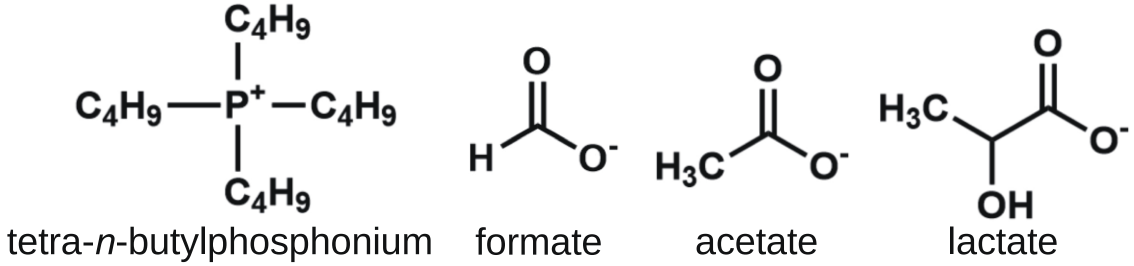


Figure 1. Ionic species used in the present study.

2. EXPERIMENTAL SECTION

The chemicals used in this study were listed in **Table 1**. Tetra-*n*-butylphosphonium carboxylates (TBP-carboxylate) were synthesized by aqueous neutralization of tetra-*n*-butylphosphonium hydroxide with the corresponding carboxylic acids. The aqueous solutions were completely evaporated to isolate the salts, and then the products thus obtained were dried i*n vacuo* at 323 K for 72 h. The products were confirmed by ^{1}H, ^{13}C, ^{31}P NMRs and FAB-MS. More detail synthetic procedure and physicochemical properties of the products have been reported elsewhere. [24] 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.

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
formic acid	Wako Pure Chemical Industries	> 0.995
acetic acid	Wako Pure Chemical Industries	> 0.999
L-(+)-lactic acid	Wako Pure Chemical Industries	0.820 mass fraction in aqueous solution
water	homemade (distilled and deionized)	resistivity is 0.46 MΩcm

The aqueous solutions were prepared at different compositions from w = 0.10–0.50 (x = 0.007–0.056 for TBP-For, x = 0.006–0.054 for TBP-Ace, and x = 0.006–0.049 for TBP-Lac) with electric balance (A&D, GF-300) with an uncertainty of 1 mg. The symbols w and x represent the mass and mole fractions, respectively. Approximately 1 cm^3 of the aqueous solutions were injected into plastic tubes. The tubes were set in a water bath thermostatted with a cooling water circulator (Taitec, CL-80R). Once all the samples were crystallized by cooling to 268 K, then the system temperature was elevated with a step of 0.1 K. While the temperature was kept for 5 hours at each temperature, the sample tubes 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 dissociation enthalpy of semiclathrate hydrates was investigated by a micro differential scanning calorimeter (Setaram, µDSC VII evo) at atmospheric pressure. Approximately 20 mg of the prepared TBP-Carboxylate 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 and then increased to a desired temperature at the heating rate of 0.1 K/min. 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 $J \cdot g^{-1}$.

All the *ab initio* calculations were carried out using the Gaussian09 software program.[26] In order to calculate the atomic charge distributions, we cited the X-ray structural data of TBA and TBP cations in semiclathrate hydrates reported by Muromachi et al.[16, 27-29] The atomic charge distributions of TBA and TBP cations were calculated by electrostatic potential (ESP) fitting, with the Merz-Singh-Kollman scheme[30, 31] from the MP2/6-311G** basis set of isolated ions.

3. RESULTS AND DISCUSSION

3.1. Phase equilibrium data of TBP-carboxylate semiclathrate hydrates

The phase equilibrium data (temperature T -composition x relations) measured by direct observation in the present study are summarized in **Tables 2-4**. The equilibrium T-x relations of TBP-For, -Ace, and -Lac semiclathrate hydrates are also shown in **Figure 2**. The highest equilibrium temperatures of TBP-For, TBP-Ace, and TBP-Lac semiclathrate hydrates were 280.9 K, 284.6 K, and 283.8 K, respectively, where the corresponding compositions were located at $x = 0.035 \pm 0.001$ in every system. The highest equilibrium temperature of TBP-Ace semiclathrate hydrates was 3.7 K higher than that of TBP-For. Similar trend has been reported in TBA-carboxylate semiclathrate hydrates.[14, 15] The oxygen atoms in the carboxyl group are replaced with water molecules to form an edge of a hydrate cage, whereas the hydrophobic group of the anion occupies the cavity of the water framework.[32, 33] Therefore, it is considered that the more precisely the hydrophobic group of a carboxylate anion fits to hydrate cage, the more stable the semiclathrate hydrate becomes. It should be noted that, in the case of TBP-Lac, the highest phase equilibrium temperature of 283.8 K was located at $x = 0.035$. Despite the fact that the lactate anion has a carbon chain longer than acetate anion, the T-x relation of TBP-Lac semiclathrate hydrate exhibited similar behavior to TBP-Ace one. Muromachi et al.[15] reported the reason why the dissociation temperature of TBA-Lac hydrate is lower than that of the propionate-based TBA hydrates, indicating the hydroxyl group in the lactate anion destabilizes the hydrate structure compared with that of the TBA propionate hydrate.

Recently, Arai et al.[25] reported that the highest equilibrium temperature of TBP-Ace semiclathrate hydrate is 284.2 K at $x = 0.031$. The comparison of the T-x relation in the present study with that of ref 25 is shown in **Figure 3**. The highest equilibrium temperature obtained in the present study was approximately 0.4 K higher than that reported value[25].

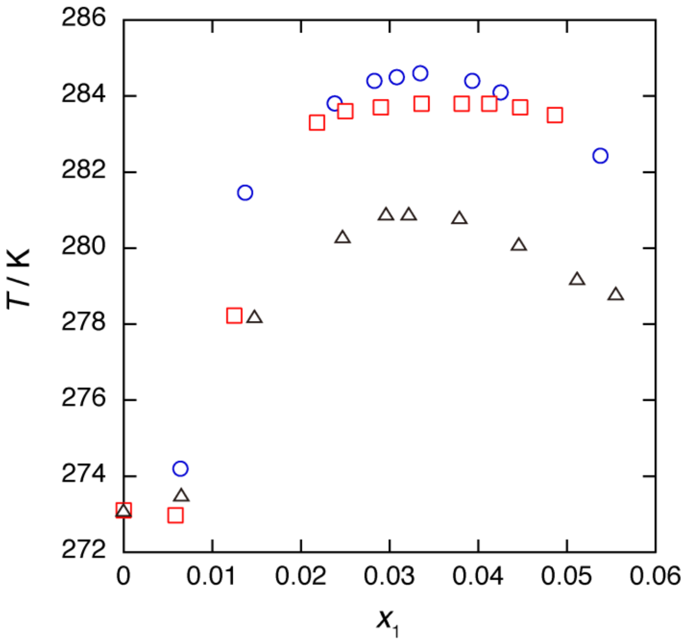


Figure 2. Equilibrium temperature-composition diagrams of TBP-Ace (1) + water (2) system, circles; TBP-Lac (1) + water (2) system, squares; TBP-For (1) + water (2) system, triangles.

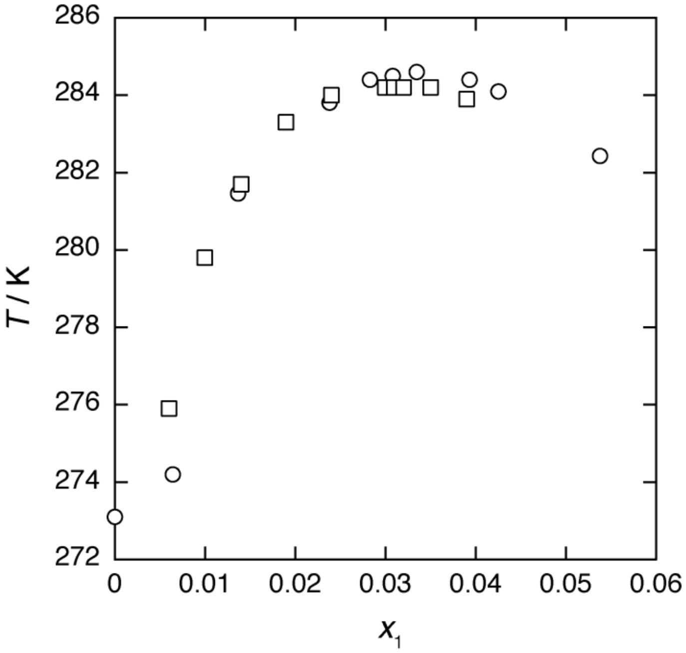


Figure 3. Comparison of phase equilibrium data of TBP-Ace semiclathrate hydrate in the present study (circles) with those in ref 25 (squares).

Table 2 Equilibrium Temperature (T) - Composition (Mass Fraction w, Mole Fraction x) Relation of TBP-For Semiclathrate Hydrate (TBP-For: 1, Water: 2)[a]

w_1	x_1	T / K
0.099	0.007	273.5
0.203	0.015	278.2
0.302	0.025	280.3
0.341	0.030	280.9
0.362	0.032	280.9
0.402	0.038	280.8
0.441	0.045	280.1
0.477	0.051	279.2
0.499	0.056	278.8

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

Table 3 Equilibrium Temperature (*T*) - Composition (Mass Fraction *w*, Mole Fraction *x*) Relation of TBP-Ace Semiclathrate Hydrate (TBP-Ace: 1, Water: 2)[a]

w_1	x_1	T / K
0.103	0.006	274.2
0.201	0.014	281.5
0.306	0.024	283.8
0.340	0.028	284.4
0.358	0.031	284.5
0.373	0.033	284.6
0.421	0.039	284.4
0.440	0.043	284.1
0.502	0.054	282.4

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

Table 4 Equilibrium Temperature (T) - Composition (Mass Fraction w, Mole Fraction x) Relation of TBP-Lac Semiclathrate Hydrate (TBP-Lac: 1, Water: 2)[a]

w_1	x_1	T / K
0.104	0.006	273.0
0.194	0.012	278.2
0.302	0.022	283.3
0.332	0.025	283.6
0.367	0.029	283.7
0.402	0.034	283.8
0.434	0.038	283.8
0.454	0.041	283.8
0.475	0.045	283.7
0.497	0.049	283.5

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

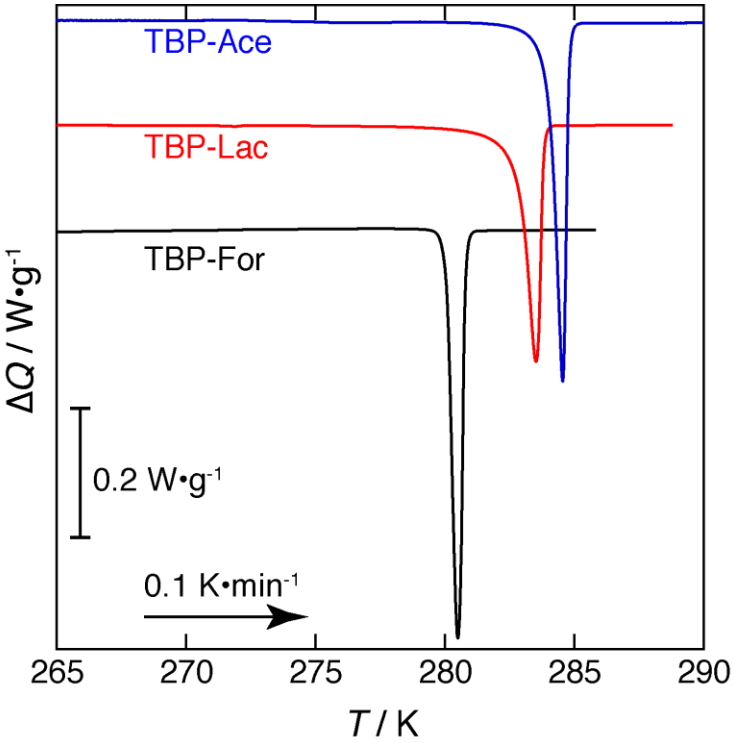


Figure 4. DSC curves (heat flow Δ*Q*, temperature *T*) of the TBP-For; black line, TBP-Ace; blue line, TBP-Lac; red line at atmospheric pressure.

3.2. Dissociation enthalpies of TBP-carboxylate semiclathrate hydrates

The DSC curves of the TBP-carboxylate semiclathrate hydrate dissociation at $x = 0.035$ are shown in **Figure 4**, where each semiclathrate hydrate has the highest equilibrium temperature. The onset, peak, higher inflection, and offset temperatures and dissociation enthalpy are listed in **Table 5**. All DSC curves had neither metastable nor ice peak. The higher inflection and offset temperatures of DSC were in good agreement with the equilibrium temperatures by direct observation. This behavior was the same as that in the literature[34, 35]. The dissociation enthalpies of TBP-carboxylate semiclathrate hydrates were around (180 to 195) J•g^{-1}. The dissociation enthalpy of TBAB semiclathrate hydrate (TBAB・$26H_2O$) is (192±3) J•g^{-1}.[36] This means that

TBP-carboxylate semiclathrate hydrates are also allowable as thermal storage media for an air-conditioner system. The TBP-Ace semiclathrate hydrate system has the largest enthalpy (193±3) J•g^{-1} among three TBP-carboxylate semiclathrate hydrates, which agrees well with the literature value of 192 J•kg^{-1}.[25]

Table 5 Experimental Dissociation Temperature (Onset Temperature T_{on}, Peak Temperature T_{peak}, Higher Inflection Temperature T_{end}, Offset Temperature T_{off}) and Dissociation Enthalpy $\Delta_{\mathrm{d}}H$ of the TBP-For, TBP-Ace, and TBP-Lac Semiclathrate Hydrates at Mole Fraction of TBP-Carboxylate $x = 0.035 \pm 0.001$[a].

Semiclathrate hydrate	T_{on}/K	T_{peak}/K	T_{end}/K	T_{off}/K	$\Delta_{\mathrm{d}}H$/J g^{-1}
TBP-For	280.04	280.50	280.69	280.78	187
TBP-Ace	283.99	284.57	284.69	284.80	193
TBP-Lac	282.85	283.56	283.72	283.84	177

[a] Standard uncertainties u are $u(T) = 0.06$ K, and $u(H) = 3$ J·g^{-1}.

3.3. Effects of cations and anions on equilibrium temperatures

The equilibrium temperature of TBA-Ace semiclathrate hydrate was 288.0 K.[14] Therefore, the difference between the equilibrium temperatures of TBP-Ace and TBA-Ace was 3.4 K. This difference is similar to that (4.0 K) between TBA-Br (285.2 K) and TBP-Br (281.2 K). **Figure 5** indicates the comparison of the equilibrium temperatures of the TBP-carboxylate semiclathrate hydrates (obtained in the present study) with those of TBA-carboxylate semiclathrate hydrates.[15] The differences (ΔT) of equilibrium temperature between TBA with TBP semiclathrate hydrates were decreased with increasing the carbon numbers of anions.

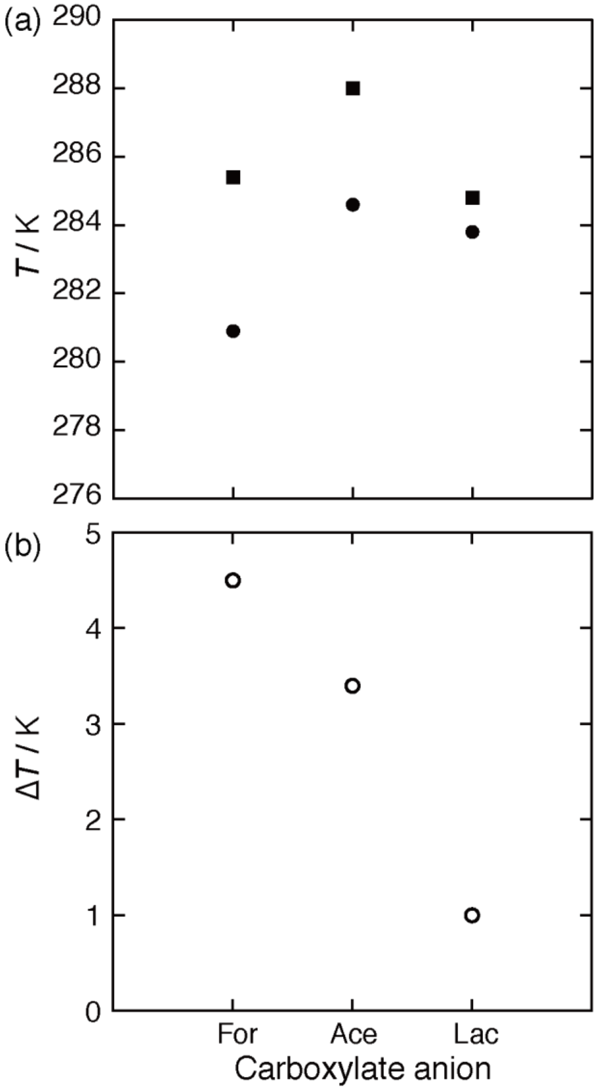
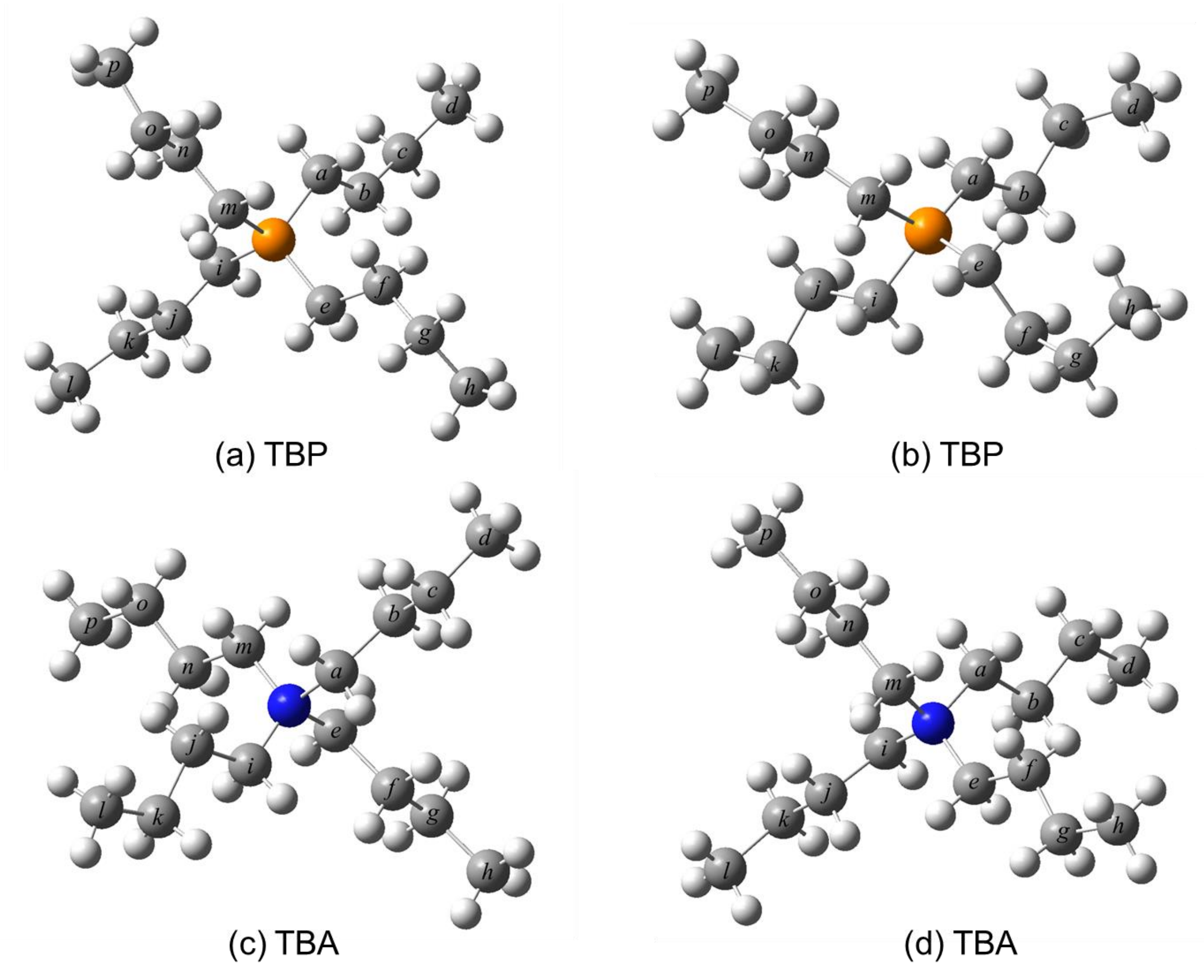


Figure 5. Highest equilibrium temperatures (a) and their difference (b) of semiclathrate hydrates based on formate, acetate and lactate anions. Closed circles and squares represent TBP and TBA[15] carboxylate systems, respectively.

Muromachi et al. have suggested the differences of equilibrium temperature between TBA and TBP semiclathrate hydrates from the viewpoint of the cation sizes.[16] The C-P bond length of TBP cation was 0.02 nm longer than the C-N bond of TBA cation. The TBA cation mainly contained trans-type chains; however, the butyl groups in TBP become gauche type. Therefore, the difference of cation size considerably influenced the equilibrium temperature of semiclathrate hydrates. On the other hand, it is still unclear how anions influence the equilibrium temperatures comprehensively, even though the size of anions is one of the important factors.

Another possibility is the effect of the atomic charge distributions on ammonium and phosphonium cations. The calculated cation structures were depicted in **Figure 6** and the obtained atomic charge distributions were listed in **Table 6**. A cation accommodated in hydrate cages has some different stable structures. In order to ensure the reliability of the charge density calculation of cations, two reliable conformation models were selected according to published papers. The data of TBP shown in **Figures 6** (a) and (b) are cited in references[16,27]. Similarly, the data of TBA shown in **Figures 6** (c) and (d) are cited in references[28, 29].

The calculation of atomic charge distributions showed that the nitrogen and phosphorus atoms in TBA and TBP cations were positively charged; however, a large difference was observed in atomic charge distribution in each cation. In the TBP cation, the atomic charge distributions on the phosphorus atom (0.638 and 0.736 in Figures 6 (a) and (b), respectively) were more positive than that on the nitrogen atom (0.382 and 0.380 in Figures 6 (c) and (d), respectively) in the TBA cation. Such a difference allows us to infer that the hydrate cages might be distorted by the interaction between positively charged center atom in phosphonium cation and negatively charged oxygen atoms in water molecules, resulting in the lower equilibrium temperatures of the TBP semiclathrate hydrate. The atomic charge distribution on the hydrocarbon chain of TBP cation tended to show slightly less positive charge distribution than that on the hydrocarbon chains of the TBA cation. However, the differences of the atomic charge distribution on the hydrocarbon chains between TBP and TBA cations were smaller than those on the center atoms of cations.



(a) TBP

(b) TBP

(c) TBA

(d) TBA

Figure 6. Structural illustrations of calculated cation models. (a) TBP[16]; (b) TBP[27]; (c) TBA[28]; (d) TBA[29] were cited as calculated cation structures. The atoms constituting the cation were defined as nitrogen atom (●), phosphorus atom (●), carbon atom (●), hydrogen atom (●).

Table 6 Atomic Charges Obtained by Electrostatic Potential Fitting Using Kollman's Scheme from the MP2/6-311G** Wave Functions. The Atoms Constituting the Molecule are shown in the Labels of Figure 6.

Atom	Atomic charge			
	(a) TBP	(b) TBP	(c) TBA	(d) TBA
P	0.638	0.736	-	-
N	-	-	0.382	0.380
a	0.094	0.098	-0.085	-0.034
b	-0.098	-0.094	0.080	0.053
c	0.184	0.226	0.159	0.158
d	-0.045	-0.049	-0.032	-0.037
e	0.043	-0.031	-0.012	-0.106
f	-0.040	0.000	0.078	0.120
g	0.166	0.134	0.135	0.151
h	-0.037	-0.036	-0.032	-0.044
i	-0.167	-0.173	-0.020	0.008
j	0.139	0.072	0.034	0.067
k	0.134	0.190	0.152	0.130
l	-0.043	-0.064	-0.031	-0.032
m	-0.232	-0.291	0.027	0.050
n	0.182	0.228	0.050	-0.007
o	0.125	0.113	0.161	0.188
p	-0.042	-0.058	-0.044	-0.046

4. CONCLUSIONS

We have proposed a new class of semiclathrate hydrates in combination with TBP cation and carboxylate anions, demonstrating their phase equilibrium and thermal behaviors. TBP-For, TBP-Ace, and TBP-Lac semiclathrate hydrates showed the maximum phase equilibrium temperatures of 280.9 K, 284.6 K, and 283.8 K at the atmospheric pressure with mole fraction $x = 0.035 \pm 0.001$, which indicated that the TBP-based semiclathrate hydrates showed lower phase equilibrium temperature than TBA-based semiclathrate hydrates. These findings were also supported by the estimated results on the bond lengths and atomic charge distributions in cations. Furthermore, the dissociation enthalpies of TBP-For, TBP-Ace, and TBP-Lac semiclathrate hydrates were (187±3) $\mathrm{J \bullet g^{-1}}$, (193±3) $\mathrm{J \bullet g^{-1}}$, and (177±3) $\mathrm{J \bullet g^{-1}}$, respectively.

AUTHOR INFORMATION

Corresponding Author

*KT: Tel: +81 738 29 8413; Fax: +81-738-29-8439. E-mail: tsunashima@wakayama-nct.ac.jp

*TS: Tel and Fax: +81-6-6850-6293. E-mail: sugahara@cheng.es. osaka-u.ac.jp

ORCID

Katsuhiko Tsunashima: 0000-0002-4563-351X

Takeshi Sugahara: 0000-0002-5236-5605

Funding Sources

KT and TS are grateful for the financial support provided by the Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan (No. 26410104 for KT and 18K05032 for TS).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

TS acknowledges scientific support from the Gas-Hydrate Analyzing System (GHAS) of the Division of Chemical Engineering, Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University.

REFERENCES

(1) Jeffrey, G. A.; Atwood, J. L.; Davies, J. E.; MacNicol, D. D.; Vogtle, F., Eds. *Hydrate Inclusion Compounds*. In Comprehensive Supramolecular Chemistry. Solid State Supramolecular Chemistry: Crystal Engineering. **1996**, 6, 757–788.

(2) Dyadin, Y.A.; Udachin, K. A. Clathrate polyhydrates of peralkylonium salts and their analogs. *J. Struct. Chem.* **1987**, *28*, 394–432.

(3) Sakamoto, H.; Sato, K.; Shiraiwa, K.; Takeya, S.; Nakajima, K.; 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.

(4) Fukushima, S.; Takao, S.; Ogoshi, H.; Ida, H.; Matsumoto, S.; Akiyama, T.; Otsuka. T. Development of high-density cold latent heat with clathrate hydrate. *NKK Technical Report* **1999**, *166*, 65–70.

(5) Aladko, L. S.; Dyadin, Y. A.; Rodionova, T. V.; Terekhova, I. S. Clathrate Hydrates of Tetrabutylammonium and Tetraisoamylammonium Halides. *J. Struct. Chem.* **2002**, *43*, 990–994.

(6) Shimada, W.; Ebinuma, T.; Oyama, H.; Kamata, Y.; Takeya, S.; Uchida, T.; Nagao, J.; Narita, H. Separation of gas molecule using tetra-*n*-butyl ammonium bromide semi-clathrate hydrate crystals. *Jpn. J. Appl. Phys.* **2003**, *42*, L129–L131.

(7) Fowler, D. L.; Loebenstein, W. V.; Pall, D. B.; Kraus, C. A. Some unusual hydrates of quaternary ammonium salts. *J. Am. Chem. Soc.* **1940**, *62*, 1140–1142.

(8) Sakamoto, J.; Hashimoto, S.; Tsuda, T.; Sugahara, T.; Inoue, Y.; Ohgaki, K. Thermodynamic and Raman Spectroscopic Studies on Hydrogen + Tetra-*n*-Butyl Ammonium Fluoride Semi-Clathrate Hydrates. *Chem. Eng. Sci.* **2008**, *63*, 5789–5794.

(9) 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.

(10) Lipkowski, J.; Komarov, V. Y.; Rodionova, T. V.; Dyadin, Y. A.; Aladko, L. S. The Structure of Tetrabutylammonium Bromide Hydrate $(C_4H_9)_4NBr\cdot 2^1/_3H_2O$. *J. Supramol. Chem.* **2002**, *2*, 435–439.

(11) Ogoshi, H.; Takao, S. Air-Conditioning System Using Clathrate Hydrate Slurry. *JFE Technical Report* **2004**, *3*, 1–5.

(12) Tsuda, T.; Nemoto, N.; Kawakami, K.; Mochizuki, E.; Kishida, S.; Tajiri, T.; Kushibiki, T.; Kuwabata, S. SEM Observation of Wet Biological Specimens Pretreated with Room Temperature Ionic Liquid, *ChemBioChem* **2011**, *12*, 2547−2550.

(13) McMullan, R.; Jeffrey, G. A. Hydrates of the Tetra *n*-butyl and Tetra *i*-amyl Quaternary Ammonium Salts. *J. Chem. Phys.* **1959**, *31*, 1231–1234.

(14) Nakayama, H.; Torigata, S. Hydrates of Organic Compounds. VIII. The Effect of Carboxylate Anions on the Formation of Clathrate Hydrates of Tetrabutylammonium Carboxylates. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 171–174.

(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.; Takeya, S.; Yamamoto, Y.; Ohmura, R. Characterization of tetra-*n*-butylphosphonium bromide semiclathrate hydrate by crystal structure analysis. *CrystEngComm* **2014**, *16*, 2056–2060.

(17) Fujisawa, Y.; Tsuda, T.; Hashimoto, S.; Sugahara, T.; Ohgaki, K. Thermodynamic stability of hydrogen+tetra-*n*-butyl phosphonium bromide mixed semi-clathrate hydrate. *Chem. Eng. Sci.* **2012**, *68*, 660–662.

(18) Sales Silva, L. P.; Dalmazzone, D.; Stambouli, M.; Lesort, A-L.; Arpentinier, P.; Trueba, A.; Fürst, W. Phase equilibria of semi-clathrate hydrates of tetra-*n*-butyl phosphonium bromide at atmospheric pressure and in presence of CH_4 and CO_2 + CH_4. *Fluid Phase Equilib.* **2016**, *413*, 28–35.

(19) Suginaka, T.; Sakamoto, H.; Iino, K.; Sakakibara, Y.; Ohmura, R. Phase equilibrium for ionic semiclathrate hydrate formed with CO_2, CH_4, or N_2 plus tetrabutylphosphonium bromide. *Fluid Phase Equilib.* **2013**, *344*, 108–111.

(20) Tsunashima, K.; Sugiya, M. Physical and electrochemical properties of low-viscosity phosphonium ionic liquids as potential electrolytes. *Electrochem. Commun.* **2007**, *9*, 2353–2358.

(21) Tsunashima, K.; Sugiya, M. Physical and Electrochemical Properties of Room Temperature Ionic Liquids Based on Quaternary Phosphonium Cations. *Electrochem.* **2007**, *75*, 734–736.

(22) Tsunashima, K.; Kawabata, A.; Matsumiya, M.; Kodama, S.; Enomoto, R.; Sugiya, M.; Kunugi, Y. Low viscous and highly conductive phosphonium ionic liquids based on bis(fluorosulfonyl)amide anion as potential electrolytes. *Electrochem. Commun.* **2011**, *13*, 178–181.

(23) Tsunashima, K.; Sakai, Y.; Matsumiya, M. Physical and electrochemical properties of phosphonium ionic liquids derived from trimethylphosphine. *Electrochem. Commun.* **2014**, *39*, 30–33.

(24) Shimada, J.; Tsunashima, K.; Ue, M.: Iwasaki, T.; Tsuda, K.; Kuwabata. S.; Kanematsu, H.; Hirai, N.; Kogo, T.; Ogawa, A. Physical and Electrochemical Properties of Ionic Liquids Based on Quaternary Phosphonium Cations and Carboxylate Anions as Electrolytes *ECS Transactions* **2017**, *75*, 105–111.

(25) Arai, Y.; Yamauchi, Y.; Tokutomi, H.; Endo, F.; Hotta, A; Alavi, S.; Ohmura, R. Thermophysical property measurements of tetrabutylphosphonium acetate (TBPAce) ionic semiclathrate hydrate as thermal energy storage medium for general air conditioning systems, *Int. J. Refrig.* **2018**, *88*, 102–107.

(26) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G,; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr. J. A.; Peralta, J. E. ; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09 Program*; Gaussian, Inc.: Wallingford, CT, 2009.

(27) Kobori, T.; Muromachi, S.; Yamasaki, T.; Takeya, S.; Yamamoto, Y.; Alavi, S.; Ohmura, R. Phase Behavior and Structural Characterization of Ionic Clathrate Hydrate Formed with Tetra-*n*-butylphosphonium Hydroxide: Discovery of Primitive Crystal Structure. *Cryst. Growth Des.*, **2015**, *15*, 3862–3867.

(28) Muromachi, S.; Udachin, K. A.; Shin, K.; Alavi, S.; Moudrakovski, I. L.; Ohmura, R.; Ripmeester, J. A. Guest-induced symmetry lowering of an ionic clathrate material for carbon capture. *Chem. Commun.*, **2014**, *50*, 11476–11479.

(29) Muromachi, S.; Udachin, K. A.; Alavi, S.; Ohmura, R.; Ripmeester, J. A. Selective occupancy of methane by cage symmetry in TBAB ionic clathrate hydrate. *Chem. Commun.*, **2016**, *52*, 5621–5624.

(30) Besler, B. H.; Merz, Jr. K. M.; Kollman, P. A. Atomic charges derived from semiempirical methods. *J. Comp. Chem.*, **1990**, *11*, 431–439.

(31) Singh, U. C.; Kollman, P. A. An approach to computing electrostatic charges for molecules. *J. Comp. Chem.*, **1984**, *5*, 129–145.

(32) Beurskens, G.; Jeffrey, G. A.; McMullan, R. K. Polyhedral Clathrate Hydrates. VI. Lattice Type and Ion Distribution in Some New Peralkyl Ammonium, Phosphonium, and Sulfonium Salt Hydrates. *J. Chem. Phys.* **1963**, *39*, 3311–3315.

(33) Dyadin, Y. A.; Gaponenko, L. A.; Aladko, L. S.; Bogatyryova, S. V. Clathrate Hydrates of Tetrabutylammonium Carboxylates and Dicarboxylates. *J. Incl. Phenom.* **1984**, *2*, 259–266.

(34) Lin, W.; Dalmazzone, D.; Fürst, W.; Delahaye, A.; Fournaison, L.; Clain, P. Accurate DSC measurement of the phase transition temperature in the TBPB–water system. *J. Chem. Thermodynamics* **2013**, 61, 132–37.

(35) Kousksou, T.; Jamil, A.; Zeraouli, Y.; Dumas, J.P. Equilibrium liquidus temperatures of binary mixtures from differential scanning calorimetry. *Chem. Eng. Sci.* **2007**, *62*, 6516–6523.

(36) 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.

For Table of Contents Only