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Phase Equilibrium Relations for Tetra-*n*-butylphosphonium Acetate Semiclathrate Hydrate Systems in the Presence of Methane, Carbon Dioxide, Nitrogen, or Ethane

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ABSTRACT

Thermodynamic stabilities of tetra-*n*-butylphosphonium acetate (TBP-Ace) semiclathrate hydrates in the presence of methane (CH_4), carbon dioxide (CO_2), nitrogen (N_2), or ethane (C_2H_6) were measured in a pressure range up to approximately 5 MPa. The dissociation temperature of TBP-Ace+CH_4, TBP-Ace+CO_2, and TBP-Ace+N_2 semiclathrate hydrates increased drastically with an increase in pressure, which means that CH_4, CO_2, and N_2 molecules occupy the vacant cages of the TBP-Ace semiclathrate hydrate. On the other hand, the C_2H_6 molecules hardly occupied the cages, resulting in small pressure dependence of the dissociation temperature. Raman spectra and powder X-ray diffraction patterns of TBP-Ace+CO_2 semiclathrate hydrate reveal that the phase transition occurs at 1.04±0.04 MPa and 285.88±0.05 K. One of the possible reasons why the phase transition occurs is that the carbonate and/or hydrogen carbonate anions derived

from the CO_2 molecules are replaced with some of acetate anions in the TBP-Ace+CO_2 semiclathrate hydrate.

Keywords

Semiclathrate hydrate, Phase equilibria, Gas separation, Phase transition, Spectroscopy

1. Introduction

Clathrate hydrates are ice-like crystalline solids that consist of hydrogen-bonded water cages and guest molecules [1]. Generally, guest molecules have the van der Waals diameter smaller than the void of hydrate cages. Ionic guest substances having the van der Waals diameter larger than the void of hydrate cages, such as quaternary alkyl onium salts, are enclathrated in several compartment hydrate cages, known as semiclathrate hydrates or ionic clathrate hydrates [2-6]. Four alkyl chains of cations are incorporated in each compartment hydrate cage, and the counter anions replace some water molecules in hydrate frameworks [5]. The vacant pentagonal dodecahedron (5^{12}) cages exist in the hydrate lattice. Semiclathrate hydrates, therefore, have an ability to enclathrate gas molecules in 5^{12} cages selectively. Enclathrating the gas molecules in the vacant 5^{12} cages enhances the thermodynamic stability of the semiclathrate hydrate [7-13]. Taking this advantage, semiclathrate hydrates have been expected as gas storage and separation media.

Although quaternary alkyl onium salts have the ability to fine-tune the structure [14-16], almost of the researches on semiclathrate hydrates are on tetra-*n*-butylammonium halides (TBA-Halide), such as tetra-*n*-butylammonium bromide (TBAB) [2, 3], tetra-*n*-butylammonium chloride (TBAC) [17] and tetra-*n*-butylammonium fluorine (TBAF) [18]. Especially, TBAB is one of the most common guest substances for semiclathrate hydrate formation. TBAB semiclathrate hydrate has been researched for cool storage media [19], gas separation and storage media [7, 9, 10, 13, 20-24]. However, the usage of TBA-Halide often causes both unfavorable severe metal corrosion and/or environmental pollution. Therefore, the developments of halogen-free semiclathrate hydrate are inevitably required. Recently, carboxylate anions have been investigated for semiclathrate hydrate applications [25-27], because carboxylate anions have better biocompatibility than halide anions. The number of reports on semiclathrate hydrates including carboxylate anions have been recently increased. Muromachi et al.

[27] have reported the structures of carboxylate semiclathrate hydrates using an X-ray diffraction (XRD) measurement. Although ammonium semiclathrate hydrates have been reported, phosphonium salts are known to have higher thermal stability than the corresponding ammonium salts [14-16]. However, the researches on phosphonium semiclathrate hydrates have been rarely reported, expect an investigation on the phase equilibria of tetra-*n*-butylphosphonium acetate (TBP-Ace) published by Arai et al. [28]. We also have reported the phase equilibria of tetra-*n*-butylphosphonium formate (TBP-For), acetate, and lactate (TBP-Lac) semiclathrate hydrates [29].

In the present study, the thermodynamic stabilities of semiclathrate hydrates for TBP-Ace+CH_4, +CO_2, +N_2 or +C_2H_6 systems were investigated (mole fraction of TBP-Ace in the aqueous solution (x) was 0.035), as a first fundamental step to apply TBP-Ace semiclathrate hydrate to gas storage and separation media. Raman spectra and powder X-ray diffraction (PXRD) patterns were also measured to clarify why the TBP-Ace+CO_2 semiclathrate hydrate exhibits a characteristic behavior around 1 MPa.

2. Experimental section

Fig. 1 represents a schematic illustration of an experimental apparatus. The experimental instrument contained the following parts: a pressure-proof glass cell (Taiatsu Techno Co., Ltd., HPG), a pressure gauge (Valcom, VPRT, maximum uncertainty: 0.02 MPa), and a temperature control unit (Taitec, CL-80R). The inner volume and maximum working pressure of the glass cell were 10 cm^3 and 5 MPa, respectively. Temperature in the thermostatted bath was measured by a thermistor thermometer (Takara., D632, reproducibility: 0.02 K).　The maximum uncertainties of equilibrium temperature and pressure were 0.05 K and 0.02 MPa, respectively.
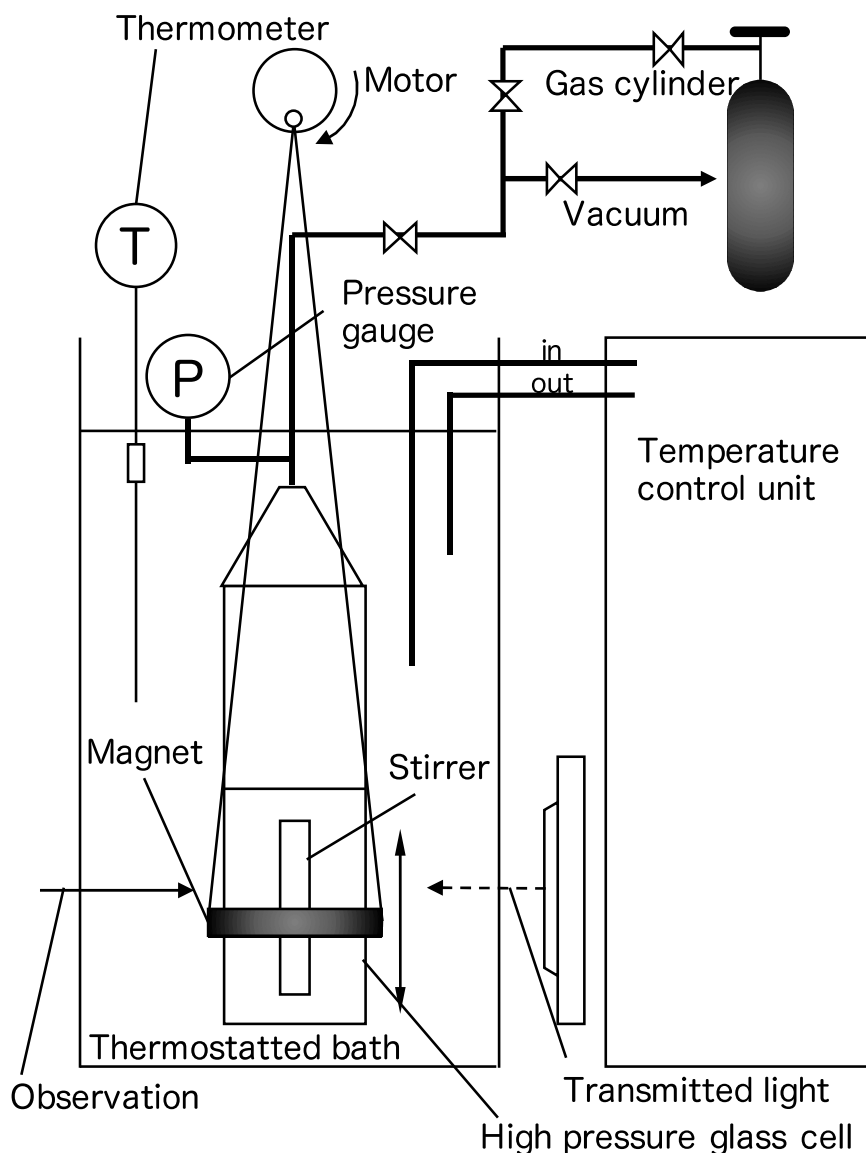
Fig. 1 Schematic illustration of the experimental apparatus.

The chemicals used in this study are listed in Table 1. TBP-Ace was synthesized by an aqueous neutralization of equimolar amounts of tetra-*n*-butylphosphonium hydroxide and acetic acid. The aqueous solution was evaporated at 308 K for 24 h. The obtained product was confirmed by ^{1}H, ^{13}C, and ^{31}P NMRs. The purity of the synthesized TBP-Ace was higher than those of tetra-*n*-butylphosphonium hydroxide (on a water free basis) and acetic acid. Majority of the impurity was tributylphosphine oxide derivatives. The impurity effect on the mass fraction purity of TBP-Ace was less than 0.01. Concentration of the recovered aqueous solution was measured by Karl Fischer titration

using a Karl Fischer moisture meter (CA-200, Mitsubishi Chemical) with an uncertainty of 0.5 %. The aqueous solution of TBP-Ace was prepared at $x = 0.035\pm0.001$ ($w = 0.380\pm0.002$) using an electric balance (A&D, GF-300). The symbols x and w represent the mole and mass fractions, respectively. The highest equilibrium temperature of TBP-Ace semiclathrate hydrate was previously reported to be 284.6 ± 0.1 K at $x = 0.035$ [29], whereas Arai et al. [28] reported that it was 284.2 K at $x = 0.031$.

Table1 List of chemicals used in the present study.

Component	Source	Purity
Tetra-*n*-butylphosphonium hydroxide	Tokyo Chemical Industry	0.402 in aqueous solution (mass fraction)
Acetic acid	Wako Pure Chemical Industries	> 0.999 (mass fraction)
Water	distilled and deionized	Resistivity is 0.46 MΩcm
Methane	Osaka Gas Liquid	0.9999
Carbon dioxide	Nippon Ekitan Corporation	0.9999
Nitrogen	Air Liquide Japan	0.999999
Ethane	Takachicho Chemical Industrial	0.999

Approximately 5 cm^3 of the TBP-Ace aqueous solution was introduced into the glass cell and sufficiently degassed with a bubbling method by each gas. The cell was immersed in a thermostatted bath, where programming temperature controller circulated the thermostatted water. Then, the solution was cooled down to 2 K lower than an expected equilibrium temperature and stirred to generate the semiclathrate hydrates. A magnetic stirrer was manipulated in a vertical direction to stir the solution. The phase behavior was straightforwardly observed. The temperature in thermostatted bath was increased very deliberately (0.1 K per step). When the last crystalline semiclathrate hydrate was dissociated, the temperature was determined as a three-phase (gas, aqueous solution and hydrate) equilibrium temperature at each pressure.

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 atmospheric pressure and 77 K. The back-

scattering was taken in with the same lens. 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}. The crystal structure of the prepared samples was analyzed by 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 CuKα X-ray (45 kV, 40 mA). The PXRD measurements were performed in the stepscan mode with scan rate of 2.7 deg./min and step size of approximately 0.02 deg. TBP-Ace+CO_2 semiclathrate hydrates were prepared at 0.83±0.05 MPa and 1.98±0.05 MPa with continuously fed with CO_2. The glass cell was moved from the bath to a cold room at 253 K. After kept there for a couple of hours, the pressure in the cell was then released and allowed to reach atmospheric pressure for Raman and PXRD analyses. Once released, the sample was kept at 77 K.

3. Results and discussion

The three-phase equilibrium relations of TBP-Ace+CH_4, TBP-Ace+CO_2, TBP-Ace+N_2, and TBP-Ace+C_2H_6 systems are listed in Tables 2-5, respectively. The symbols of p and T stand for the pressure and temperature.

Table 2 Thermodynamic stability boundary of the semiclathrate hydrate in TBP-Ace +CH$_4$ system at $x = 0.035\pm0.001$ ($w = 0.380\pm0.002$).[a]

T / K	p / MPa
284.48	0.11
284.57	0.20
284.75	0.36
284.91	0.47
285.08	0.60
285.44	0.74
286.04	0.98
286.76	1.30
287.19	1.49
287.66	1.77
288.14	2.15
288.91	2.68
289.30	3.01
289.82	3.57
290.21	4.04
290.64	4.49
290.93	4.97

[a] Standard uncertainties u are $u(p) = 0.02$ MPa, and $u(T) = 0.05$ K.

Table 3 Thermodynamic stability boundaries of the semiclathrate hydrate in TBP-Ace +CO$_2$ system at $x = 0.035\pm0.001$ ($w = 0.380\pm0.002$).[a]

T / K	p / MPa	T / K	p / MPa
284.76	0.22	286.87	1.70
285.13	0.41	287.14	2.00
285.31	0.57	287.35	2.23
285.57	0.79	287.52	2.48
285.59	0.83	287.78	2.70
285.69	0.89	287.96	3.06
285.75 [m]	1.00 [m]	288.03	3.23
285.79 [m]	1.02 [m]	288.06	3.32
285.84 [m]	1.05 [m]	288.18	3.45
285.96	1.08	288.22	3.47
285.95 [m]	1.14 [m]	288.30	3.79
285.99 [m]	1.22 [m]	288.37	4.09
286.07	1.15	288.45	4.33
286.14	1.15	288.55	4.56
286.25	1.23	288.55	4.78
286.35	1.24	288.65	4.96
286.44	1.38	288.68 [q]	5.15 [q]
286.53	1.45		

[m] metastable; [q] quadruple point of hydrate, aqueous, CO$_2$-rich liquid, gas phases.

[a] Standard uncertainties u are $u(p) = 0.02$ MPa, and $u(T) = 0.05$ K.

Table 4 Thermodynamic stability boundary of the semiclathrate hydrate in TBP-Ace +N$_2$ system at x = 0.035±0.001 (w = 0.380±0.002).[a]

T / K	p / MPa
284.35	0.10
284.45	0.18
284.54	0.44
284.63	0.69
284.76	1.06
284.84	1.29
284.94	1.50
285.04	1.89
285.14	2.24
285.23	2.58
285.33	2.91
285.53	3.49
285.73	3.99
285.83	4.39
285.91	4.77
286.01	5.05

[a] Standard uncertainties u are $u(p)$ = 0.02 MPa, and $u(T)$ = 0.05 K.

Table 5 Thermodynamic stability boundary of the semiclathrate hydrate in TBP-Ace
+C_2H_6 system at x = 0.035±0.001 (w = 0.380±0.002).[a]

T / K	p / MPa
284.38	0.11
284.36	0.23
284.39	0.49
284.46	0.75
284.51	1.01
284.62	1.34
284.67	1.49
284.71	1.78
284.75	2.00
284.78	2.21
284.83	2.47
284.85	2.70
284.94	3.07
284.95 [q]	3.15 [q]

[q] quadruple point of hydrate, aqueous, C_2H_6-rich liquid, gas phases.

[a] Standard uncertainties u are $u(p)$ = 0.02 MPa, and $u(T)$ = 0.05 K.

Fig. 2 shows the phase diagram of the semiclathrate hydrates for the TBP-Ace aqueous solution (x= 0.035) +CH_4, +CO_2, +N_2, or +C_2H_6 systems. The four-phase equilibrium points of (hydrate + aqueous + C_2H_6 (or CO_2)-rich liquid + gas phases) were located at (284.95 K, 3.15 MPa) and (288.68 K, 5.51 MPa) in the TBP-Ace+water+C_2H_6 and TBP-Ace+water+CO_2 systems, respectively. The equilibrium temperatures of TBP-Ace+N_2, TBP-Ace+CH_4 and TBP-Ace+CO_2 semiclathrate hydrates increased drastically with an increase in pressure, whereas the pressure dependence of the equilibrium temperature in the TBP-Ace+C_2H_6+water system, which is slightly larger than that of the TBAC+ C_2H_6+water system [9], was quite small. This is because the van der Waals diameter of C_2H_6 molecule is slightly larger than the void size of 5^{12} cage, resulting in low cage occupancy of C_2H_6 [6, 9]. At a pressure lower than 1.0 MPa, the equilibrium pressure-temperature relations of TBP-Ace+CH_4 and TBP-Ace+CO_2 semiclathrate hydrates

exhibit similar behavior. At a pressure higher than 1.0 MPa, the equilibrium temperature of TBP-Ace+CH$_4$ semiclathrate hydrate is much higher than that of TBP-Ace+CO$_2$ semiclathrate hydrate. The 5^{12} cage should prefer the occupancy by CH$_4$ to that by CO$_2$ because of the molecular size. These results in the present study seem to be reasonable. However, the tendency was different from that of the other semiclathrate hydrate systems, *i.e.,* TBAB, TBAC, and tetra-*n*-butylphosphonium bromide (TBPB) [7, 9, 10, 30, 31], where the CO$_2$-containing systems showed higher equilibrium temperature than that of the CH$_4$-containing systems. The different behavior in the TBP-Ace semiclathrate hydrate, as described later, would be due to the existence of carbonate (CO$_3^{2-}$) and/or hydrogen carbonate (HCO$_3^-$) anion in the TBP-Ace+CO$_2$ semiclathrate hydrate crystal.

The difference of equilibrium condition is essential to gas separation process by using semiclathrate hydrates. The results reveal that TBP-Ace semiclathrate hydrate as well as other ones could be used as gas separation media. Especially, TBP-Ace semiclathrate hydrate, not containing halide anion, would be more easily and environmental-friendly adhibited than the other ones.
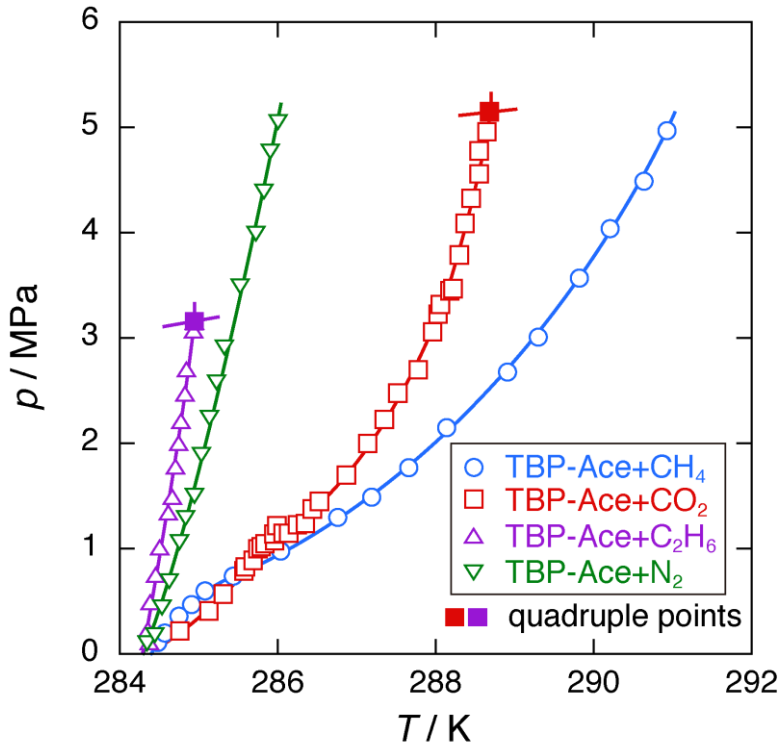

Fig. 2 Thermodynamic stability boundaries of the semiclathrate hydrates in the TBP-Ace+water+CH$_4$, +CO$_2$, +N$_2$, or +C$_2$H$_6$ systems at $x = 0.035\pm0.001$.
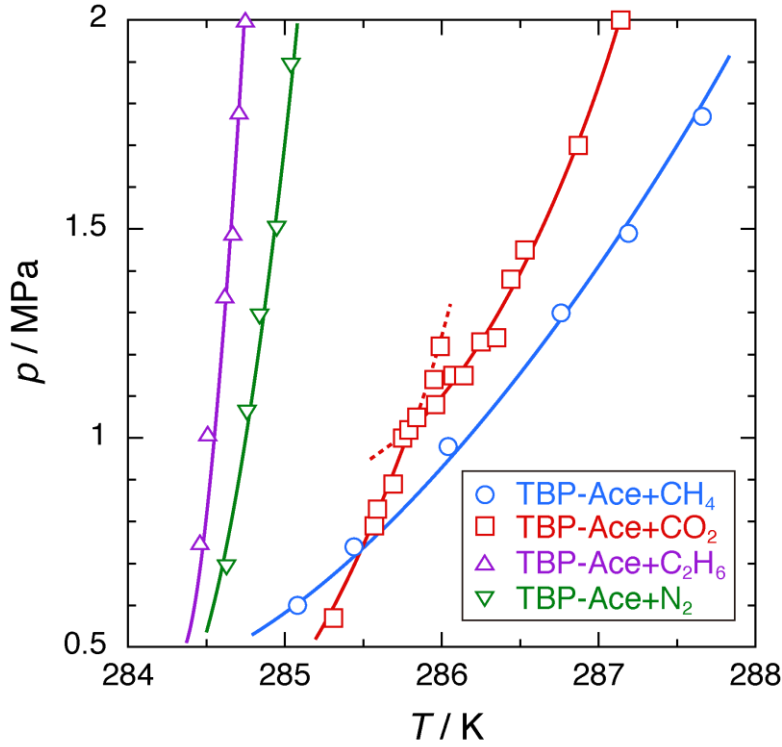
Fig. 3 Enlarged Figure 2 around 1 MPa.

In the TBP-Ace+CO_2 system, as shown in Fig. 3, the behavior considered as the existence of a structural phase transition was observed at 285.88±0.05 K and 1.04±0.04 MPa. Fig. 4 shows the Raman spectra in the TBP-Ace+CO_2 semiclathrate hydrates prepared at 1.98 MPa and 0.83 MPa. The overall changes between the spectra imply that the phase behavior around 1.04 MPa is derived from the phase transition. In both samples, the Fermi resonance peaks (highlighted in orange) corresponding to the CO_2 molecules in the 5^{12} cage were detected at 1276 cm^{-1} and 1380 cm^{-1}, which agree well with those of the structure II CO_2+cyclopropane clathrate hydrate [32] and TBAF+CO_2 semiclathrate hydrate [33]. The peak intensities of CO_2 in the sample prepared at 1.98 MPa are stronger than those of 0.83 MPa, which means that the cage occupancy of CO_2 molecules increases with an increase in pressure. The solubility of CO_2 in water also increased with an increase in pressure, so that the concentration of CO_3^{2-} and/or HCO_3^- anions in the aqueous solution increased. There are three Raman-active bonds (highlighted in blue) derived from CO_3^{2-} [34, 35] and HCO_3^- [36]. The carboxy group (COO$^-$) has six main Raman-active bonds (highlighted in green) [37, 38].

Comparing these bands between two spectra, the peak intensities of both anions derived from CO_2 seem to increase with an increase in pressure, whereas the intensities of carboxy group seem to decrease. These results imply that several CO_3^{2-} and/or HCO_3^- anions are replaced with acetate anion in the TBP-Ace+CO_2 semiclathrate hydrate because of chemical equilibrium between CO_3^{2-}, HCO_3^-, and acetate anions. The highest equilibrium temperatures of $(TBA)_2$-CO_3 (291.5 K) [39] and TBA-HCO_3 (291.0 K) [40] semiclathrate hydrates are higher than that (288.0 K) of TBA-acetate one [27].
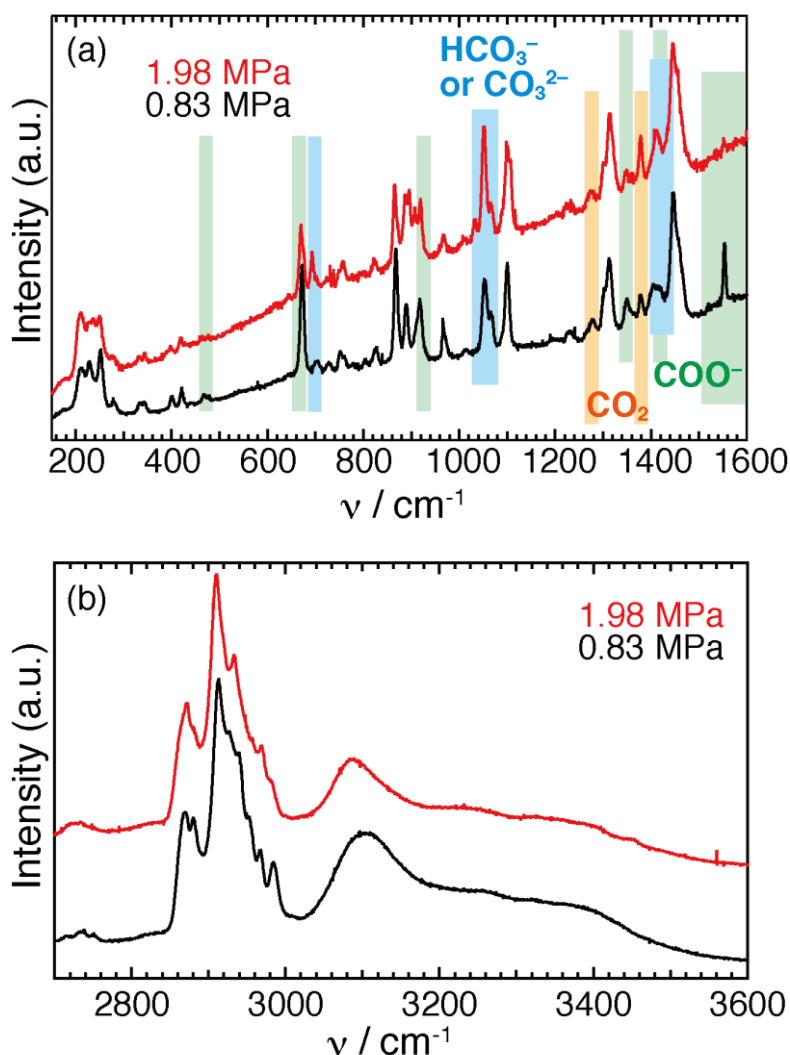
Fig. 4 Raman spectra ((a) 150-1600 cm^{-1}; (b) 2700-3600 cm^{-1}) of TBP-Ace+CO_2 semiclathrate hydrates prepared at 1.98 MPa (upper, red) and 0.83 MPa (lower, black). The spectra were recorded at 0.1 MPa and 77 K. The regions highlighted in orange, blue, and green represent typical peak positions derived from CO_2 [32, 33], carbonate [34, 35] or hydrogen carbonate anion [36], and carboxy group [37, 38], respectively.

PXRD patterns of the TBP-Ace+CO_2 semiclathrate hydrates prepared at 0.83 MPa and 1.98 MPa as well as the simple TBP-Ace one are shown in Fig. 5. PXRD patterns of the simple TBP-Ace semiclathrate hydrate and the TBP-Ace+CO_2 one prepared at 0.83 MPa were roughly fitted with a tetragonal structure of ($a = 2.353\pm0.002$ nm, $c = 1.242\pm0.001$ nm at 150 K) and ($a = 2.350\pm0.001$ nm, $c = 1.240\pm0.001$ nm at 150 K), respectively, whereas the pattern of the TBP-Ace+CO_2 one prepared at 1.98 MPa was apparently different from others. The former two are similar to the unit lattice of the TBA-acetate semiclathrate hydrate reported by McMullan and Jeffrey ($a = 2.362$ nm, $c = 1.238$ nm at 253 K) [40] and Dyadin et al. ($a = 2.36$ nm, $c = 1.22$ nm at 263 K) [41]. The PXRD results also support the existence of the phase transition around 1 MPa.
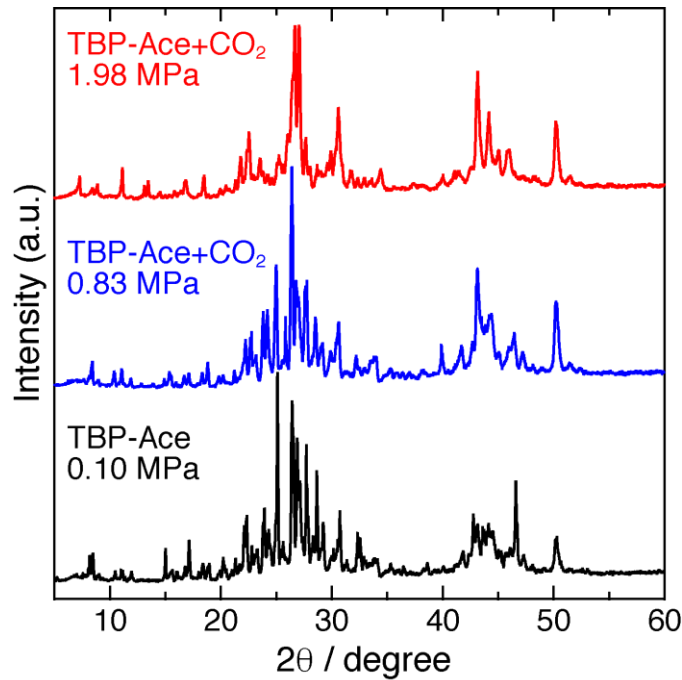

Fig. 5 PXRD patterns of TBP-Ace+CO_2 semiclathrate hydrates prepared at 1.98 MPa (top) and 0.83 MPa (middle) and simple TBP-Ace semiclathrate hydrate (bottom). All the patterns were recorded at 150 K and atmospheric pressure.

4. Conclusion

The thermodynamic stabilities of TBP-Ace aqueous solution +CH_4, +CO_2, +N_2, or +C_2H_6 systems were investigated. The CH_4, CO_2, and N_2 molecules are enclathrated in the 5^{12} cage of the TBP-Ace semiclathrate hydrate. The phase equilibrium temperatures

of TBP-Ace+CH$_4$, TBP-Ace+CO$_2$, and TBP-Ace+N$_2$ semiclathrate hydrate systems drastically increased with an increase in pressure. Especially, the increasing amount of temperature in the TBP-Ace+CH$_4$ semiclathrate hydrate system was the largest of four systems measured in the present study. The results imply that the TBP-Ace semiclathrate hydrate would be regarded as a possible gas separation medium in the CH$_4$+CO$_2$ (only above 1 MPa), CO$_2$+N$_2$, CH$_4$+N$_2$, CO$_2$+C$_2$H$_6$, and CH$_4$+C$_2$H$_6$ gas mixtures.

The phase behavior, Raman spectra, and PXRD patterns in the TBP-Ace+CO$_2$ semiclathrate hydrate reveal that the phase transition occurs at 1.04±0.04 MPa and 285.88±0.05 K. The Raman spectrum indicates that the anions derived from CO$_2$ are included in the TBP-Ace+CO$_2$ semiclathrate hydrate. The carbonate (CO$_3^{2-}$) and/or hydrogen carbonate (HCO$_3^-$) anions are partially replaced with acetate anion and the semiclathrate hydrate formed in the TBP-Ace+CO$_2$+water system would be an anion-mixed TBP-(Ace)$_{1-(2y+z)}$(CO$_3^{2-}$)$_y$(HCO$_3^-$)$_z$+CO$_2$ semiclathrate hydrate.

References

[1] E. D. Sloan, C. A. Koh, Clathrate Hydrates of Natural Gases, 3rd ed., Taylor & Francis, New York, 2008.

[2] Y. A. Dyadin, K. A. Udachin, Clathrate Polyhydrates of Peralkylonium Salts and Their Analogs, Journal of Structure Chemical 28 (1987) 394-432. https://doi.org/10.1007/BF00753818.

[3] H. Oyama, W. Shimada, T. Ebinuma, Y. Kamata, S. Takeya, T. Uchida, J. Nagao, H. Narita, Phase diagram, latent heat, and specific heat of TBAB semiclathrate hydrate crystals, Fluid Phase Equilib. 234 (2005) 131-135. https://doi.org/10.1016/j.fluid.2005.06.005.

[4] W. Shimada, T. Ebinuma, H. Oyama, Y. Kamata, H. Narita, Free-growth forms and growth kinetics of tetra-*n*-butylammonium bromide semi-clathrate hydrate crystals, J. Cryst. Growth 274 (2005) 246-250. https://doi.org/10.1016/j.jcrysgro.2004.09.071.

[5] W. Shimada, M. Shiro, H. Kondo, S. Takeya, H. Oyama, T. Ebinuma, H. Narita, Tetra-*n*-butylammonium bromide water (1/38) Acta Crystallogr. Sect. C 61 (2005) 65-66. https://doi.org/10.1107/S0108270104032743.

[6] T. Kobori, S. Muromachi, T. Yamasaki, S. Takeya, Y. Yamamoto, S. Alavi, R. Ohmura, Phase Behavior and Structural Characterization of Ionic Clathrate Hydrate Formed with Tetra-*n*-butylphosphonium Hydroxide: Discovery of Primitive Crystal Structure, Cryst. Growth Design 57 (2015) 171-174. https://doi.org/10.1021/acs.cgd.5b00484.

[7] W. Shimada, T. Ebinuma, H. Oyama, Y. Kamata, S. Takeya, T. Uchida, J. Nagao, H. Narita, Separation of Gas Molecule Using Tetra-*n*-butyl Ammonium Bromide Semi-Clathrate Hydrate Crystals, Jpn. J. Appl. Phys 42 (2003) 129-131. https://doi.org/10.1143/JJAP.42.L129.

[8] J. Sakamoto, S. Hashimoto, T. Tsuda, T. Sugahara, Y. Inoue, K. Ohgaki, Thermodynamic and Raman spectroscopic studies on hydrogen+tetra-*n*-butyl ammonium fluoride semi-clathrate hydrates, Chem. Eng. Sci. 63 (2008) 5789-5794. https://doi.org/10.1016/j.ces.2008.08.026.

[9] T. Makino, T. Yamamoto, K. Nagata, H. Sakamoto, S. Hashimoto, T. Sugahara, K. Ohgaki, Thermodynamic Stabilities of Tetra-*n*-butyl Ammonium Chloride + H_2, N_2, CH_4, CO_2, or C_2H_6 Semiclathrate Hydrate Systems, J. Chem. Eng. Data 55 (2010) 839-841. https://doi.org/10.1021/je9004883.

[10] A. Mohammadi, M. Manteghian, A. H. Mohammadi, Dissociation Data of Semiclathrate Hydrates for the Systems of Tetra-*n*-butylammonium Fluoride (TBAF) + Methane + Water, TBAF + Carbon Dioxide + Water, and TBAF + Nitrogen + Water, J. Chem. Eng. Data 58 (2013) 3545-3550. https://doi.org/10.1021/je4008519.

[11] A. Fukumoto, L. P. S. Silva, P. Paricaud, D. Dalmazzone, W. Furst, Modeling of the dissociation conditions of H_2 + CO_2 semiclathrate hydrate formed with TBAB, TBAC, TBAF, TBPB, and $TBNO_3$ salts. Application to CO_2 capture from syngas, Int. J. Hydrogen Energy 40 (2015) 9254-9266. https://doi.org/10.1016/j.ijhydene.2015.05.139.

[12] S. Muromachi, S. Takeya, Gas-containing semiclathrate hydrate formation by tetra-*n*-butylammonium carboxylates: Acrylate and butyrate, Fluid Phase Equilib. 441 (2017) 59-63. https://doi.org/10.1016/j.fluid.2017.01.008.

[13] T. Sugahara, H. Machida, Dissociation and Nucleation of Tetra-*n*-butyl Ammonium Bromide Semi-Clathrate Hydrates at High Pressures, J. Chem. Eng. Data 62 (2017) 2721-2725. https://doi.org/10.1021/acs.jced.7b00115.

[14] K. Tsunashima, E. Niwa, S. Kodama, M. Sugiya, and Y. Ono, Thermal and Transport Properties of Ionic Liquids Based on Benzyl-Substituted Phosphonium Cations, J. Phys. Chem. B 113 (2009) 15870-15874. https://doi.org/10.1021/jp908356c.

[15] K. Tsunashima, S. Kodama, M. Sugiya, Y. Kunugi, Physical and electrochemical properties of room-temperature dicyanamide ionic liquids based on quaternary phosphonium cations, Electrochimica Acta 56 (2010) 762-766. https://doi.org/10.1016/j.electacta.2010.08.106.

[16] J. Shimada, K. Tsunashima, M. Ue, K. Iwasaki, T. Tsuda S. Kuwabata, H. Kanematsu, N.Hirai, T. Kogo, A. Ogawa, Physical and Electrochemical Properties of Ionic Liquids Based on Quaternary Phosphonium Cations and Carboxylate Anions as Electrolytes, ECS Transactions 75 (2017) 105-111. https://doi.org/10.1149/07552.0105ecst.

[17] Z.-G. Sun, C.-G. Liu, B. Zhou, L.-Z. Xu, Phase Equilibrium and Latent Heat of Tetra-*n*-butylammonium Chloride Semi-Clathrate Hydrate, J. Chem. Eng. Data 56 (2011) 3416-3418. https://doi.org/10.1021/je2004116.

[18] V. Y. Komarov, T. V. Rodionova, I. S. Terekhova, N. V. Kuratieva, The Cubic Superstructure-I of Tetrabutylammonium Fluoride $(C_4H_9)_4NF \cdot 29.7H_2O$ Clathrate Hydrate, J. Incl. Phenom. Macrrocycl. Chem. 59 (2007) 11-15. https://doi.org/10.1007/s10847-006-9151-9.

[19] H. Ogoshi, S. Takao, Air-Conditioning System Using Clathrate Hydrate Slurry, JFE TECHNICAL REPORT 3 (2004) 1-5.

[20] Y. Kamata, H. Oyama, W. Shimada, T. Ebinuma, S. Takeya, T. Uchida, J. Nagao, H. Narita, Gas Separation Method Using Tetra-*n*-butyl Ammonium Bromide Semi-Clathrate Hydrate, Jpn. J. Appl. Phys. 43 (2004) 362-365. https://doi.org/10.1143/JJAP.43.362.

[21] Y. Kamata, Y. Yamakoshi, T. Ebinuma, H. Oyama, W. Shimada, H. Narita, Hydrogen Sulfide Separation Using Tetra-*n*-butyl Ammonium Bromide Semi-clathrate (TBAB) Hydrate, Energy & Fuels 19 (2005) 1717-1722. https://doi.org/10.1021/ef0497098.

[22] M. Arjmandi, A. Chapoy, and B. Tohidi, Equilibrium Data of Hydrogen, Methane, Nitrogen, Carbon Dioxide, and Natural Gas in Semi-Clathrate Hydrates of Tetrabutyl Ammonium Bromide, J. Chem. Eng. Data 52 (2007) 2153-2158. https://doi.org/10.1021/je700144p.

[23] S. Hashimoto, T. Sugahara, M. Moritoki, H. Sato, K. Ohgaki, Thermodynamic stability of hydrogen + tetra-*n*-butyl ammonium bromide mixed gas hydrate in nonstoichiometric aqueous solutions, Chem. Eng. Sci. 63 (2008) 1092-1097. https://doi.org/10.1016/j.ces.2007.11.001.

[24] J. Deschamps, D. Dalmazzone, Dissociation enthalpies and phase equilibrium for TBAB semi-clathrate hydrates of N_2, CO_2, $N_2 + CO_2$ and $CH_4 + CO_2$, J. Therm. Anal. Calorim. 98 (2009) 113–118. https://doi.org/10.1007/s10973-009-0399-3.

[25] H. Nakayama and K. Watanabe, Hydrates of Organic Compounds. III. The Formation of Clathrate-like Hydrate of Tetrabutylammonium Dicarboxylates, Bull. Chem. Soc. Jpn. 51 (1978) 2518-2522. https://doi.org/10.1246/bcsj.51.2518.

[26] H. Nakayama, S. Torigata, Hydrates of Organic Compounds. VIII. The Effect of Carboxylate Anions on the Formation of Clathrate Hydrates of Tetrabutylammonium Carboxylates, Bull. Chem. Soc. Jpn. 57 (1984) 171-174. https://doi.org/10.1246/bcsj.57.171.

[27] S. Muromachi, M. Kida, S. Takeya, Y. Yamamoto, R. Ohmura, Characterization of the ionic clathrate hydrate of tetra-n-butylammonium acrylate, Can. J. Chem 93 (2015) 954-959. https://doi.org/10.1139/cjc-2014-0539.

[28] Y. Arai, Y. Yamauchi, H. Tokutomi, F. Endo, A. Hotta, S. Alavi, R. Ohmura, Thermophysical property measurements of tetrabutylphosphonium acetate (TBPAce) ionic semiclathrate hydrate as thermal energy storage medium for general air conditioning systems, Int. J. Refrigeration 88 (2018) 102-107. https://doi.org/10.1016/j.ijrefrig.2017.12.020.

[29] J. Shimada, M. Shimada, T. Sugahara, K. Tsunashima, A. Tani, Y. Tsuchida, M. Matsumiya, Phase Equilibrium Relations of Semiclathrate Hydrates Based on Tetra-*n*-butylphosphonium Formate, Acetate, and Lactate, J. Chem. Eng. Data 63 (2018) 3615-3620. https://doi.org/10.1021/acs.jced.8b00481.

[30] S. Lee, S. Park, Y. Lee, J. Lee, H. Lee, Y. Seo, Guest Gas Enclathration in Semiclathrates of Tetra-*n*-butylammonium Bromide: Stability Condition and Spectroscopic Analysis, Langmuir 27 (2011) 10597-10603. https://doi.org/10.1021/la202143t.

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

http://dx.doi.org/10.1016/j.fluid.2013.01.018.

[32] T. Makino, Y. Ogura, Y. Matsui, T. Sugahara, K. Ohgaki, Isothermal phase equilibria and structural phase transition in the carbon dioxide + cyclopropane mixed-gas hydrate system, Fluid Phase Equilib. 284 (2009) 19-25. https://doi.org/10.1016/j.fluid.2009.05.020.

[33] S. Lee, Y. Lee, S. Park, Y. Kim, J. D. Lee, Y. Seo, Thermodynamic and Spectroscopic Identification of Guest Gas Enclathration in the Double Tetra-*n*-butylammonium Fluoride Semiclathrates, J. Phys. Chem. B 116 (2012) 9075-9081. https://doi.org/10.1021/jp302647c.

[34] S. M.-Ramirez, S. S.-Cortes, J.V. G.-Ramos, C. Domingo, C. Fortes, M.T. B.-Varela, Micro-Raman spectroscopy applied to depth profiles of carbonates formed in lime mortar, Cem. Concr. Res. 33 (2003) 2063-2068. https://doi.org/10.1016/S0008-8846(03)00227-8.

[35] J. Wu, S Wang, H. Zheng, The influence of ionic strength on carbonate-based spectroscopic barometry for aqueous fluids: an *in-situ* Raman study on Na_2CO_3-NaCl solutions, Sci. Rep. 6 (2016) 1-9. https://doi.org/10.1038/srep39088.

[36] J. D. Frantz, Raman spectra of potassium carbonate and bicarbonate aqueous fluids at elevated temperatures and pressures: comparison with theoretical simulations, Chem. Geolo. 152 (1998) 211-225. https://doi.org/10.1016/S0009-2541(98)00058-8.

[37] D. W. Mayo, F. A. Miller, R. W. Hannah, Course Notes on the Interpretation of Infrared and Raman Spectra, John Wiley & Sons, Inc., Hoboken, New Jersey, 2004. https://doi.org/10.1002/0471690082.

[38] H. Noma, Y. Miwa, I. Yokoyama, K. Machida, Infrared and Raman Intensity Parameters of Sodium Acetate and Their Intensity Distributions, J. Mol. Struct. 242 (1991) 207-219. https://doi.org/10.1016/0022-2860(91)87136-6.

[39] H. Nakayama, Hydrates of Organic Compounds. VII. The Effect of Anions on the Formation of Clathrate Hydrate of Tetrabutylammonium Salts, Bull. Chem. Soc. Jpn. 56 (1983) 877-800. https://doi.org/10.1246/bcsj.56.877.

[40] R. McMullan, G. A. Jeffrey, Hydrates of the Tetra *n*-butyl and Tetra *i*-amyl Quaternary Ammonium Salts, J. Chem. Phys. 31 (1959) 1231–1234. https://doi.org/10.1063/1.1730574.

[41] Y. A. Dyadin, L. A. Gaponenko, L. S. Aladko, S. V. Bogatyryova, Clathrate Hydrates of Tetrabutylammonium Carboxylates and Dicarboxylates, J. Incl. Phenom. 2 (1984)

259–266. https://doi.org/10.1007/BF00663264.

Graphic Abstract