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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 (CH₄), carbon dioxide (CO₂), nitrogen (N₂), or ethane (C₂H₆) were measured in a pressure range up to approximately 5 MPa. The dissociation temperature of TBP-Ace+CH₄, TBP-Ace+CO₂, and TBP-Ace+N₂ semiclathrate hydrates increased drastically with an increase in pressure, which means that CH₄, CO₂, and N₂ molecules occupy the vacant cages of the TBP-Ace semiclathrate hydrate. On the other hand, the C₂H₆ 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+CO₂ 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 CO₂ molecules are replaced with some of acetate anions in the TBP-Ace+CO₂ 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, except 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+CH₄, +CO₂, +N₂ or +C₂H₆ 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+CO₂ 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 cm³ 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.

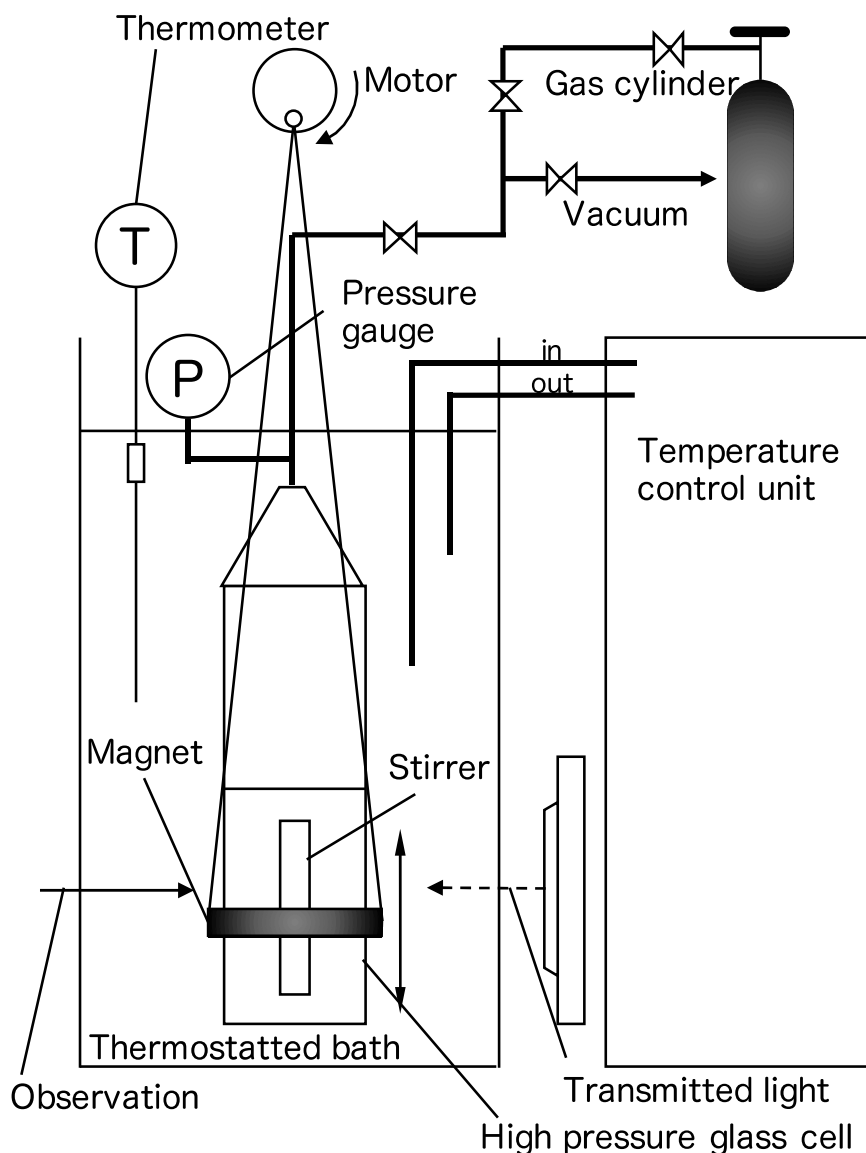


Fig. 1 Schematic illustration of the experimental apparatus.

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 ^1H , ^{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 $x = 0.035 \pm 0.001$ ($w = 0.380 \pm 0.002$) 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- <i>n</i> -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 cm³ 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 $\text{CuK}\alpha$ 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 $0.83\pm 0.05 \text{ MPa}$ and $1.98\pm 0.05 \text{ MPa}$ 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
+CH₄ system at $x = 0.035 \pm 0.001$ ($w = 0.380 \pm 0.002$).^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 +CO₂ system at $x = 0.035 \pm 0.001$ ($w = 0.380 \pm 0.002$).^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, CO₂-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
 +N₂ system at $x = 0.035 \pm 0.001$ ($w = 0.380 \pm 0.002$).^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 +C₂H₆ system at $x = 0.035 \pm 0.001$ ($w = 0.380 \pm 0.002$).^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, C₂H₆-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 ($x= 0.035$) +CH₄, +CO₂, +N₂, or +C₂H₆ systems. The four-phase equilibrium points of (hydrate + aqueous + C₂H₆ (or CO₂)-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+C₂H₆ and TBP-Ace+water+CO₂ systems, respectively. The equilibrium temperatures of TBP-Ace+N₂, TBP-Ace+CH₄ and TBP-Ace+CO₂ semiclathrate hydrates increased drastically with an increase in pressure, whereas the pressure dependence of the equilibrium temperature in the TBP-Ace+C₂H₆+water system, which is slightly larger than that of the TBAC+C₂H₆+water system [9], was quite small. This is because the van der Waals diameter of C₂H₆ molecule is slightly larger than the void size of 5¹² cage, resulting in low cage occupancy of C₂H₆ [6, 9]. At a pressure lower than 1.0 MPa, the equilibrium pressure-temperature relations of TBP-Ace+CH₄ and TBP-Ace+CO₂ semiclathrate hydrates

exhibit similar behavior. At a pressure higher than 1.0 MPa, the equilibrium temperature of TBP-Ace+CH₄ semiclathrate hydrate is much higher than that of TBP-Ace+CO₂ semiclathrate hydrate. The 5¹² cage should prefer the occupancy by CH₄ to that by CO₂ 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 CO₂-containing systems showed higher equilibrium temperature than that of the CH₄-containing systems. The different behavior in the TBP-Ace semiclathrate hydrate, as described later, would be due to the existence of carbonate (CO₃²⁻) and/or hydrogen carbonate (HCO₃⁻) anion in the TBP-Ace+CO₂ 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.

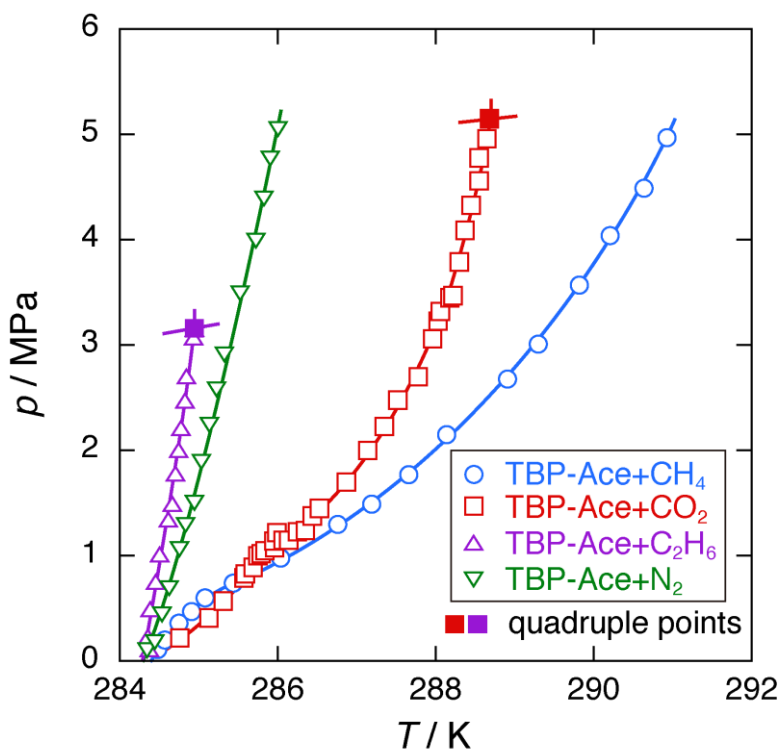


Fig. 2 Thermodynamic stability boundaries of the semiclathrate hydrates in the TBP-Ace+water+CH₄, +CO₂, +N₂, or +C₂H₆ systems at $x = 0.035 \pm 0.001$.

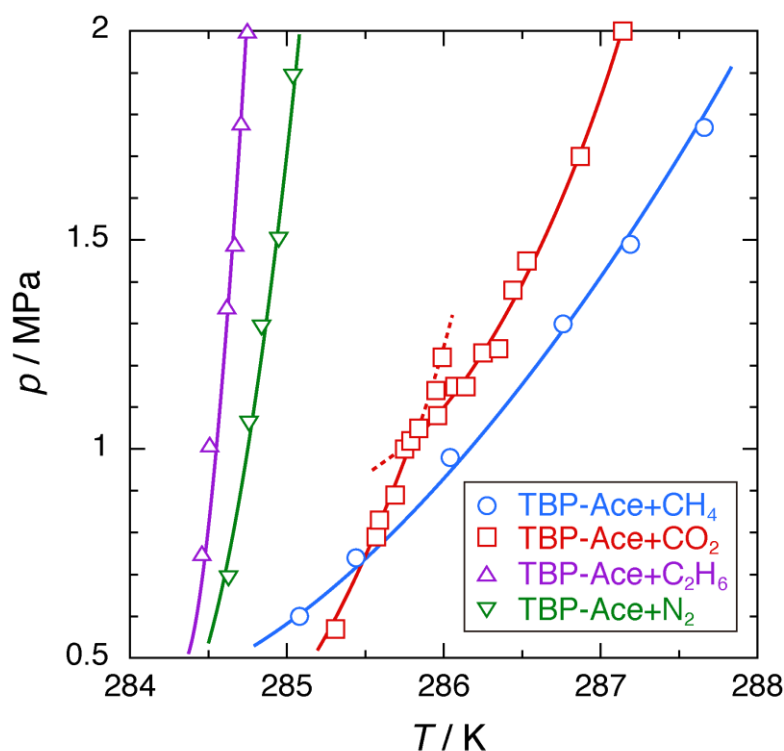


Fig. 3 Enlarged Figure 2 around 1 MPa.

In the TBP-Ace+CO₂ 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+CO₂ 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 CO₂ molecules in the 5¹² cage were detected at 1276 cm⁻¹ and 1380 cm⁻¹, which agree well with those of the structure II CO₂+cyclopropane clathrate hydrate [32] and TBAF+CO₂ semiclathrate hydrate [33]. The peak intensities of CO₂ in the sample prepared at 1.98 MPa are stronger than those of 0.83 MPa, which means that the cage occupancy of CO₂ molecules increases with an increase in pressure. The solubility of CO₂ in water also increased with an increase in pressure, so that the concentration of CO₃²⁻ and/or HCO₃⁻ anions in the aqueous solution increased. There are three Raman-active bonds (highlighted in blue) derived from CO₃²⁻ [34, 35] and HCO₃⁻ [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 $(\text{TBA})_2\text{-CO}_3$ (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].

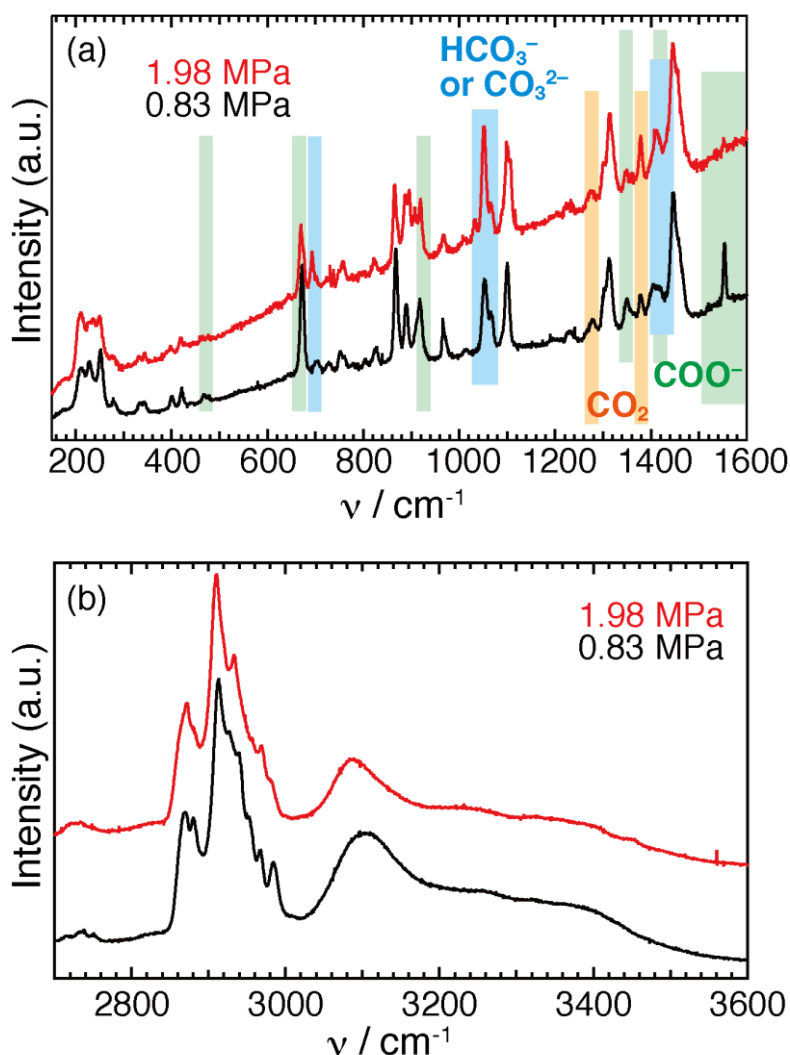


Fig. 4 Raman spectra ((a) 150-1600 cm^{-1} ; (b) 2700-3600 cm^{-1}) of TBP-Ace+ CO_2 semiclathrate hydrates prepared at 1.98 MPa (upper, red) and 0.83 MPa (lower, black). The spectra were recorded at 0.1 MPa and 77 K. The regions highlighted in orange, blue, and green represent typical peak positions 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+CO₂ 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+CO₂ one prepared at 0.83 MPa were roughly fitted with a tetragonal structure of ($a = 2.353 \pm 0.002$ nm, $c = 1.242 \pm 0.001$ nm at 150 K) and ($a = 2.350 \pm 0.001$ nm, $c = 1.240 \pm 0.001$ nm at 150 K), respectively, whereas the pattern of the TBP-Ace+CO₂ 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.

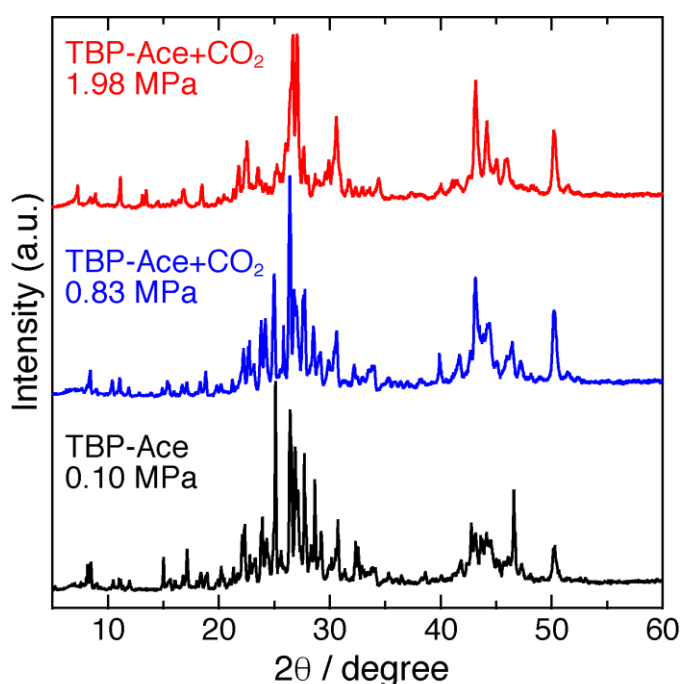


Fig. 5 PXRD patterns of TBP-Ace+CO₂ semiclathrate hydrates prepared at 1.98 MPa (top) and 0.83 MPa (middle) and simple TBP-Ace semiclathrate hydrate (bottom). All the patterns were recorded at 150 K and atmospheric pressure.

4. Conclusion

The thermodynamic stabilities of TBP-Ace aqueous solution +CH₄, +CO₂, +N₂, or +C₂H₆ systems were investigated. The CH₄, CO₂, and N₂ molecules are enclathrated in the 5¹² cage of the TBP-Ace semiclathrate hydrate. The phase equilibrium temperatures

of TBP-Ace+CH₄, TBP-Ace+CO₂, and TBP-Ace+N₂ semiclathrate hydrate systems drastically increased with an increase in pressure. Especially, the increasing amount of temperature in the TBP-Ace+CH₄ 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 CH₄+CO₂ (only above 1 MPa), CO₂+N₂, CH₄+N₂, CO₂+C₂H₆, and CH₄+C₂H₆ gas mixtures.

The phase behavior, Raman spectra, and PXRD patterns in the TBP-Ace+CO₂ 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 CO₂ are included in the TBP-Ace+CO₂ semiclathrate hydrate. The carbonate (CO₃²⁻) and/or hydrogen carbonate (HCO₃⁻) anions are partially replaced with acetate anion and the semiclathrate hydrate formed in the TBP-Ace+CO₂+water system would be an anion-mixed TBP-(Ace)_{1-(2y+z)}(CO₃²⁻)_y(HCO₃⁻)_z+CO₂ semiclathrate hydrate.

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Graphic Abstract

