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Note	

Dissociation and Nucleation of Tetra-*n*-Butyl Ammonium Bromide Semi-Clathrate Hydrates at High Pressures

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ABSTRACT: The equilibrium pressure–temperature relations of the tetra-*n*-butyl ammonium bromide (TBAB) semi-clathrate hydrate were measured at pressures up to 80 MPa by the high-pressure differential scanning calorimetry. As a pressurizing medium, tetrafluoromethane (CF_4), which cannot occupy any hydrate cages in the TBAB semi-clathrate hydrate at the present experimental pressures, was used. The dissociation temperature of tetragonal TBAB semi-clathrate hydrate ($TBAB\cdot 26H_2O$) increases with the increase in pressure, while the dissociation enthalpy is (192±3) $J\cdot g^{-1}$ and almost constant at pressures up to 80 MPa. The temperature difference between formation and dissociation at the same pressure, that is, the maximum allowable degree of supercooling, is (17.7±0.7) K and independent of the pressure.

KEYWORDS. Gas hydrate; Phase equilibria; Enthalpy; Calorimetry; Nucleation

1. INTRODUCTION

Gas hydrate or clathrate hydrate is a crystalline solid that consists of the host framework of hydrogen-bonded water molecules and the guest molecules in the void (cage) of the framework. There are some hydrate unit-cells formed by the combination of several different-shaped cages, for example, structure-I (sI) consists of 2 small cages (dodecahedron, 5^{12}) and 6 middle cages (tetrakaidecahedron, $5^{12}6^{2}$).[1] The enclathration of guest species stabilizes the hydrate structure.

Among clathrate hydrates, the hydrate formed from tetra-*n*-butyl ammonium salt aqueous solutions has been known well as a semi-clathrate hydrate where the quaternary ammonium cation and anion are incorporated with the water molecules to construct the hydrate framework.[2–6] Tetra-*n*-butyl ammonium bromide (TBAB) is one of the most famous semi-clathrate hydrate formers. Aladko *et al.*[3] have reported the existence of crystals with various hydration numbers for pure TBAB hydrate: TBAB·24H_2O, TBAB·26H_2O, TBAB·32H_2O, and TBAB·36H_2O. Other researchers[4,7-10] have reported that there are two TBAB hydrates, that is, the hydration numbers are 26 and 38. The ideal unit cells of TBAB·26H_2O and TBAB·38H_2O consist of 10(5^{12}-cages)+16($5^{12}6^{2}$-cages)+4($5^{12}6^{3}$-cages) and 6(5^{12}-cages)+4($5^{12}6^{2}$-cages)+4($5^{12}6^{3}$-cages), respectively, where $5^{12}6^{3}$-cage stands for the pentakaidecahedron. Recently, Rodionova *et al.*[6] demonstrated that the structural variety of the TBAB semi-clathrate hydrate results from the difference in the way of including bromide anions and arranging tetra-*n*-butyl ammonium cations.

TBAB semi-clathrate hydrate has a potential as a cold storage material for air conditioning[6,8,11,12] as well as a thermodynamic hydrate promoter of hydrogen storage,[9,13-18] gas absorption[18–22], and gas separation[18,19,23–27]. In the case of the TBAB mixed semi-clathrate hydrates enclathrating hydrogen (H_2)[15], krypton (Kr)[22], or xenon (Xe)[20], it has been reported that the structural phase transition occurs at high pressures. Also in the argon+TBAB mixed semi-clathrate hydrate system, the phase behavior implies the existence of the structural phase transition, although the authors did not state it.[21] The structural phase transition of TBAB semi-clathrate hydrate implies that the semi-clathrate hydrate structure is relatively soft and easily disordered. And the difference of the chemical potential between stable and metastable phases is relatively small. To elucidate why the structural variety of the TBAB semi-clathrate hydrate occurs and to solve why the large supercooling is required for the nucleation of the TBAB semi-clathrate hydrate, it is necessary to investigate the thermodynamic stability of TBAB semi-clathrate hydrate itself in a high-pressure region. In the present study, we investigated the phase equilibrium relation as well as the nucleation behavior of the TBAB semi-clathrate hydrate at high pressures up to 80 MPa by high-pressure micro-differential scanning calorimeter (microDSC).

2. EXPERIMENTAL SECTION

Materials used in the present study are summarized in Table 1. All of them were used without further purification.

The microDSC (Setaram, μDSC VII evo) with the high-pressure cells (maximum working pressure, 100 MPa) was used to investigate the thermodynamic stability and dissociation enthalpy of TBAB semi-clathrate hydrate at pressures up to 80 MPa. These DSC cells were connected with the pressure control apparatus and purged and pressurized to a given pressure with gases. The TBAB aqueous solution with the mole fraction $x_{\mathrm{TBAB}} = 0.0356 \pm 0.0003$ (the mass fraction $w_{\mathrm{TBAB}} = 0.398 \pm 0.002$) was prepared with the electric balance (Shimadzu, BL-220H).

The TBAB concentration is slightly smaller or larger than the stoichiometric concentration of the tetragonal TBAB semi-clathrate hydrate (TBAB·26H_2O) reported by ref 8 (w_{TBAB} = 0.40) and ref 6 (0.404±0.004) or ref 12 (0.35 to 0.37), respectively.

Approximately 20 mg of the prepared TBAB aqueous solution was loaded into the DSC cell by microsyringe (Hamilton, 80400). The precise sample mass of the loaded TBAB aqueous solutions was measured with the electric balance (A&D, BM-22) with the uncertainty of 0.02 mg. The air dissolved in the solution was purged with CF_4 three times. After CF_4 was introduced into both the sample and reference cells of DSC simultaneously to the desired pressure, the furnace temperature was decreased to 258.2 K at the cooling rate of 0.5 K/min. The temperature was held at 258.2 K for 10 min and then increased to 295.2 K at the heating rate of 0.1 K/min. When the dissociation temperature is determined with DSC, the effect of the heating rate may be unable to be ignored. The heating rate was slower than the cooling rate to minimize its effect. To confirm the effect, the dissociation temperatures at 0.1 MPa with the heating rate of 0.05 K/min and 0.1 K/min were compared. The obtained results agreed within the uncertainty of the temperature measurement. The pressure was measured with the pressure gauge (Valcom, VPRT, maximum uncertainty: 0.4 MPa). The pressure fluctuation caused by the temperature ramping was within the uncertainty of the pressure gauge.

We calibrate the microDSC with a dedicated Joule heat calibrator (Setaram, EJ3). In addition, the water was adopted as a reference. The uncertainty of the dissociation enthalpy is less than 2 $J\cdot g^{-1}$.

In the present study, we adopted tetrafluoromethane (CF_4) as a pressurizing medium. The CF_4 molecule, an sI clathrate hydrate former[1], does not occupy 5^{12}-cages of the sI CF_4 hydrate at pressures below 70 MPa.[28] In addition, the vapor-liquid critical temperature of CF_4 is 227.6 K.[29]

That is, CF_4 itself has no phase transition in the present experimental temperature range of (258.2 to 295.2) K. We believe that CF_4 is one of the best pressurizing media for the investigation of pressure effect in the semi-clathrate hydrate systems having vacant 5^{12}-cages. Only disadvantage of the CF_4 usage would be the solubility of CF_4 to the aqueous solution, which slightly affects the activity of water. To confirm the unoccupancy of CF_4 in the TBAB semi-clathrate hydrate, Raman spectra of the TBAB semi-clathrate hydrates prepared with and without CF_4 pressurization were measured. A laser Raman microprobe spectrometer with a multichannel CCD detector (JASCO, NRS-1000) was used. The Diode Pumped Solid State (DPSS) laser (Cobolt, Fandango) was irradiated to the samples at atmospheric pressure and 110 K (by using the temperature control stage (Linkam Scientific Instruments, THMS600)). The backscatter was taken in with same lens. The wavelength of the DPSS laser was 514.5 nm and the output power was adjusted to 100 mW. The obtained Raman spectra are shown in Figure 1. Both spectra are very similar. The spectrum of the TBAB semi-clathrate hydrate, which was pressurized to approximately 80 MPa with CF_4, does not include the peaks derived from the CF_4 molecules. In general, the strong peaks derived from CF_4 are detected around 435 cm^{-1}, 631 cm^{-1}, and 909 cm^{-1} in CF_4 fluid phase.[30] The peak derived from CF_4 in 5^{12}-cages is detected around 917 cm^{-1} at 80 MPa and 918 cm^{-1} at 150 MPa.[28]

3. RESULTS AND DISCUSSION

The DSC curves of the TBAB semi-clathrate hydrate dissociation at various pressures are shown in Figure 2. The onset and peak temperatures in the DSC curves as well as the enthalpy of dissociation at various pressures are listed in Table 2. The dissociation temperature of the TBAB semi-clathrate hydrate depends on the pressure, while the enthalpy of tetragonal TBAB semi-clathrate hydrate dissociation is independent of pressure and (192±3) $J \cdot g^{-1}$ ($TBAB \cdot 26H_2O$). The dissociation temperature and enthalpy at 0.1 MPa obtained in the present study agree well with the literature.[6-10] The slope (dp/dT) of the tetragonal TBAB semi-clathrate hydrate dissociation is positive as shown in Figure 3, where the onset temperature was adopted. The positive slope (dp/dT) indicates the volume shrinkage in TBAB semi-clathrate hydrate formation, unlike ice formation and, moreover, the pressure-induced nucleation[31] at a constant temperature is possible. According to the literature[32], the hydrate dissociation temperature of TBAB semi-clathrate hydrate with $w_{TBAB} = 0.10$ at high pressures up to 20.9 MPa has negative slope (dp/dT). The eutectic temperature of (TBAB semi-clathrate hydrate + ice + aqueous solution) should be dropped at high pressures because the melting curve of Ice Ih has negative slope. The high-pressure equilibria with $w_{TBAB} = 0.10$ close to the eutectic concentration $w_{TBAB} = 0.06$ would exhibit opposite behavior to that of $w_{TBAB} = 0.398 \pm 0.002$. Further experiments at various TBAB concentrations are needed.

Interestingly, the very tiny peak occasionally detected at 282 K and 0.1 MPa in Figure 2, which would be derived from the metastable structure of TBAB semi-clathrate hydrate (probably, orthorhombic $TBAB \cdot 38H_2O$), exhibits different pressure dependence as shown in Figures 2 and S1. The slope (dp/dT) of the metastable $TBAB \cdot 38H_2O$ is smaller than that of thermodynamically stable $TBAB \cdot 26H_2O$. With further increasing pressure up to 180±20 MPa where the extrapolated curves of $TBAB \cdot 26H_2O$ and $TBAB \cdot 38H_2O$ intersects (shown in Figure S2 in supporting information), the $TBAB \cdot 38H_2O$ should become the thermodynamically stable structure. If the CF_4 molecules partially occupy 5^{12}-cages, the pressure of the structural phase transition would descend to a pressure lower than 180±20 MPa like the H_2+TBAB,[15] Xe+TBAB,[20] and Kr+TBAB[22] mixed semi-clathrate hydrate systems.

The DSC curves of the TBAB semi-clathrate hydrate nucleation at various pressures are shown in Figure 4. The heat flows in nucleation exceeded the detection limit of the microDSC. We focused only on the onset temperature of the spontaneous nucleation. There was no significant difference between the results at the cooling rate of 0.5 K/min and 1.0 K/min. The spontaneous nucleation temperature also depends on the pressure and increases with the increase in pressure. The slope ($\mathrm{d}p/\mathrm{d}T$) is very similar to that of the TBAB semi-clathrate hydrate dissociation as shown in Figure 3. These results reveal that the pressure acts as a driving force for the TBAB semi-clathrate hydrate nucleation. The temperature difference between dissociation and spontaneous nucleation, corresponding to the maximum allowable degree of supercooling, is shown in Figure 5. It is (17.7±0.7) K and independent of pressure.

4. CONCLUSIONS

The tetragonal TBAB semi-clathrate hydrate ($\mathrm{TBAB \cdot 26H_2O}$) prepared from the stoichiometric TBAB aqueous solution is thermodynamically stable at a pressure up to at least 80 MPa. The equilibrium dissociation temperature depends on the pressure and the equilibrium curve has a positive slope ($\mathrm{d}p/\mathrm{d}T$) in the pressure-temperature projection. The temperature of the spontaneous nucleation of the tetragonal TBAB semi-clathrate hydrate also depends on the pressure. The pressure-nucleation temperature relation has a similar slope to the pressure-dissociation temperature relation. In other words, the pressure-induced nucleation[31] at a constant temperature is possible from the thermodynamic viewpoint.

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

chemical name	source	mole fraction purity
tetrafluoromethane (CF_4)	Kanto Denka Kogyo	> 0.99999
tetra-*n*-butyl ammonium bromide (TBAB)	Wako Pure Chemical Industries	> 0.98
water	Wako Pure Chemical Industries	> 0.9999

Table 2. Experimental Dissociation Temperature (Onset Temperature T_{on}, Peak Temperature T_{peak}) and Dissociation Enthalpy $\Delta_{\mathrm{d}}H$ of TBAB Semi-clathrate Hydrate at Mole Fraction x_{TBAB} = 0.0356±0.0003 (Mass Fraction w_{TBAB} = 0.398±0.002) and Pressure p^{a}

p / MPa	T_{on} / K	T_{peak} / K	$\Delta_{\mathrm{d}}H$ / J·g^{-1}
0.1	285.08	285.54	192
0.1	285.10	285.56	192
10.0	285.80	286.28	191
10.2	285.76	286.21	191
20.0	286.52	286.89	193
20.4	286.47	286.97	188
30.1	287.06	287.60	190
31.5	287.14	287.70	192
39.8	287.67	288.21	187
44.0	287.91	288.52	192
50.7	288.33	288.91	190
59.7	288.86	289.44	192
59.7	288.87	289.48	194
70.1	289.48	290.06	194
72.9	289.60	290.24	195
79.0	289.99	290.56	194

[a] Standard uncertainties u are $u(p)$ = 0.4 MPa, $u(T)$ = 0.06 K, and $u(H)$ = 2 J·g^{-1}.

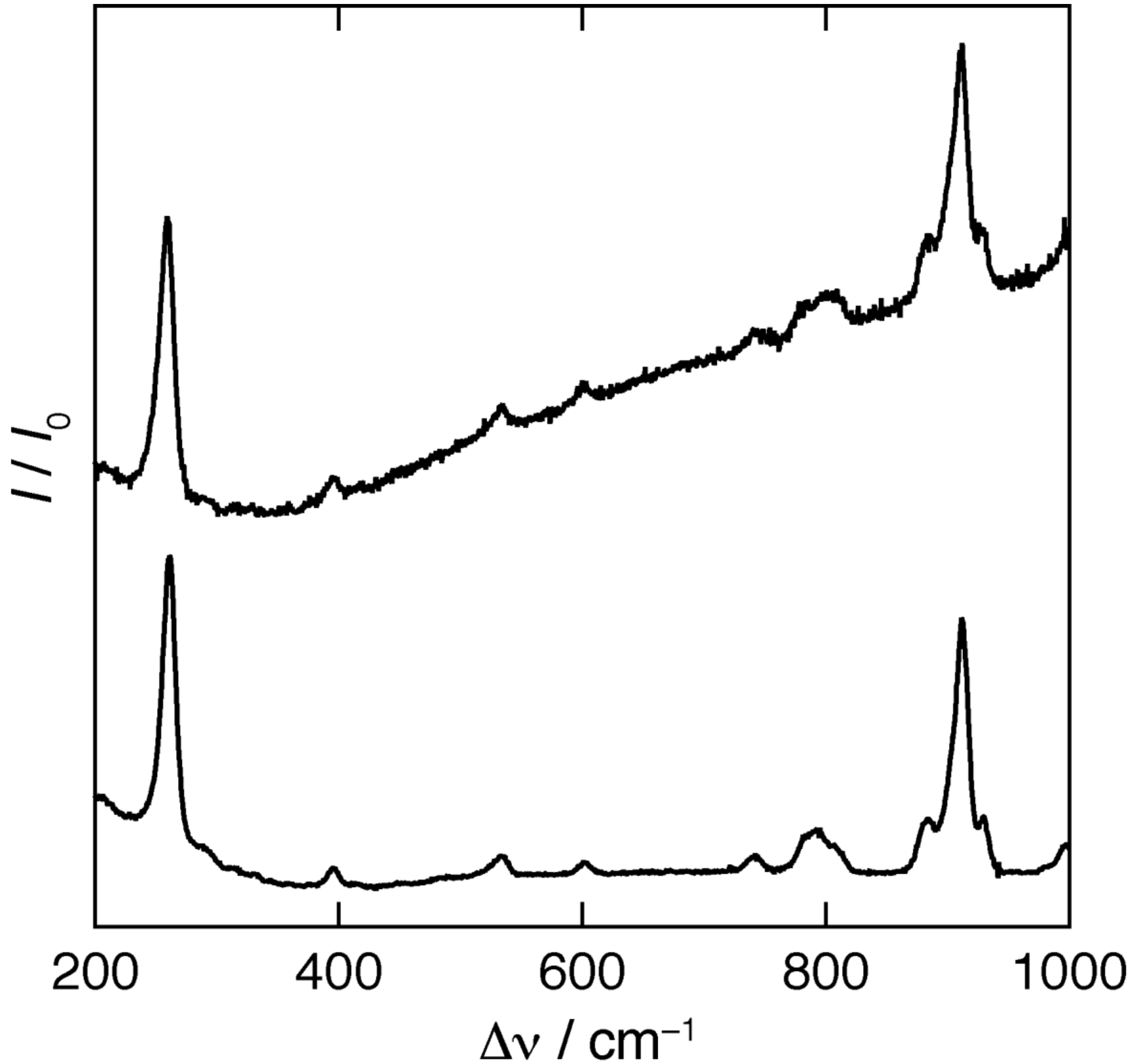

Figure 1. Raman spectra (Intensity *I*, Raman shift Δν) of TBAB semi-clathrate hydrates prepared under CF_4 pressurization at approximately 80 MPa (top) and at 0.1 MPa (bottom). The spectra were measured at 0.1 MPa and 110 K.

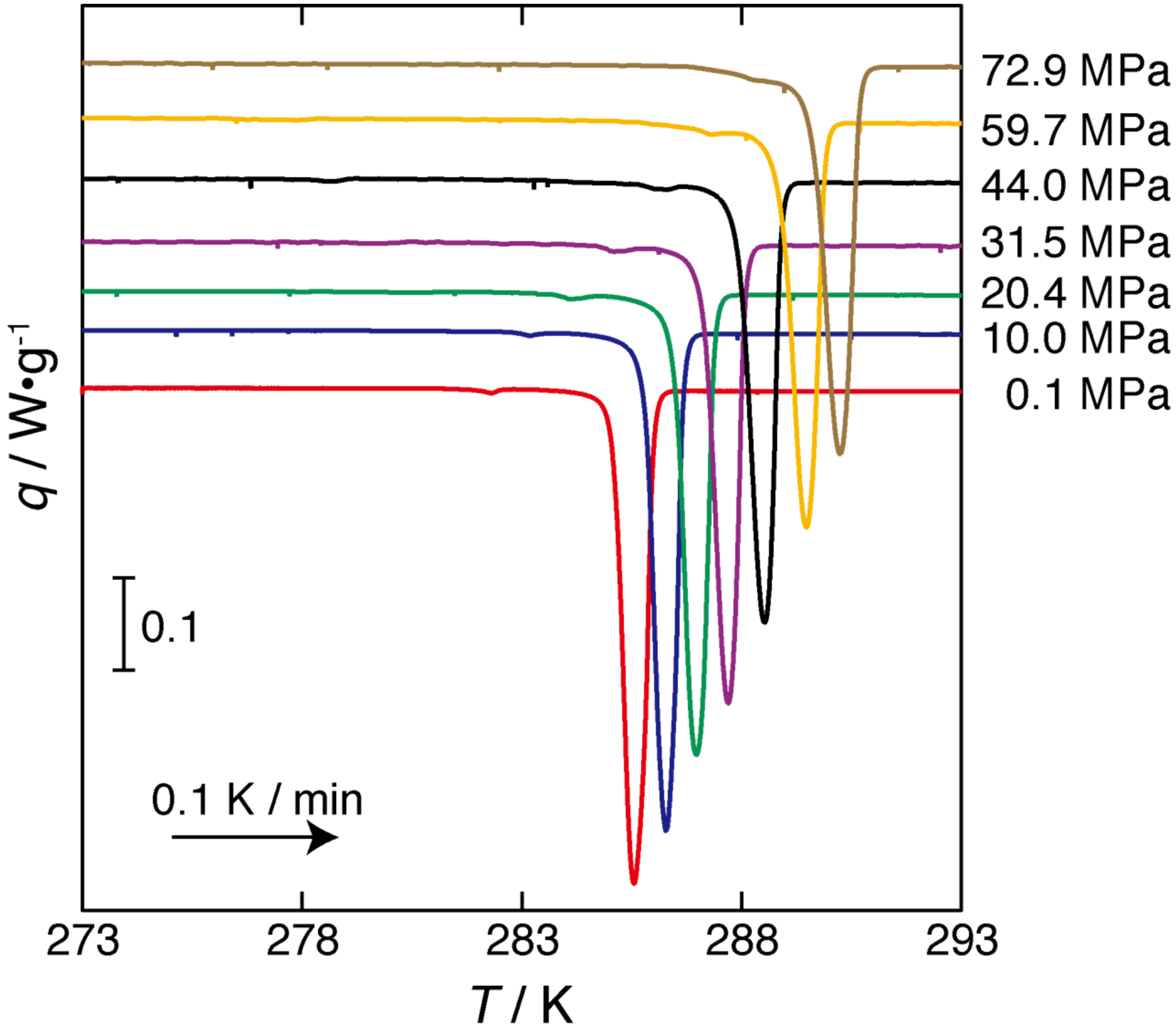

Figure 2. DSC curves (heat flow *q*, Temperature *T*) of the TBAB semi-clathrate hydrate dissociation pressurized with CF_4 at 0.1 MPa, 10.0 MPa, 20.4 MPa, 31.5 MPa, 44.0 MPa, 59.7 MPa, and 72.9 MPa (from the bottom to the top). Each curve was vertically shifted to be easily recognized.

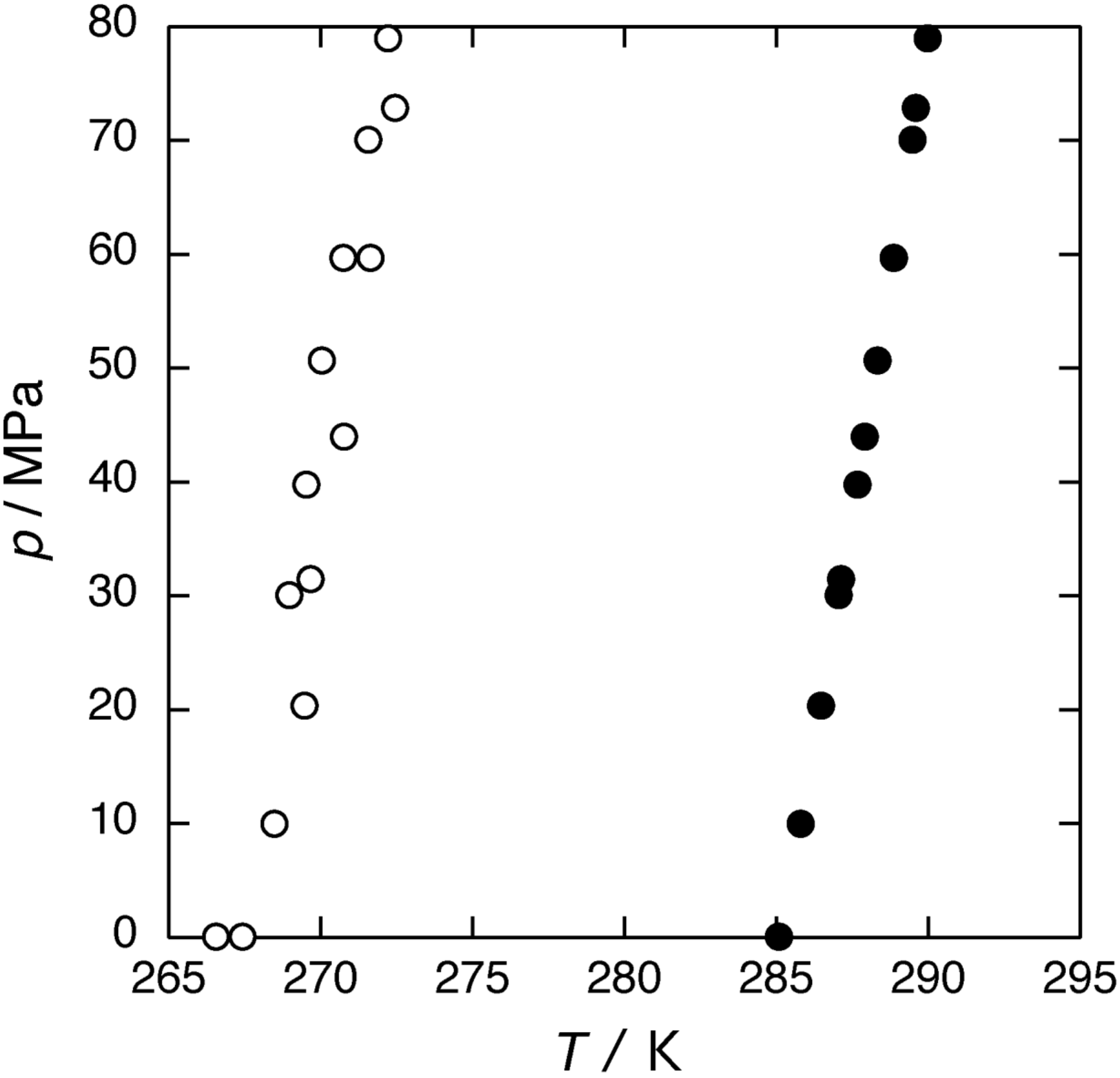

Figure 3. Pressure (*p*) – temperature (*T*) relations of the dissociation (closed keys) and spontaneous nucleation (open keys) of TBAB semi-clathrate hydrates (TBAB·26H_2O) pressurized with CF_4. The onset temperatures of dissociation and nucleation in the DSC curves were adopted in the plot.

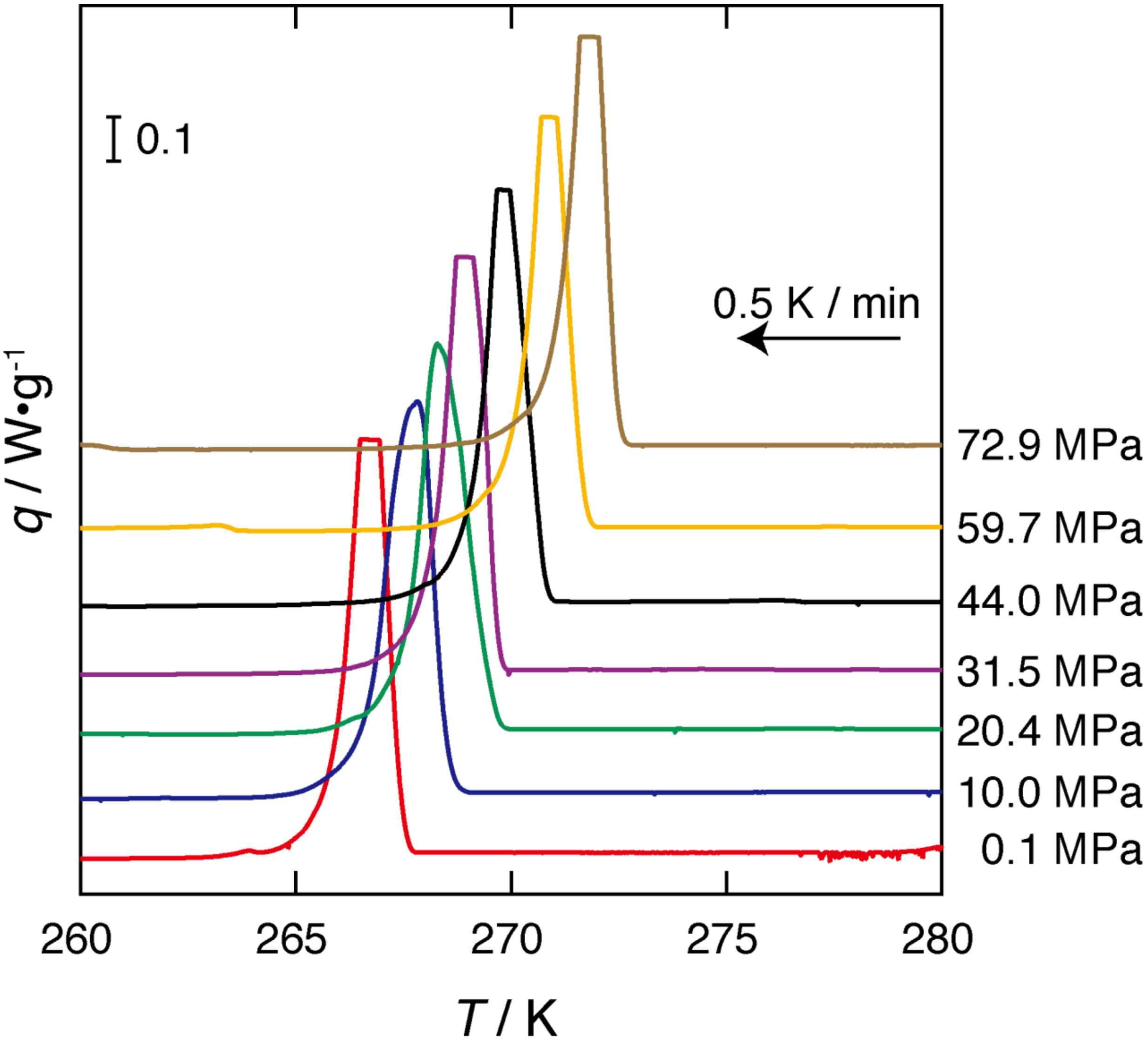

Figure 4. DSC curves of the TBAB semi-clathrate hydrate nucleation pressurized with CF_4 at 0.1 MPa, 10.0 MPa, 20.4 MPa, 31.5 MPa, 44.0 MPa, 59.7 MPa, and 72.9 MPa (from the bottom to the top). Some of the heat flows in nucleation exceeded the detection limit. Each curve was vertically shifted to be easily recognized.

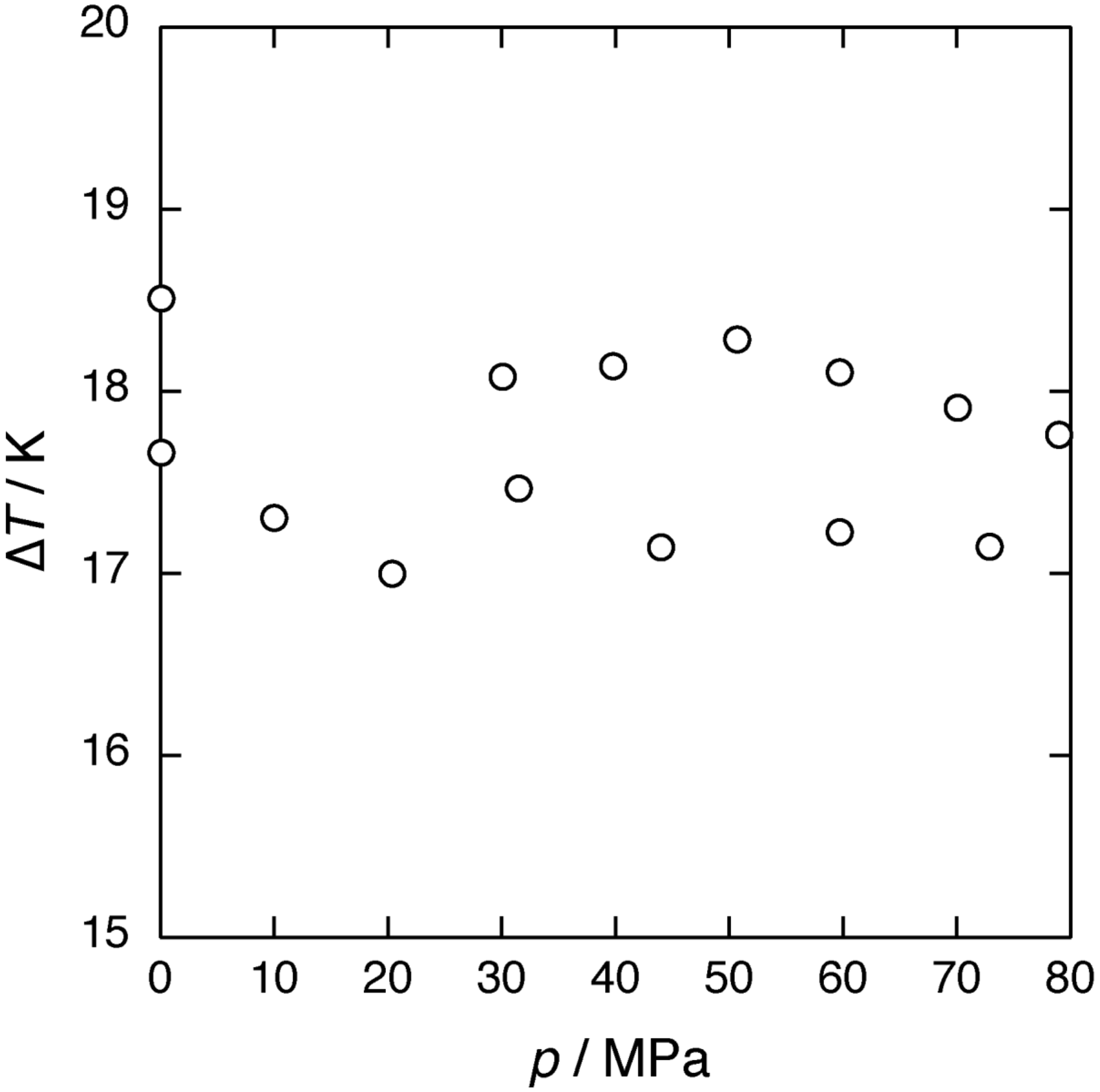

Figure 5. Pressure effect of maximum allowable degree of supercooling (Δ*T*) in the TBAB semi-clathrate hydrate nucleation (TBAB·26H_2O) under CF_4 pressurization.

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Notes

The authors declare no competing financial interest.

Supporting Information

Pressure-temperature relations of stable and metastable structures and the extrapolated difference between the dissociation temperatures of stable and metastable structures are shown in Figures S1 and S2, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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REFERENCES

(1) Sloan, E. D.; Koh, C. A. *Clathrate Hydrates of Natural Gases*, 3rd ed.; Taylor & Francis-CRC Press: Boca Raton, FL, 2008.

(2) 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.

(3) 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.

(4) Shimada, W.; Shiro, M.; Kondo, H.; Takeya, S.; Oyama, H.; Ebinuma, T.; Narita, H. Tetra-*n*-butylammonium bromide-water (1/38). *Acta Cryst. C* **2005**, *61*, o65–o66.

(5) 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.

(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) Shimada, W.: Ebinuma, T.: Oyama, H.: Kamata, Y.: Takeya, S.: Uchida, T.; Nagao, J.; Narita, H. Separation of gas molecules using tetra-*n*-butyl ammonium bromide semi-clathrate hydrate crystals. *Jpn. J. Appl. Phys.* **2003**, *42*, 129–131.

(8) Oyama, H.; Shimada, W.; Ebinuma, T.; Kamata, Y.; Takeya, S.; Uchida, T.; Nagao, J.; Narita, H. Phase diagram, latent heat, and specific heat of TBAB semiclathrate hydrate crystals. *Fluid Phase Equilib.* **2005**, *234*, 131–135.

(9) Hashimoto, S.; Sugahara. T.; Moritoki, M.; Sato, H.; Ohgaki, K. Thermodynamic stability of hydrogen+tetra-*n*-butyl ammonium bromide mixed gas hydrate in nonstoichiometric aqueous solutions. *Chem. Eng. Sci.* **2008**, *63*, 1092–1097.

(10) 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.

(11) Sun, Z.-G.; Jiang, C.-M.; Xie, N.-L. Hydrate Equilibrium Conditions for Tetra-*n*-butyl Ammonium Bromide. *J. Chem. Eng. Data* **2008**, *53*, 2375–2377.

(12) Sato, K.; Tokutomi, H.; Ohmura, R. Phase equilibrium of ionic semiclathrate hydrates formed with tetrabutylammonium bromide and tetrabutylammonium chloride. *Fluid Phase Equilib*. **2013**, *337*, 115–118.

(13) Hashimoto, S.; Murayama, S.; Sugahara, T.; Sato, H.; Ohgaki, K. Thermodynamic and Raman spectroscopic studies on H_2 + tetrahydrofuran + water and H_2 + tetra-*n*-butyl ammonium bromide + water mixtures containing gas hydrates. *Chem. Eng. Sci.* **2006**, *61*, 7884–7888.

(14) Chapoy, A.; Anderson, R.; Tohidi, B. Low-pressure molecular hydrogen storage in semi-clathrate hydrates of quaternary ammonium compounds. *J. Am. Chem. Soc.* **2007**, *129*, 746–747.

(15) Hashimoto, S.; Tsuda, T.; Ogata, K.; Sugahara, T.; Inoue, Y.; Ohgaki, K. Thermodynamic Properties of Hydrogen + Tetra-*n*-Butyl Ammonium Bromide Semi-Clathrate Hydrate. *J. Thermodyn.* **2010**, *2010*, 170819-1–5.

(16) Chapoy, A.; Gholinezhad, J.; Tohidi, B. Experimental Clathrate Dissociations for the Hydrogen + Water and Hydrogen + Tetrabutylammonium Bromide + Water Systems. *J. Chem. Eng. Data* **2010**, *55*, 5323–5327.

(17) Komatsu, H.; Hayasaka, A.; Ota, M.; Sato, Y.; Watanabe, M.; Smith, R. L. Jr. Measurement of pure hydrogen and pure carbon dioxide adsorption equilibria for THF clathrate hydrate and tetra-*n*-butyl ammonium bromide semi-clathrate hydrate. *Fluid Phase Equilib.* **2013** *357*, 80–85.

(18) Mohammadi, A. H.; Eslamimanesh, A.; Belandria, V.; Richon, D. Phase Equilibria of Semiclathrate Hydrates of CO_2, N_2, CH_4, or H_2 + Tetra-*n*-butylammonium Bromide Aqueous Solution. *J. Chem. Eng. Data* **2011**, *56*, 3855–3865.

(19) Mohammadi, A. H.; Richon, D. Phase Equilibria of Semi-Clathrate Hydrates of Tetra-*n*-butylammonium Bromide + Hydrogen Sulfide and Tetra-*n*-butylammonium Bromide + Methane. *J. Chem. Eng. Data* **2010**, *55*, 982–984.

(20) Jin, Y.; Nagao, J. Change in the Stable Crystal Phase of Tetra-*n*-butylammonium Bromide (TBAB) Hydrates Enclosing Xenon. *J. Phys. Chem. C* **2013**, *117*, 6924−6928.

(21) Babaee, S.; Hashemi, H.; Mohammadi, A. H.; Naidoo, P.; Ramjugernath, D. Experimental Measurement and Thermodynamic Modeling of Hydrate Dissociation Conditions for the Argon + TBAB + Water System. *J. Chem. Eng. Data* **2014**, *59*, 3900−3906.

(22) Jin, Y.; Kida, M.; Nagao, J. Phase Transition of Tetra-*n*-butylammonium Bromide Hydrates Enclosing Krypton. *J. Chem. Eng. Data* **2016**, *61*, 679−685.

(23) Lin, W.; Delahaye, A.; Fournaison, L. Phase equilibrium and dissociation enthalpy for semi-clathrate hydrate of CO_2+TBAB. *Fluid Phase Equilib.* **2008**, *264*, 220–227.

(24) Fan, S.; Li, S.; Wang, J.; Lang, X.; Wang, Y. Efficient Capture of CO_2 from Simulated Flue Gas by Formation of TBAB or TBAF Semiclathrate Hydrates. *Energy Fuels* **2009**, *23*, 4202–4208.

(25) Babu, P.; Chin, W. I.; Kumar, R.; Linga, P. Systematic Evaluation of Tetra-*n*-butyl Ammonium Bromide (TBAB) for Carbon Dioxide Capture Employing the Clathrate Process. *Ind. Eng. Chem. Res.* **2014**, *53*, 4878−4887.

(26) Kobori, T.; Muromachi, S.; Ohmura, R. Phase Equilibrium for Ionic Semiclathrate Hydrates Formed in the System of Water + Tetra-*n*-butylammonium Bromide Pressurized with Carbon Dioxide. *J. Chem. Eng. Data* **2015**, *60*, 299−303.

(27) Li, Q.; Fan, S.; Wang, Y.; Lang, X.; Chen, J. CO_2 Removal from Biogas Based on Hydrate Formation with Tetra-*n*-Butylammonium Bromide Solution in the Presence of 1-Butyl-3-Methylimidazolium Tetrafluoroborate. *Energy Fuels* **2015**, *29*, 3143−3148.

(28) Sugahara, K.; Yoshida, M.; Sugahara, T.; Ohgaki, K. High-pressure phase behavior and cage occupancy for the CF_4 hydrate system. *J. Chem. Eng. Data* **2004**, *49*, 326–329.

(29) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1986.

(30) Shimanouchi, T. *Tables of Molecular Vibrational Frequencies*, consolidated, Vol. I; National Bureau of Standards Department of Commerce: Washington, DC, 1972.

(31) Moritoki, M. Fractional Crystallization Process Applying High Pressure. *Kagaku Kogaku Ronbunshu* **1979**, *5*, 79–84.

(32) Arjmandi, M.; Chapoy, A.; Tohidi, B. Equilibrium Data of Hydrogen, Methane, Nitrogen, Carbon Dioxide, and Natural Gas in Semi-Clathrate Hydrates of Tetrabutyl Ammonium Bromide. *J. Chem. Eng. Data* **2007**, *52*, 2153–2158.

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