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Dissociation Data of Semiclathrate Hydrates for the Systems of Tetra-*n*-butylammonium Fluoride (TBAF) + Methane + Water, TBAF + Carbon Dioxide + Water, and TBAF + Nitrogen + Water

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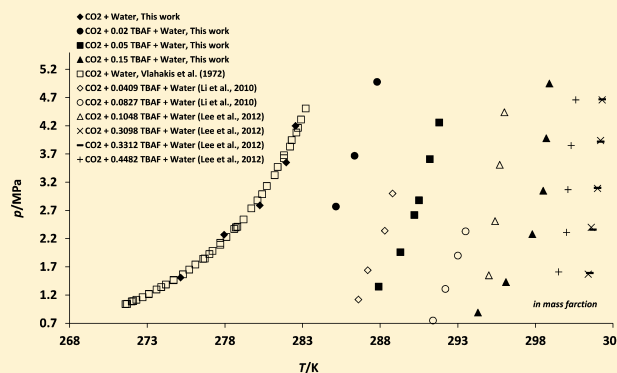
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ABSTRACT: One of the limitations in the process of hydrate formation to benefit its positive application is high pressure and low temperature conditions. Design and construction of a unit with the aforementioned conditions is therefore expensive and unsafe. Thus, an investigation of methods for moderation of hydrate formation conditions seems to be very important. As mentioned in literature, utilization of ammonium salts in water normally promotes the hydrate formation conditions. One of these salts is tetra-*n*-butylammonium fluoride (TBAF). In this research, the dissociation data of semiclathrate hydrates for the systems of methane + TBAF + water, carbon dioxide + TBAF + water, and nitrogen + TBAF + water have been measured and reported. Experimental measurements were performed at three concentrations of TBAF, that is, (0.02, 0.05, and 0.15) mass fraction. A comparison of hydrate dissociation data in the presence or absence of TBAF shows the promotion effect of TBAF on methane, carbon dioxide, and nitrogen hydrate formation. By increasing the concentration of TBAF from (0.02 to 0.15) mass fraction, its promotion effect increases, and the *p*–*T* curves of the double gas + TBAF semiclathrate systems shift to the low pressure and high temperature regions (moderate conditions). Results of the experiments show that, contrary to clathrate hydrates, a small increase in temperature of semiclathrate hydrates, studied herein, leads to a noticeable increase in dissociation pressure.



1. INTRODUCTION

Gas hydrates (sometimes called clathrate hydrates) are ice-like nonstoichiometric crystalline solids composed of a lattice of water molecules and trapped small (guest) molecules in water cavities. In the clathrate hydrates, the guest molecules are trapped and do not participate in the hydrate lattice structure.¹

Gas hydrates are formed under certain conditions of relatively high pressure and low temperature.^{1,2} Utilization of thermodynamic promoters is one of the common ways for moderating the gas hydrate formation condition. Oxolane, 1,4-dioxane, cyclohexane (CH), cyclopentane (CP), cyclobutane (CB), methylcyclohexane (MCH), methylcyclopentane (MCP), cycloheptane (CHP), 1,4-dimethylcyclohexane, 2,2-dimethylbutane, or cyclooctane (CO) are among some of the proposed promoters. However, using these additives introduces some problems such as toxicity, volatility, or flammability.^{3–6}

In 1940, a new structure of the hydrate was discovered by Fowler et al.⁷ The structural nature of discovered hydrates was different from clathrate hydrates. In this type of hydrates the guest molecules participate in the lattice structure; therefore

these structures are called semiclathrates. In the semiclathrate hydrates, some cages are broken to encapsulate the guest molecules, and water molecules of the framework are partially replaced by the atom of the guest species.⁸ Fowler et al.⁷ reported on the formation of semiclathrate hydrates by the tetra-*n*-butyl and tetraisoamyl quaternary salts. They also found that the aqueous solutions of tetra-*n*-butylphosphonium salts and tri-*n*-butylsulphonium salts form the semiclathrate hydrates. In the formation of semiclathrate hydrates, anion species participate in the hydrate framework, and cation species occupy the large cavities, while the small cavities may remain vacant or partially occupied with water molecules or small gas molecules (called auxiliary gas).^{9–12} When the promoter molecules occupy the large cavities and the gas molecules occupy the small cavities, the double hydrates (also called mixed hydrates) are formed.

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Semiclathrates are sometimes called ionic clathrates, because the guest component of this type of clathrates is a salt.¹³ The most characteristic structural types of the ionic clathrate hydrates of tetraalkylammonium salts are superstructures of cubic structure I (CSS-I), tetragonal structure I (TS-I), and hexagonal structure I (HS-I).^{13–16}

Tetraalkylammonium salts such as tetra-*n*-butylammonium bromide (TBAB), tetra-*n*-butylammonium chloride (TBAC), and tetra-*n*-butylammonium fluoride (TBAF) are not volatile and form semiclathrate hydrates with high dissociation temperature (semiclathrate hydrates can be formed at atmospheric pressure (0.101325 MPa) close to room temperature (298.15 K)).

In this paper, we report the experimental data of dissociation condition of semiclathrate hydrates formed from methane + TBAF + water, carbon dioxide + TBAF + water, and nitrogen + TBAF + water mixtures.

2. EXPERIMENTAL SECTION

2.1. Materials. The purities and suppliers of the materials used in this work are reported in Table 1. Distilled water was

Table 1. Purities and Suppliers of Materials Used in This Work

chemical name	supplier	purity
TBAF·3H ₂ O ^a	Daejung	0.98 mass fraction
methane	Varian Gas	0.99995 mole fraction
nitrogen	Varian Gas	0.9995 mole fraction
carbon dioxide	Varian Gas	0.999 mole fraction

^aTBAF·3H₂O = tetra-*n*-butylammonium fluoride trihydrate.

used to prepare the TBAF aqueous solutions with $W_{\text{TBAF}} = (0.02, 0.05, \text{ and } 0.15)$ mass fraction. Aqueous solutions were prepared with a gravimetric method using an accurate analytical balance (mass uncertainty: ± 0.0001 g).

2.2. Apparatus. The schematic diagram of the experimental apparatus is shown in Figure 1. The reactor is a jacketed stainless steel cell (with an effective volume of 460 cm³). It has a valve for charging and discharging water and gas. For appropriate mixing of the gas and aqueous solution, an electromotor is used to rock the cell. The rocking motion of the cell always makes the existing phases in the reactor (hydrate, liquid, and gas phases), being in contact together even after the hydrate formation, which is necessary for obtaining true equilibrium data. The jacket of the reactor has an inlet and an outlet for the coolant which is a mixture of commercial ethanol and water. The temperature of the coolant is controlled by a programmable coolant circulator and a thermocouple. The cell temperature and pressure are also measured by means of a platinum resistance thermometer (Pt100) and a BD pressure transducer. The temperature measurement uncertainty is estimated to be less than 0.1 K. This estimation comes from calibration against a 25 Ω reference platinum resistance thermometer. The pressure measurement accuracies are estimated to be better than 5 kPa. A JB Platinum vacuum pump is used for evacuating the cell. Through a data acquisition board, the reactor pressure and temperature are transmitted to a PC and are recorded at 20 s intervals.

2.3. Procedure. The semiclathrate hydrate dissociation conditions are measured using the isochoric pressure search method. The reliability of this method has been examined and proven in a number of previous studies.^{17–21} At first, the cell

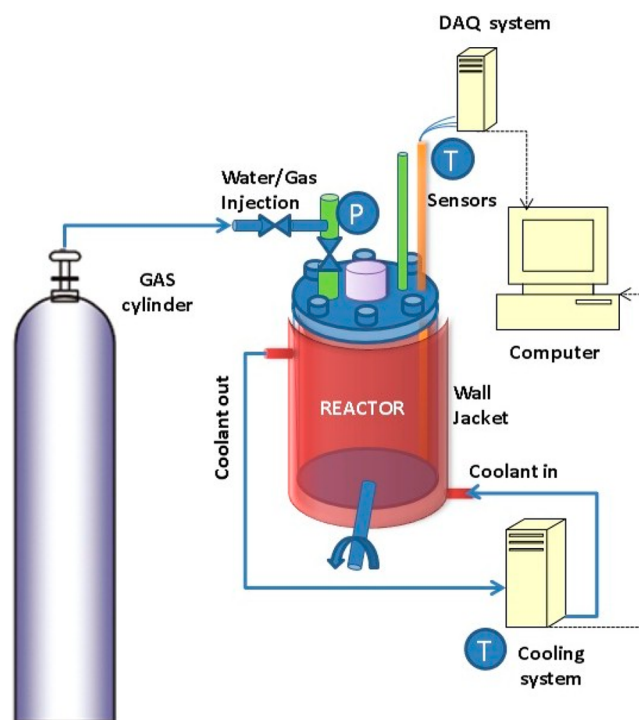


Figure 1. Schematic illustration of the experimental apparatus.

was washed with distilled water, and then the air inside the cell was evacuated with the vacuum pump. After loading of 100 cm³ of aqueous solution into the cell, once again the vacuum pump was used to remove the air inside the reactor. The vacuum pump was used just for a few seconds, and the cell inlet valve was instantly closed after removing the air inside the reactor. A certain amount of gas (methane, carbon dioxide, or nitrogen) was charged into the cell to reach the desired pressure. After the cell was pressurized with the gas, the electromotor with speed of 25 rpm was turned on, followed by cooling the cell in a slow rate of lowering the temperature until 274.15 K. The cell pressure decreased continuously due to double semiclathrate hydrate formation, and while reaching a steady state condition, the system was rapidly heated at a rate of 1.5 K·h^{−1} until the temperature was within 3 K of the expected dissociation point. The temperature was then raised slowly at the rate of 0.2 K·h^{−1}. During the experiment, both the cell temperature and the pressure were recorded, and in this way for each experimental run, a pressure–temperature diagram was obtained, from which the hydrate dissociation point was determined.^{17–21}

3. RESULTS AND DISCUSSION

TBAF semiclathrate hydrate has two crystal structures: One of them is cubic structure (CSS-I), and the hydration number is 28.6 (TBAF·28.6H₂O). The other one of tetragonal structure with a hydration number of 32.3 (TS-I) (TBAF·32.3H₂O), which seems to be a metastable structure.^{10,13,22–24} The stoichiometric ratio for small guest gas molecules such as methane, carbon dioxide, and nitrogen is 16.4 molecules of water per molecule of gas in tetragonal structure.⁹ Figure 2 represents the phase diagram (temperature–composition relation) of TBAF semiclathrate hydrate under atmospheric pressure ($p = 0.101325$ MPa). Our results have been compared with some literature data, and they are in a good agreement with literature data. The measured experimental data are listed in Table 2. The stoichiometric concentration of TBAF in water

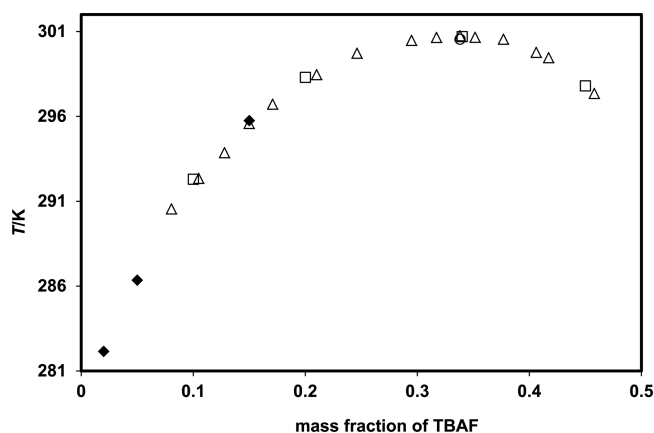


Figure 2. Phase diagram of TBAF semicathrates under atmospheric pressure ($p = 0.101325$ MPa). Symbols represent experimental data: \triangle , ref 24; \square , ref 23; \circ , ref 22; \blacklozenge , this work.

Table 2. Measured Dissociation Temperature (T_{diss}) of TBAF Hydrate at Atmospheric Pressure ($p = 0.10325$ MPa)

mass fraction of TBAF ^a	T_{diss} ^b /K
0.02	282.1
0.05	286.3
0.15	295.7

^aThe maximum uncertainty in the measured mass fraction of TBAF in aqueous solution is 0.0001 mass fraction. ^bThe maximum uncertainty in the measured temperature is expected to be 0.2 K.

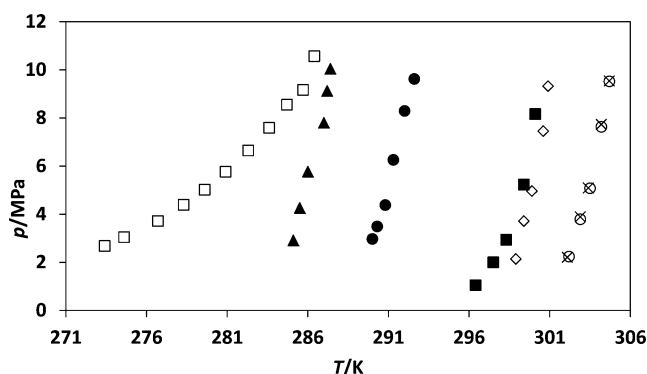


Figure 3. Hydrate dissociation conditions of the methane + TBAF + water systems. Symbols represent experimental data: \square , methane + water, ref 29; \times , 0.310 mass fraction TBAF aqueous solution, ref 28; \circ , 0.331 mass fraction TBAF aqueous solution, ref 28; \diamond , 0.448 mass fraction TBAF aqueous solution, ref 28; \blacktriangle , 0.02 mass fraction TBAF aqueous solution, this work; \bullet , 0.05 mass fraction TBAF aqueous solution, this work; \blacksquare , 0.15 mass fraction TBAF aqueous solution, this work.

is 0.34 mass fraction, and as shown in Figure 2, the maximum dissociation temperature for TBAF semicathrate hydrate under atmospheric pressure ($p = 0.101325$ MPa) is observed in this concentration. The stable structure of TBAF semicathrate hydrate is CSS-I, and in the phase diagram of TBAF semicathrate hydrate (Figure 2), the hydration number in all concentration of TBAF is 28.6.

The results of our measurements of semicathrate hydrate dissociation conditions (pressure–temperature data) for the systems of (a) methane + TBAF ((0.02, 0.05, and 0.15) mass fraction) + water, (b) carbon dioxide + TBAF ((0.02, 0.05, and

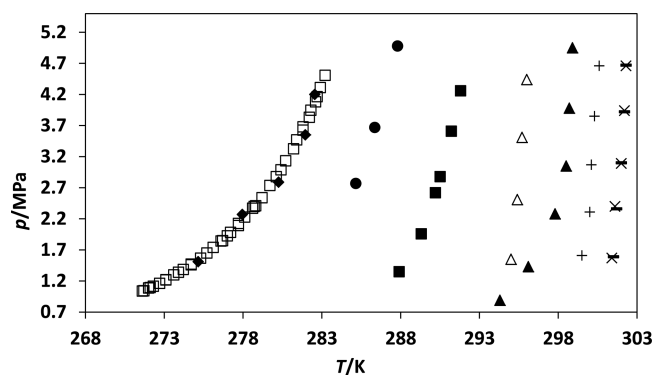


Figure 4. Hydrate dissociation conditions of the carbon dioxide + TBAF + water systems. Symbols represent experimental data: \square , carbon dioxide + water, ref 27; \triangle , 0.105 mass fraction TBAF aqueous solution, ref 28; \times , 0.310 mass fraction TBAF aqueous solution, ref 28; \circ , 0.331 mass fraction TBAF aqueous solution, ref 28; $+$, 0.448 mass fraction TBAF aqueous solution, ref 28; \blacklozenge , carbon dioxide + water, this work; \bullet , 0.02 mass fraction TBAF aqueous solution, this work; \blacksquare , 0.05 mass fraction TBAF aqueous solution, this work; \blacktriangle , 0.15 mass fraction TBAF aqueous solution, this work.

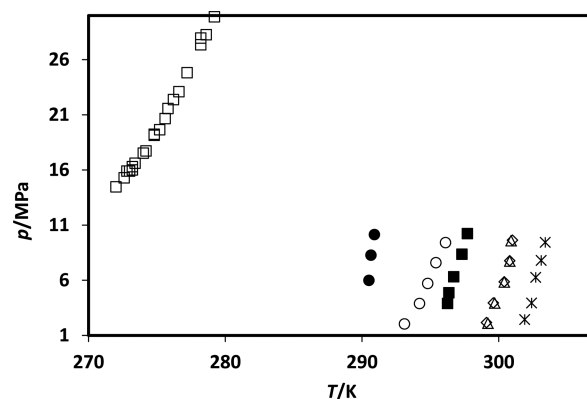


Figure 5. Hydrate dissociation conditions of the nitrogen + TBAF + water systems. Symbols represent experimental data: \square , nitrogen + water, ref 26; \circ , 0.10 mass fraction TBAF aqueous solution, ref 23; \diamond , 0.20 mass fraction TBAF aqueous solution, ref 23; $*$, 0.34 mass fraction TBAF aqueous solution, ref 23; \triangle , 0.45 mass fraction TBAF aqueous solution, ref 23; \bullet , 0.05 mass fraction TBAF aqueous solution, this work; \blacksquare , 0.15 mass fraction TBAF aqueous solution, this work.

0.15) mass fraction) + water, and (c) nitrogen + TBAF ((0.05 and 0.15) mass fraction) + water are given in Figures 3 to 5, respectively. All of the obtained p – T dissociation data are summarized in Table 3. The literature data for some systems are also depicted in the Figures 3 to 5. The measured dissociation data for all systems are in good agreement with the literature values. As can be seen in these figures, the equilibrium conditions for double TBAF semicathrate were noticeably moderated, and the p – T dissociation curves were greatly shifted to low pressure and high temperature regions. By increasing the concentration of TBAF from 0.02 mass fraction to 0.15 mass fraction (the concentration ranges studied in this work), the p – T curves of the double gas + TBAF semicathrate systems were shifted to the right side (moderate condition). Literature data (see Figures 2 to 5) show the less stabilization effect for the TBAF semicathrate and double gas + TBAF

Table 3. Measured Dissociation Data of Semiclathrate Hydrates for the Systems of Methane + TBAF + Water, Carbon Dioxide + TBAF + Water, and Nitrogen + TBAF + Water

T^a/K	system ^b	p^c/MPa
CH ₄ + TBAF (0.02 mass fraction) + water		
287.0		7.80
287.2		9.12
287.4		10.04
286.0		5.77
285.5		4.26
285.1		2.91
CH ₄ + TBAF (0.05 mass fraction) + water		
292.6		9.62
292.0		8.29
291.3		6.26
290.8		4.38
290.3		3.49
290.0		2.97
CH ₄ + TBAF (0.15 mass fraction) + water		
300.1		8.16
299.4		5.23
298.3		2.94
297.5		2.00
296.4		1.05
CO ₂ + TBAF (0.02 mass fraction) + water		
287.8		4.98
286.3		3.67
285.1		2.77
CO ₂ + TBAF (0.05 mass fraction) + water		
291.8		4.26
291.2		3.61
290.5		2.88
290.2		2.62
289.3		1.96
287.9		1.35
CO ₂ + TBAF (0.15 mass fraction) + water		
298.9		4.95
298.7		3.98
298.5		3.05
297.8		2.28
296.1		1.43
294.3		0.89
N ₂ + TBAF (0.05 mass fraction) + water		
290.9		10.15
290.6		8.28
290.5		6.00
N ₂ + TBAF (0.15 mass fraction) + water		
297.7		10.24
297.3		8.37
296.7		6.33
296.3		4.88
296.2		3.91

^aThe maximum uncertainty in the measured temperature is expected to be 0.2 K. ^bThe maximum uncertainty in the measured mass fraction of TBAF in aqueous solution is 0.0001 mass fraction. ^cThe maximum uncertainty in the measured pressure is expected to be 0.05 MPa.

semiclathrate when the concentration of TBAF is more than the stoichiometric amount (0.34 mass fraction). For all systems the maximum stabilization effect is observed in stoichiometric concentration. Figures 3 to 5 show that, contrary to clathrate

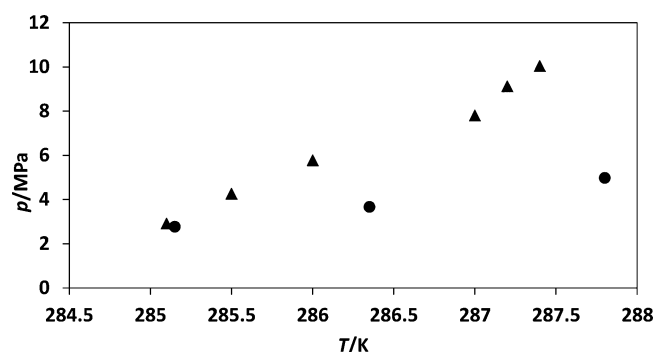


Figure 6. Semiclathrate hydrate dissociation conditions of the methane + TBAF (0.02 mass fraction) + water and carbon dioxide + TBAF (0.02 mass fraction) + water systems. Symbols represent experimental data: ▲, methane + TBAF (0.02 mass fraction) + water; ●, carbon dioxide + TBAF (0.02 mass fraction) + water.

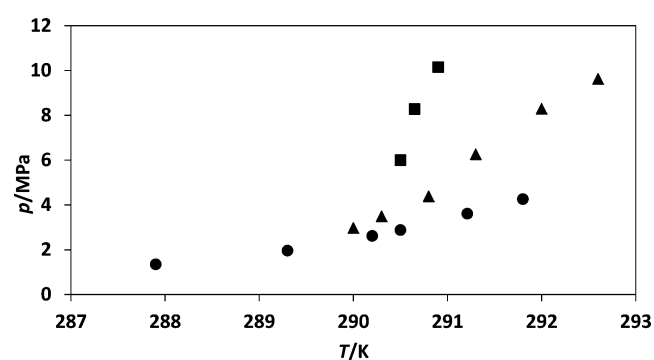


Figure 7. Semiclathrate hydrate dissociation conditions of the methane + TBAF (0.05 mass fraction) + water, carbon dioxide + TBAF (0.05 mass fraction) + water, and nitrogen + TBAF (0.05 mass fraction) + water systems. Symbols represent experimental data: ▲, methane + TBAF (0.05 mass fraction) + water; ●, carbon dioxide + TBAF (0.05 mass fraction) + water; ■, nitrogen + TBAF (0.05 mass fraction) + water.

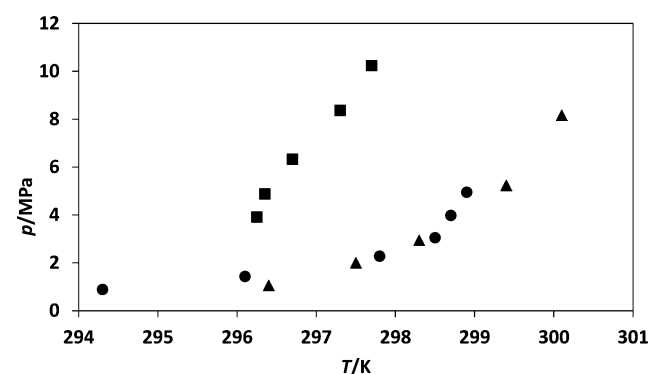


Figure 8. Semiclathrate hydrate dissociation conditions of the methane + TBAF (0.15 mass fraction) + water, carbon dioxide + TBAF (0.15 mass fraction) + water, and nitrogen + TBAF (0.15 mass fraction) + water systems. Symbols represent experimental data: ▲, methane + TBAF (0.15 mass fraction) + water; ●, carbon dioxide + TBAF (0.15 mass fraction) + water; ■, nitrogen + TBAF (0.15 mass fraction) + water.

hydrates, a small increase in temperature of semiclathrate hydrates increases the dissociation pressure noticeably (in the ranges studied in the present work).

Dissociation data of double hydrates for systems of methane + TBAF, carbon dioxide + TBAF, and nitrogen + TBAF are compared in Figures 6 to 8. According to Figures 6 and 7, for the concentrations of (0.02 and 0.05) mass fraction of TBAF, the isobaric dissociation temperatures of the double TBAF + nitrogen (a), + carbon dioxide (b), and + methane (c) hydrates increase as $T_{ib} (a) > T_{ib} (b) > T_{ib} (c)$.

Figure 8 depicts the dissociation data of methane, carbon dioxide, and nitrogen + TBAF (0.15 mass fraction) semiclathrate hydrates. At this concentration of TBAF, the isobaric dissociation temperatures of methane + TBAF semiclathrate hydrates are very close to the isobaric dissociation temperatures of carbon dioxide + TBAF semiclathrate hydrates.

4. CONCLUSION

In this study, the dissociation data of semiclathrate hydrates for the systems of methane + TBAF + water, carbon dioxide + TBAF + water, and nitrogen + TBAF + water were measured and reported (Table 3). The experimental results show that TBAF has a drastic promotion effect on semiclathrate hydrate formation. The utilization of TBAF greatly shift the hydrate dissociation conditions of gas to the low pressure and high temperature regions. Another conclusion of this study is that the promotion effect of TBAF increases by increasing the concentration of TBAF before the stoichiometric amount (0.34 mass fraction).

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Notes

The authors declare no competing financial interest.

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