

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/228478994>

# Semiclathrate Hydrate Phase Equilibria for CO<sub>2</sub> in the Presence of Tetra-*n*-butyl Ammonium Halide (Bromide, Chloride, or Fluoride)

ARTICLE in JOURNAL OF CHEMICAL & ENGINEERING DATA · SEPTEMBER 2010

Impact Factor: 2.04 · DOI: 10.1021/jc100059h

CITATIONS

78

READS

118

## 5 AUTHORS, INCLUDING:



Shifeng Li

Shenyang University

21 PUBLICATIONS 289 CITATIONS

SEE PROFILE



Shuanshi Fan

South China University of Technology

169 PUBLICATIONS 8,121 CITATIONS

SEE PROFILE



Xuemei Lang

South China University of Technology

28 PUBLICATIONS 542 CITATIONS

SEE PROFILE



Yanhong Wang

Northeast Agricultural University

27 PUBLICATIONS 356 CITATIONS

SEE PROFILE

# Semiclathrate Hydrate Phase Equilibria for CO<sub>2</sub> in the Presence of Tetra-*n*-butyl Ammonium Halide (Bromide, Chloride, or Fluoride)

Shifeng Li,<sup>†,\*</sup> Shuanshi Fan,<sup>\*,‡</sup> Jingqu Wang,<sup>†</sup> Xuemei Lang,<sup>‡</sup> and Yanhong Wang<sup>‡</sup>

State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116012, China, and Key Laboratory of Enhanced Heat Transfer and Energy Conversation, Ministry of Education, South China University of Technology, Guangzhou 510640, China

Phase equilibrium data for the semiclathrate hydrates formed in three three-component systems, the CO<sub>2</sub> + tetra-*n*-butyl ammonium bromide (TBAB) + water system, the CO<sub>2</sub> + tetra-*n*-butyl ammonium chloride (TBAC) + water system, and the CO<sub>2</sub> + tetra-*n*-butyl ammonium fluoride (TBAF) + water system, were measured in the pressure range of (0.40 to 3.77 MPa) and temperature range of (280.2 to 293.5 K) at (2.93·10<sup>-3</sup> and 6.17·10<sup>-3</sup>) mole fraction of tetra-*n*-butyl ammonium halide. The experimental data were generated using an isochoric pressure-search method. The equilibrium data for the CO<sub>2</sub> + TBAB + water system were compared with some experimental data from the literature. The effects of tetra-*n*-butyl ammonium halide concentration on the stability zone of the semiclathrate hydrates were studied. It was shown that TBAB, TBAC, and TBAF all can enlarge the hydrate stability zone, and as the tetra-*n*-butyl ammonium halide concentration increases, so does the hydrate stability zone. The three-phase equilibrium pressure of the CO<sub>2</sub> + TBAF + water system is lower than others at the same temperature.

## Introduction

Clathrate hydrates are crystalline inclusion compounds which form through the combination of water and suitably sized “guest” molecules, typically under low temperature and elevated pressure conditions.<sup>1</sup> Within the clathrate lattice, water molecules form a network of hydrogen-bonded cavity structures that enclose the guests. Of more than 130 compounds that are known to form clathrate hydrates with water molecules, the majority form sI, sII, or sH<sup>1</sup>.

Some unusual hydrate structures are formed by tetra-*n*-alkyl ammonium salts at atmospheric pressure, which were first identified by Fowler et al.<sup>2</sup> Such a hydrate is called a semiclathrate hydrate crystal, because unlike clathrate hydrates where water molecules form hydrate cages and small guest molecules like methane are trapped inside cages, in semiclathrate hydrates, the halide anion displaces the water molecule in the framework, forming H-bonds together with water molecules, and the tetra-*n*-alkyl ammonium cation occupies four cages.<sup>3,4</sup> Recently, a semiclathrate hydrate, for example, tetra-*n*-butyl ammonium bromide (TBAB) hydrate, has been introduced as a cold storage material for its higher phase change temperature compared to that of ice.<sup>5,6</sup> In addition, TBAB or tetra-*n*-butyl ammonium fluoride (TBAF) hydrate has been used as a tool for gas storage or carbon dioxide capture because these gases can easily be encaged in empty cavities of semiclathrate under moderate conditions.<sup>7–11</sup> Many studies have reported the phase equilibrium conditions of semiclathrate hydrates of tetra-*n*-butyl ammonium salts with different gases, such as H<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and so forth.<sup>12–19</sup> However, most of these studies are limited to the high-concentration tetra-*n*-butyl ammonium salt region. In

**Table 1. Experimental Materials Used in This Work**

component	purity	supplier
CO <sub>2</sub>	0.999	Guangzhou Gases Co.
TBAB	0.99	Guangzhou Guanghua Chemical Co.
TBAC	0.99	Shanghai Kefeng Chemical Co.
TBAF·3H <sub>2</sub> O	0.99	Nanjing DeBioChem Co.
water		distilled

addition, the experimental hydrate equilibrium data for CO<sub>2</sub> + TBAF have not been reported.

The objective of this work is to measure systematically the hydrate formation conditions of CO<sub>2</sub> with low-concentration tetra-*n*-butyl ammonium halides, such as TBAB, tetra-*n*-butyl ammonium chloride (TBAC), and TBAF.

## Experimental Section

**Materials.** The purities and suppliers of the materials are provided in Table 1.

**Experimental Apparatus.** Figure 1 shows the schematic diagram of the apparatus used to determine the phase equilibrium conditions. The main part of the apparatus is a stainless steel cylinder with inner dimensions of 80 mm in diameter and 60 mm in height and is equipped with a magnetic stirrer to agitate the fluids and hydrate crystals inside the vessel.

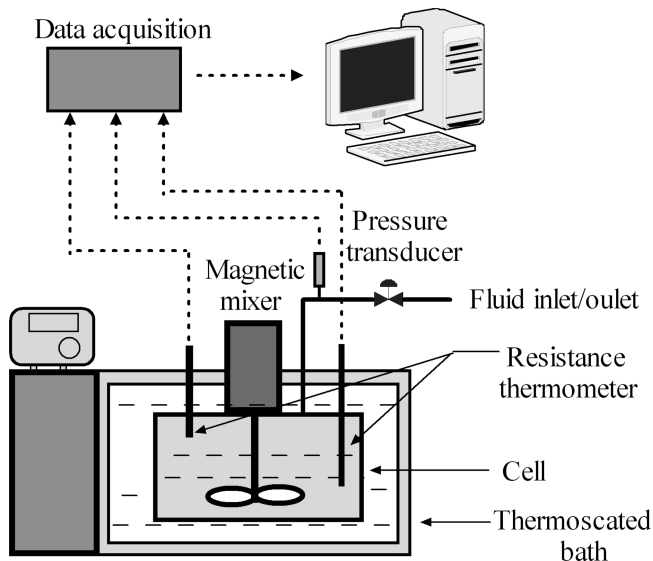
The equilibrium cell was designed to be operated at pressures up to 20 MPa. The cell was immersed in a thermostatted bath (Huber CC2-K20B) to maintain the temperature of the equilibrium cell at setting value. Two platinum resistance thermometers (Westzh WZ-PT100) within 0.1 K accuracy inserted into the cell were used to measure the temperatures in the gas and liquid phase. A pressure transducer (Senex DG-1300) within 0.01 MPa in accuracy measured the pressure inside of the vessel. The pressures and temperatures of the vessel were recorded by data logger (Agilent 34970A).

**Experimental Method.** The semiclathrate hydrate equilibria conditions were measured with an isochoric pressure-search

\* Corresponding author. Tel.: +86-20-22236581. Fax: +86-20-22236581. E-mail: ssfan@scut.edu.cn.

<sup>†</sup> Dalian University of Technology.

<sup>‡</sup> South China University of Technology.

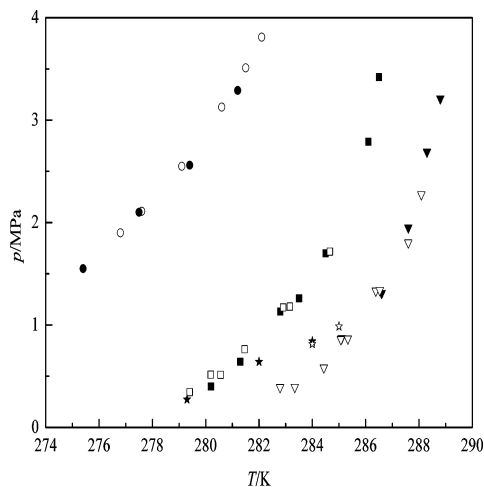


**Figure 1.** Schematic of the experimental apparatus used for phase equilibrium measurements.

**Table 2.** Measured Hydrate Formation Conditions for CO<sub>2</sub> in Water

<i>T</i> /K	<i>p</i> /MPa
275.4	1.55
277.5	2.10
279.4	2.56
281.2	3.29

method.<sup>20,21</sup> The cell containing liquids (approximately 150 mL) was immersed into the temperature-controlled bath. CO<sub>2</sub> was then supplied from a CO<sub>2</sub> gas cylinder through a pressure-regulating valve into the evacuated cell until the pressure inside the cell (*p*) was increased to the desired level. After *T* and *p* were stabilized, the valve in the line connecting the cell and cylinder was closed. Subsequently, the magnetic stirrer was initiated, and the temperature was decreased to form the hydrate. Hydrate formation in the cell was detected by a decrease in *p* and an increase in *T*. The temperature was then increased with steps of 0.1 K. At every temperature step, the temperature was held constant for 4 h to achieve



**Figure 2.** Phase equilibrium conditions for CO<sub>2</sub> + water and CO<sub>2</sub> + TBAB + water systems. CO<sub>2</sub> + water system: ●, this work; ○, ref 24. CO<sub>2</sub> + TBAB + water system: ■, 2.93·10<sup>-3</sup> mole fraction, this work; ▼, 6.17·10<sup>-3</sup> mole fraction, this work; □, 2.58·10<sup>-3</sup> mole fraction, ref 15; ▽, 5.51·10<sup>-3</sup> mole fraction, ref 15; ★, 2.90·10<sup>-3</sup> mole fraction, ref 9; ☆, 6.10·10<sup>-3</sup> mole fraction, ref 9.

**Table 3.** Hydrate Equilibrium Data for the CO<sub>2</sub> + TBAB + Water System Measured at 2.93·10<sup>-3</sup> and 6.17·10<sup>-3</sup> Mole Fraction of TBAB

<i>x</i>	<i>T</i> /K	<i>p</i> /MPa
2.93·10 <sup>-3</sup>	280.2	0.40
	281.3	0.64
	283.5	1.26
	285.1	1.71
	286.1	2.79
6.17·10 <sup>-3</sup>	286.5	3.42
	285.1	0.87
	286.6	1.31
	287.6	1.95
	288.3	2.69
	288.8	3.21

**Table 4.** Hydrate Equilibrium Data for the CO<sub>2</sub> + TBAC + Water System Measured at 2.93·10<sup>-3</sup> and 6.17·10<sup>-3</sup> Mole Fraction of TBAC

<i>x</i>	<i>T</i> /K	<i>p</i> /MPa
2.93·10 <sup>-3</sup>	280.1	0.47
	282.2	1.09
	283.5	1.93
	285.0	2.99
	285.4	3.62
6.17·10 <sup>-3</sup>	286.1	0.99
	286.8	1.41
	287.8	2.08
	288.3	2.99
	289.2	3.77

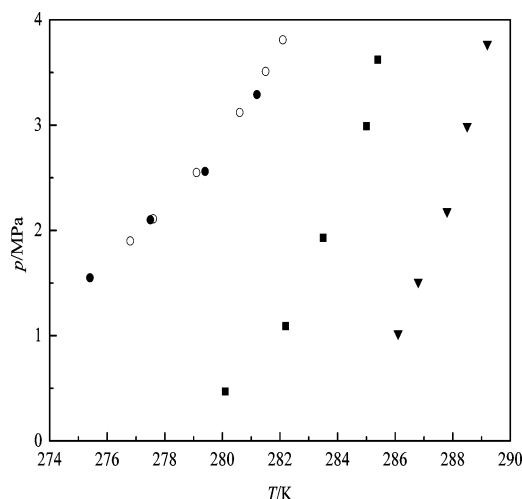
**Table 5.** Hydrate Equilibrium Data for the CO<sub>2</sub> + TBAF + Water System Measured at 2.93·10<sup>-3</sup> and 6.17·10<sup>-3</sup> Mole Fraction of TBAF

<i>x</i>	<i>T</i> /K	<i>p</i> /MPa
2.93·10 <sup>-3</sup>	285.7	0.53
	286.6	1.12
	287.2	1.64
	288.3	2.34
	288.8	3.00
6.17·10 <sup>-3</sup>	290.8	0.54
	291.4	0.75
	292.2	1.31
	293.0	1.90
	293.5	2.33

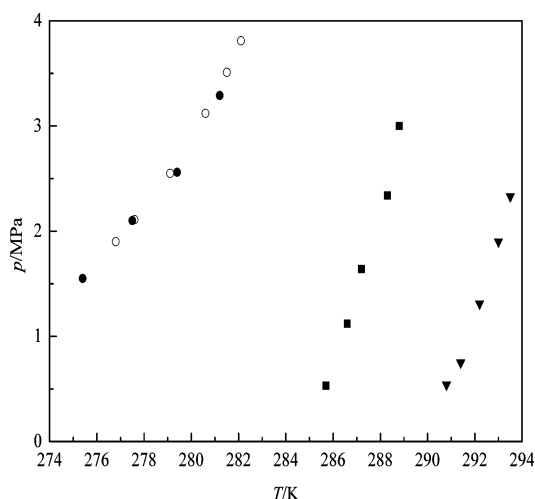
equilibrium state in the cell. In this way, a *p*–*T* diagram was obtained for each experimental run, from which the hydrate dissociation point was determined.<sup>22,23</sup> Consequently, the point at which the slope of the *p*–*T* curve plots sharply changed was considered to be the hydrate dissociation point at which all hydrate crystals have dissociated completely.

## Results and Discussion

For checking the experimental apparatus and procedure adapted in this work, the hydrate formation pressures of CO<sub>2</sub> in water were measured and compared with the data reported in the literature.<sup>24</sup> The measured data are listed in Table 2, and the comparison with literature data is plotted in Figures 2 to 4. From Figures 2 to 4, it can be seen that the data of this work match very well with the literature data. Experimental three-phase equilibrium data for CO<sub>2</sub> in the presence of different aqueous solutions of TBAB, TBAC, and TBAF are given in the Tables 3 to 5. Initially, the data for the CO<sub>2</sub> + TBAB + water system were measured and compared with the literature data. As shown in Figure 2, the experimental *p*–*T* data were consistent with those of ref 15, but there was a large discrepancy between our data and those of ref 9. In ref 15, Lin et al. had a suspicion against the remarks and results of ref 9, so our experimental data supported the point of Lin et al. again. In Figure 2, it is clearly that hydrate equilibrium pressures were decreased apparently with addition of TBAB, and the greater



**Figure 3.** Phase equilibrium conditions for the CO<sub>2</sub> + water and CO<sub>2</sub> + TBAC + water systems. CO<sub>2</sub> + water system: ●, this work; ○, ref 24. CO<sub>2</sub> + TBAC + water system: ■, 2.93·10<sup>−3</sup> mole fraction; ▼, 6.17·10<sup>−3</sup> mole fraction.



**Figure 4.** Phase equilibrium conditions for the CO<sub>2</sub> + water and CO<sub>2</sub> + TBAF + water systems. CO<sub>2</sub> + water system: ●, this work; ○, ref 24. CO<sub>2</sub> + TBAF + water system: ■, 2.93·10<sup>−3</sup> mole fraction; ▼, 6.17·10<sup>−3</sup> mole fraction.

decrease was observed with the higher mole fraction TBAB (6.17·10<sup>−3</sup>).

Similarly, the same promoter effects on hydrate formation were also found in the presence of TBAC. In Figure 3, the phase equilibrium conditions for CO<sub>2</sub> + TBAC + water were measured. It was also found that hydrate stability zone enlarged with TBAC concentration (from 2.93·10<sup>−3</sup> to 6.17·10<sup>−3</sup>). As shown in Figure 4, at a given pressure, the three-phase equilibrium temperatures with 2.93·10<sup>−3</sup> mole fraction of TBAF were higher by about 10 K than those in the CO<sub>2</sub> + water system. In comparison with the results of Figure 2 to 4, it was also notable found that with both mole fractions of tetra-*n*-butyl ammonium halide, the three-phase equilibrium pressure of CO<sub>2</sub> + TBAF + water system was lower than others at the same temperature.

## Conclusion

This work reports hydrate equilibrium data for the semiclathrate hydrates formed in three three-component systems: the CO<sub>2</sub> + TBAB + water system, the CO<sub>2</sub> + TBAC + water system, and the CO<sub>2</sub> + TBAF + water system, which were measured

in the pressure range of (0.40 to 3.77) MPa and temperature range of (280.2 to 293.5) K at 2.93·10<sup>−3</sup> and 6.17·10<sup>−3</sup> mole fraction of tetra-*n*-butyl ammonium halide. An isochoric pressure-search method was used to perform all of the measurements. The comparison of the hydrate equilibrium data for the above-mentioned systems with the CO<sub>2</sub> + water system<sup>23</sup> showed that tetra-*n*-butyl ammonium halide (TBAB, TBAC, and TBAF) can enlarge the hydrate stability zone. As the tetra-*n*-butyl ammonium halide concentration increases, so does the hydrate stability zone. The three-phase equilibrium pressure of the CO<sub>2</sub> + TBAF + water system is lower than others at the same temperature.

## Literature Cited

- (1) Sloan, E. D.; Koh, C. A. *Clathrate Hydrates of Natural Gases*, 3rd ed.; 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) Dyadin, Yu. A.; Udachin, K. A. Clathrate formation in water-peralkylonium salts systems. *J. Inclusion Phenom.* **1984**, *2*, 61–72.
- (4) Shimada, W.; Shiro, M.; Kondo, H.; Takeya, S.; Oyama, H.; Ebinuma, T.; Narita, H. Tetra-*n*-butylammonium bromide-water (1/38). *Acta Crystallogr., Sect. C* **2005**, *61*, o65–o66.
- (5) Tanasawa, I.; Takao, S. In *Clathrate hydrate slurry of tetra-*n*-butylammonium bromide as a cold-storage material*, Proceedings of the Fourth International Conference on Gas Hydrates, Yokohama, Japan, May 19–23, 2002; pp 963–967.
- (6) Darboret, M.; Cournil, M.; Herri, J. Rheological study of TBAB hydrate slurries as secondary two-phase refrigerants. *Int. J. Refrig.* **2005**, *28*, 663–671.
- (7) Strobel, T. A.; Koh, C. A.; Sloan, E. D. Hydrogen storage properties of clathrate hydrate materials. *Fluid Phase Equilib.* **2007**, *261*, 382–389.
- (8) 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.
- (9) Duc, N. H.; Chauvy, F.; Herri, J. M. CO<sub>2</sub> capture by hydrate crystallization-A potential solution for gas emission of steelmaking industry. *Energy Convers. Manage.* **2007**, *48*, 1313–1322.
- (10) Fan, S. S.; Li, S. F.; Wang, J. Q.; Lang, X. M.; Wang, Y. H. Efficient capture of CO<sub>2</sub> from simulated flue gas by formation of TBAB or TBAF semiclathrate hydrates. *Energy Fuels* **2009**, *23*, 4202–4208.
- (11) Li, S. F.; Fan, S. S.; Wang, J. Q.; Lang, X. M.; Liang, D. Q. CO<sub>2</sub> capture from binary mixture via forming hydrate with the help of tetra-*n*-butyl ammonium bromide. *J. Nat. Gas Chem.* **2009**, *18*, 15–20.
- (12) Arjmandi, M.; Chapoy, A.; Tohidi, B. Equilibrium data of hydrogen, methane, nitrogen, carbon dioxide, and natural gas in semi-clathrate hydrates of tetra-*n*-butyl ammonium bromide. *J. Chem. Eng. Data* **2007**, *52*, 2153–2158.
- (13) Li, D. L.; Du, J. W.; Fan, S. S.; Liang, D. Q.; Li, X. S.; Huang, N. S. Clathrate dissociation conditions for methane + tetra-*n*-butyl Ammonium bromide (TBAB) + Water. *J. Chem. Eng. Data* **2007**, *52*, 1916–1918.
- (14) 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.
- (15) Lin, W.; Delahaye, A.; Fournaison, L. Phase equilibrium and dissociation enthalpy semi-clathrate hydrate of CO<sub>2</sub> + TBAB. *Fluid Phase Equilib.* **2008**, *264*, 220–227.
- (16) 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.
- (17) Mayoufi, N.; Dalmazzone, D.; Furst, W.; Delahaye, A.; Fournaison, L. CO<sub>2</sub> enclathration in hydrates of peralkyl-(ammonium/phosphonium) salts: stability conditions and dissociation enthalpies. *J. Chem. Eng. Data* **2009**; DOI: 10.1021/jc9006212.
- (18) Makino, T.; Yamamoto, T.; Nagata, K.; Sakamoto, H.; Hashimoto, S.; Sugahara, T.; Ohgaki, K. Thermodynamic stabilities of tetra-*n*-butyl ammonium chloride + H<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub>, or C<sub>2</sub>H<sub>6</sub> semiclathrate hydrate systems. *J. Chem. Eng. Data* **2010**, *55*, 839–841.
- (19) Johnny, D.; Didier, D. Dissociation enthalpies and phase equilibrium for TBAB semi-clathrate hydrates of N<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub> + CO<sub>2</sub> and CH<sub>4</sub> + CO<sub>2</sub>. *J. Therm. Anal. Calorim.* **2009**, *98*, 113–118.
- (20) Tohidi, B.; Burgass, R. W.; Danesh, A.; Østergaard, K. K.; Todd, A. C. Improving the accuracy of gas hydrate dissociation point measurements. *Ann. N.Y. Acad. Sci.* **2000**, *912*, 924–931.

- (21) Majumdar, A.; Mahmoodaghdam, E.; Bishnoi, P. R. Equilibrium hydrate formation conditions for hydrogen sulfide, carbon dioxide, and ethane in aqueous solutions of ethylene glycol and sodium chloride. *J. Chem. Eng. Data* **2000**, *45*, 20–22.
- (22) Imai, S.; Okutani, K.; Ohmura, R.; Mori, Y. H. Phase equilibrium for clathrate hydrates formed with difluoromethane + either cyclopentane or tetra-*n*-butylammonium bromide. *J. Chem. Eng. Data* **2005**, *50*, 1783–1786.
- (23) Ohmura, R.; Takeya, S.; Maekawa, T.; Uchida, T. Phase equilibrium for structure-H hydrate formed with krypton and 2,2-Dimethylbutane. *J. Chem. Eng. Data* **2006**, *51*, 161–163.
- (24) Adisasmito, S.; Frank, R. J.; Sloan, E. D. Hydrates of carbon dioxide and methane mixture. *J. Chem. Eng. Data* **1991**, *36*, 68–71.

Received for review January 19, 2010. Accepted March 1, 2010. The authors greatly acknowledge the National Natural Science Foundation of China (No. 20876019) and the National High Technology Research and Development Program (“863” Program) of China (No. 2007AA03Z229).

JE100059H