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Semiclathrate Hydrate Phase Equilibria for CO_2 in the Presence of Tetra-*n*-butyl Ammonium Halide (Bromide, Chloride, or Fluoride)

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Phase equilibrium data for the semiclathrate hydrates formed in three three-component systems, the CO_2 + tetra-*n*-butyl ammonium bromide (TBAB) + water system, the CO_2 + tetra-*n*-butyl ammonium chloride (TBAC) + water system, and the CO_2 + 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 $(2.93 \cdot 10^{-3}$ and $6.17 \cdot 10^{-3})$ 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_2 + 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_2 + 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.[1] 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[1].

Some unusual hydrate structures are formed by tetra-*n*-alkyl ammonium salts at atmospheric pressure, which were first identified by Fowler et al.[2] 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.[3,4] 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.[5,6] 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 been encaged in empty cavities of semiclathrate under moderate conditions.[7-11] Many studies have reported the phase equilibrium conditions of semiclathrate hydrates of tetra-*n*-butyl ammonium salts with different gases, such as H_2, CO_2, N_2, CH_4, and so forth.[12-19] 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_2	0.999	Guangzhou Gases Co.
TBAB	0.99	Guangzhou Guanghua Chemical Co.
TBAC	0.99	Shanghai Kefeng Chemical Co.
$TBAF \cdot 3H_2O$	0.99	Nanjing DeBioChem Co.
water		distilled

addition, the experimental hydrate equilibrium data for CO_2 + TBAF have not been reported.

The objective of this work is to measure systematically the hydrate formation conditions of CO_2 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

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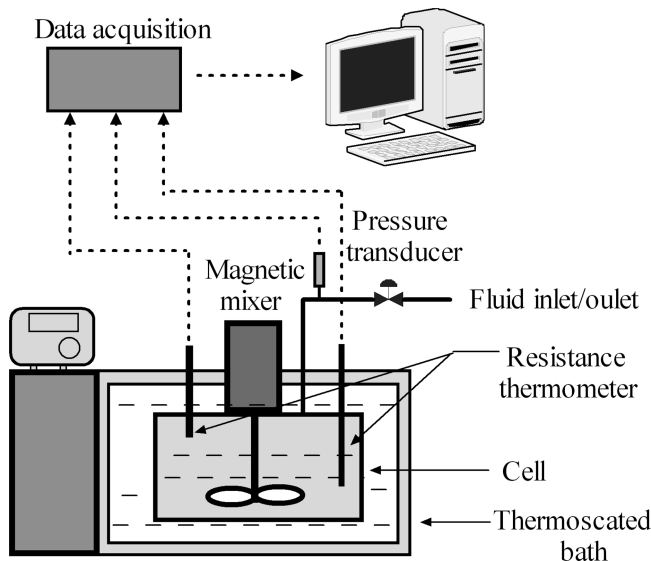**Figure 1.** Schematic of the experimental apparatus used for phase equilibrium measurements.

Table 2. Measured Hydrate Formation Conditions for CO_2 in Water

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

method.[20,21] The cell containing liquids (approximately 150 mL) was immersed into the temperature-controlled bath. CO_2 was then supplied from a CO_2 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
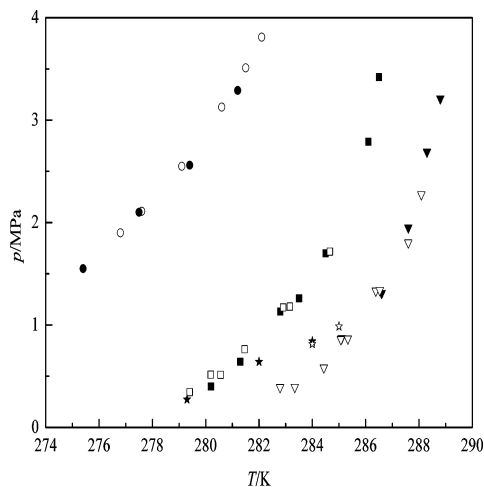

Figure 2. Phase equilibrium conditions for CO_2 + water and CO_2 + TBAB + water systems. CO_2 + water system: ●, this work; ○, ref 24. CO_2 + TBAB + water system: ■, $2.93 \cdot 10^{-3}$ mole fraction, this work; ▼, $6.17 \cdot 10^{-3}$ mole fraction, this work; □, $2.58 \cdot 10^{-3}$ mole fraction, ref 15; ▽, $5.51 \cdot 10^{-3}$ mole fraction, ref 15; ★, $2.90 \cdot 10^{-3}$ mole fraction, ref 9; ☆, $6.10 \cdot 10^{-3}$ mole fraction, ref 9.

Table 3. Hydrate Equilibrium Data for the CO_2 + TBAB + Water System Measured at $2.93 \cdot 10^{-3}$ and $6.17 \cdot 10^{-3}$ Mole Fraction of TBAB

x	T/K	p/MPa
$2.93 \cdot 10^{-3}$	280.2	0.40
	281.3	0.64
	283.5	1.26
	285.1	1.71
	286.1	2.79
	286.5	3.42
$6.17 \cdot 10^{-3}$	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_2 + TBAC + Water System Measured at $2.93 \cdot 10^{-3}$ and $6.17 \cdot 10^{-3}$ Mole Fraction of TBAC

x	T/K	p/MPa
$2.93 \cdot 10^{-3}$	280.1	0.47
	282.2	1.09
	283.5	1.93
	285.0	2.99
	285.4	3.62
$6.17 \cdot 10^{-3}$	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_2 + TBAF + Water System Measured at $2.93 \cdot 10^{-3}$ and $6.17 \cdot 10^{-3}$ Mole Fraction of TBAF

x	T/K	p/MPa
$2.93 \cdot 10^{-3}$	285.7	0.53
	286.6	1.12
	287.2	1.64
	288.3	2.34
	288.8	3.00
$6.17 \cdot 10^{-3}$	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.[22,23] 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_2 in water were measured and compared with the data reported in the literature.[24] 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_2 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_2 + 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
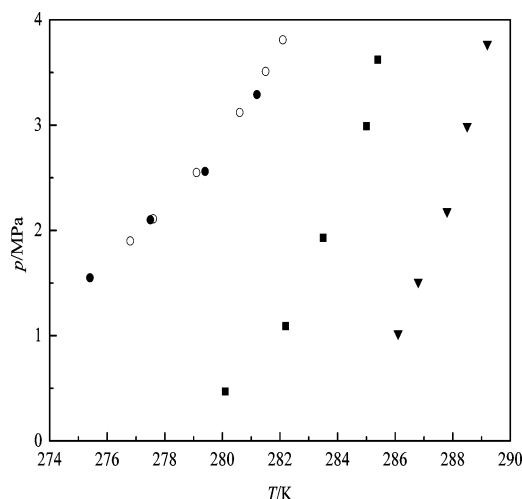
Figure 3. Phase equilibrium conditions for the CO_2 + water and CO_2 + TBAC + water systems. CO_2 + water system: ●, this work; ○, ref 24. CO_2 + TBAC + water system: ■, $2.93 \cdot 10^{-3}$ mole fraction; ▼, $6.17 \cdot 10^{-3}$ mole fraction.
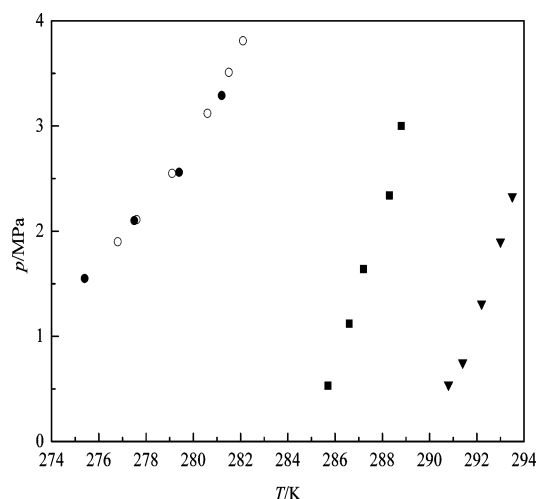

Figure 4. Phase equilibrium conditions for the CO_2 + water and CO_2 + TBAF + water systems. CO_2 + water system: ●, this work; ○, ref 24. CO_2 + TBAF + water system: ■, $2.93 \cdot 10^{-3}$ mole fraction; ▼, $6.17 \cdot 10^{-3}$ mole fraction.

decrease was observed with the higher mole fraction TBAB ($6.17 \cdot 10^{-3}$).

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_2 + TBAC + water were measured. It was also found that hydrate stability zone enlarged with TBAC concentration (from $2.93 \cdot 10^{-3}$ to $6.17 \cdot 10^{-3}$). As shown in Figure 4, at a given pressure, the three-phase equilibrium temperatures with $2.93 \cdot 10^{-3}$ mole fraction of TBAF were higher by about 10 K than those in the CO_2 + 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_2 + 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_2 + TBAB + water system, the CO_2 + TBAC + water system, and the CO_2 + 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 $2.93 \cdot 10^{-3}$ and $6.17 \cdot 10^{-3}$ 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_2 + water system[23] 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_2 + TBAF + water system is lower than others at the same temperature.

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