Hydrate Equilibrium Data for Methane + *tert*-Butylamine + Water

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Hydrate equilibrium pressures of methane + *tert*-butylamine + water were investigated in the temperature range of (281.2 to 295.2) K and in the pressure range of (2.69 to 8.46) MPa at (0.01, 0.056, and 0.097) mole fraction of *tert*-butylamine. Measurements were made using an isochoric method. The addition of *tert*-butylamine causes the hydrate equilibrium pressure to be lowered. In the case of higher mole fraction $x = (0.056, 0.097)$, the hydrate has a lower equilibrium pressure than that of mole fraction $x = (0.01)$.

Introduction

Clathrate hydrate, or gas hydrate, is a nonstoichiometric clathrate crystalline compound. It is an ice-like substance which is formed by water and gas (methane, ethane, or carbon dioxide, etc.) under certain temperature and pressure conditions. Besides academic interest, natural-gas storage and transportation based on hydrate may be a potential application. The high equilibrium pressures of gas hydrates are a major drawback in this application. By adding water-soluble organic compounds such as tetrahydrofuran and tetrabutyl ammonium bromide, hydrate equilibrium pressures can be reduced significantly.[1-4] In general, gas hydrates crystallize in three distinct structures, structures I, II, and H, depending on the nature and the size of the guest molecule.[5] In addition, there are a variety of more complex clathrate hydrate structures, named as types III to VII and structure T(sT).[6-8] The *tert*-butylamine clathrate hydrate, which was designated as a type VI structure, is a true clathrate as there is no evidence of hydrogen bonding between host water and guest amine molecules, and its structure is shown in Figure 1.[9] *tert*-Butylamine molecules occupy large complex cages with 17 sides ($4^3 5^9 6^2 7^3$), while the small cages ($4^4 5^4$) remain empty.[9] Kim et al. have reported a structural transition of the simple amine hydrate to produce a novel double (methane + *tert*-butylamine) hydrate as confirmed by using microscopic analytical methods.[10] Sloan et al.[11] have investigated a possible structural transformation for double (hydrogen + *tert*-butylamine) hydrate. So, *tert*-butylamine may be made as a stabilizer to reduce hydrate equilibrium pressure. In this paper, hydrate equilibrium pressures of methane + *tert*-butylamine + water have been measured at (0.01, 0.056, and 0.097) mole fraction of *tert*-butylamine in the temperature range of (281.2 to 295.2) K and in the pressure range of (2.69 to 8.46) MPa. Measurements were made using an isochoric method.

Experimental Section

The experimental apparatus and procedures employed in this work were described in detail by Sun et al.[12-15] Figure 2 shows the schematic diagram of the apparatus. The equilibrium cell is a "full view" sapphire variable-volume cell with a movable piston. The cell consists of a sapphire tube sealed at the top end with a stainless steel flange. The test contents were mixed
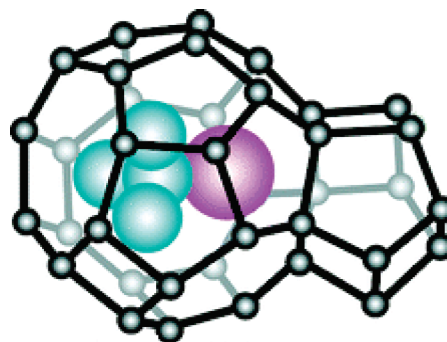

Figure 1. *tert*-Butylamine hydrate (sVI).

through a stirrer which was driven by a dc motor located at the end of the piston and a magnetic coupling mounted outside the cell. The cell pressure was measured using a TF01 400A absolute pressure transducer [(0 to 40) MPa] and gave uncertainties of about 0.06 % of full scale. The cell temperature was measured using platinum resistance thermometers with an uncertainty of ± 0.1 K. The cell volume was adjusted with the movable piston. The data from the acquisition system were saved at preset sampling intervals on a computer.

The source and purity of materials used in this work are described in Table 1. The cell was washed with distilled water and the *tert*-butylamine aqueous solutions thrice, respectively. The cell was initially charged with approximately 20 mL of solutions by an injector. Next, the cell was vacuumed, and methane was intaken subsequently. The hydrate equilibrium was established using an isochoric pressure search method. In this way, a pressure–temperature diagram was obtained for each experimental run, from which the hydrate dissociation point was determined.[16-18]

After the sample had been charged in the cell, the temperature was lowered to form hydrates. The temperature was then raised stepwise; the temperature was kept constant; and sufficient time was allowed to achieve a steady equilibrium state at each temperature. The temperature and pressure were measured continuously, and the equilibrium data were plotted. The point at which the slope of the P–T curve sharply changed was considered as the hydrate dissociation point at which all hydrate crystals have dissociated. This was also confirmed by visual observation.

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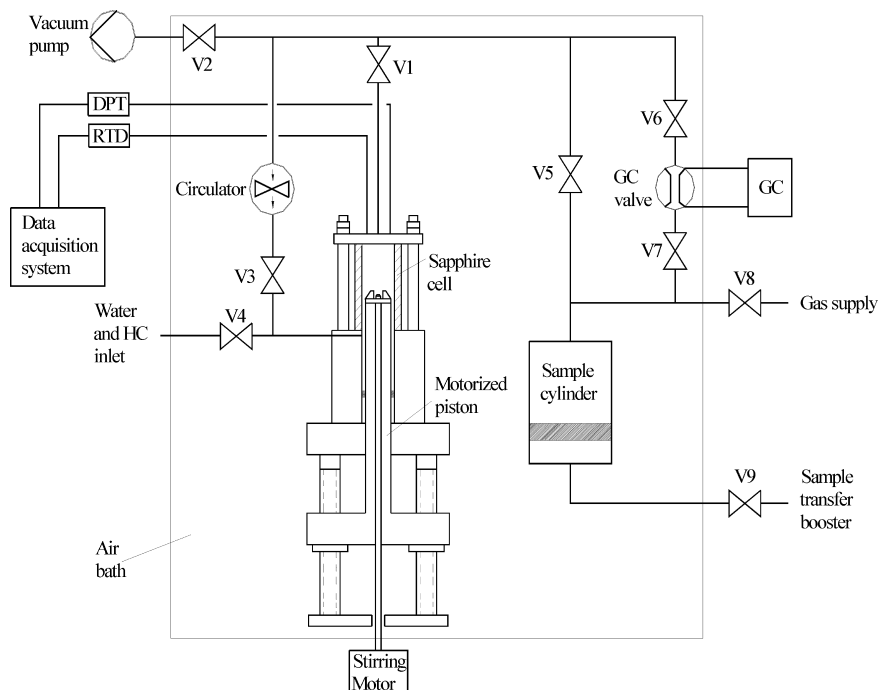
Figure 2. Schematic diagram of the experimental apparatus. DPT, differential pressure transducer; RTD, resistance temperature detector; V1 to V9, valves.
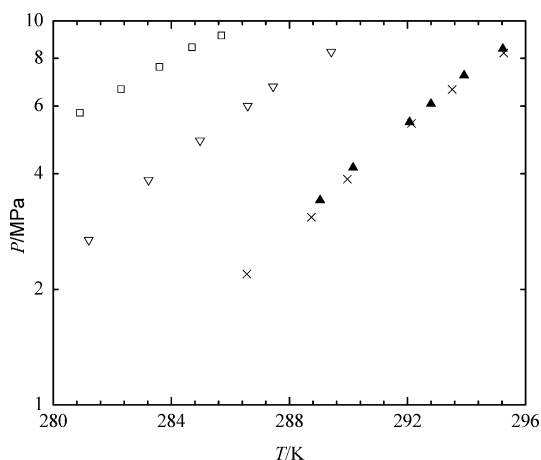
Table 1. Experimental Materials Used in This Work

component	purity	supplier
methane	99.99%	Fushan Kede Gas Co.
tert-butylamine	> 99.5%	Tianjing Bodi Chemical Co., Ltd.
water		distilled

Results and Discussion

In Figure 3, measured equilibrium data for methane + *tert*-butylamine + water hydrate are compared with those for simple methane.[19] Table 2 presents the measured hydrate equilibrium data of the methane + *tert*-butylamine + water system at (0.01, 0.056, and 0.097) mole fraction of *tert*-butylamine. Here, we note that the mixed methane (hydrogen) + *tert*-butylamine hydrate forms structure II at various *tert*-butylamine concentrations.[9,10] As shown in Figure 3, at 0.056 mole fraction of *tert*-butylamine, the stoichiometric amount of *tert*-butylamine participates in forming the mixed structure II hydrate with methane, and the equilibrium pressure is the lowest. At 0.097 mole

Table 2. Hydrate Equilibrium Pressures of the Methane + *tert*-Butylamine + Water System Measured at Three Different Mole Fractions *x* of *tert*-Butylamine

x	T/K	P/MPa
0.01	281.20	2.69
	283.23	3.85
	284.97	4.88
	286.59	6.01
	287.45	6.75
	289.42	8.31
0.056	286.56	2.19
	288.74	3.08
	289.97	3.87
	292.14	5.41
	293.52	6.63
	295.26	8.25
0.097	289.04	3.41
	290.16	4.15
	292.07	5.45
	292.80	6.08
	293.92	7.21
	295.23	8.46

fraction of *tert*-butylamine, methane molecules can occupy only the small cages of the mixed hydrate, which is same as that of 0.056 mole fraction, and the hydrate equilibrium pressures are close to those of 0.056 mole fraction of *tert*-butylamine, which indicates that the increase of *tert*-butylamine mole fraction does not show a noticeable effect on equilibrium pressures. At 0.01 mole fraction of *tert*-butylamine, methane molecules can occupy both small and large cages of the mixed hydrate, and the hydrate equilibrium pressures appear the highest among three mole fractions of *tert*-butylamine.

Figure 3 shows that the addition of *tert*-butylamine leads to the hydrate equilibrium pressure lower by from (42.8 to 79.3) % at a specified temperature depending on the mole fraction of *tert*-butylamine. *tert*-Butylamine should be a better substance for stabilizing the mixed hydrates.

Figure 3. Hydrate equilibrium pressures for □, methane + water, ref 19; and methane + *tert*-butylamine + water. ▽, 0.01 mole fraction; ×, 0.056 mole fraction; ▲, 0.097 mole fraction.

Conclusions

This work presents hydrate equilibrium data for methane + *tert*-butylamine + water at (0.01, 0.056, and 0.097) mole fraction

of *tert*-butylamine in the temperature range of (281.2 to 295.2) K and in the pressure range of (2.69 to 8.46) MPa. The data were obtained using an isochoric method. Measurements show that the addition of *tert*-butylamine causes the hydrate equilibrium pressure to be lowered. Hence, *tert*-butylamine could be used as a stabilizer for reducing hydrate equilibrium pressure.

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