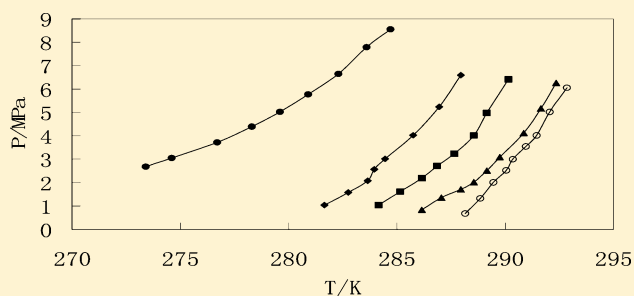


Equilibrium Conditions of Methane in Semiclathrate Hydrates of Tetra-*n*-butylammonium Chloride

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ABSTRACT: The phase equilibrium data for semiclathrate hydrates of tetra-*n*-butylammonium chloride (TBAC) + methane with TBAC mass fractions (w) of 0.0500, 0.0997, 0.2000, and 0.3001 are measured in the temperature range of (281.65 to 292.85) K using a visual high-pressure phase equilibrium apparatus. The experimental data are generated using an isochoric step-heating method (T -cycle method). Methane partially occupied the small cages of TBAC semiclathrate hydrates, which increases the stability of the hydrates. The phase equilibrium pressure of TBAC + methane hydrates increases with the increase of temperature at a specified TBAC concentration. The experimental results present that the presence of TBAC decreases the formation pressure of methane hydrate greatly. Moreover, pressure reduction is dependent on the TBAC concentration. The experimental data also show that TBAC is a kind of promoter for methane hydrate formation.



INTRODUCTION

Clathrate hydrates are ice-like crystalline compounds. Gas hydrates are formed by the combination of water molecules (the host) and suitably sized gas molecules (the guest). These hydrate cages are composed of hydrogen-bonded water molecules. Guest molecules interact with water molecules through van der Waals forces. Generally, the guest molecules encaged in the hydrate do not participate in forming hydrate lattices.¹

Some quaternary ammonium salts such as tetra-*n*-butylammonium bromide (TBAB) and chloride (TBAC) were found to form semiclathrate hydrates with water molecules at atmospheric pressure. In semiclathrate hydrates, halide anions such as Br⁻ and Cl⁻ are bound to the water molecules through hydrogen bonds and join host frameworks, some of which entrap tetra-*n*-butylammonium cations. In gas hydrates, the guest molecules are not physically bonded to water lattices, while in semiclathrate hydrates, guest molecules can both form part of the host lattice and occupy cages after breaking part of the cage structure.²

In recent years, semiclathrate hydrates have been paid more attention for different technologies such as gas separation, gas storage, and cold storage. Arjmandi et al.,³ Hashimoto et al.,⁴ Sakamoto et al.,⁵ Makino et al.,⁶ Deschamps and Dalmazzone,⁷ and Chapoy et al.⁸ showed that H₂ can be stored in the TBAB, TBAC, or TBAF semiclathrate hydrates. Shimada et al.⁹ and Lee et al.¹⁰ confirmed that small molecules such as nitrogen and methane could be incorporated into TBAB semiclathrate hydrates, while the larger gas molecules such as ethane or propane were not incorporated into the semiclathrate hydrates. Kamata et al.¹¹ reported that hydrogen sulfide was encaged during TBAB hydrate formation and separated successfully. Some researchers reported that the addition of TBAB, TBAC, or TBAF into the mixed CO₂ gas hydrates could give a remarkable

pressure reduction for hydrate formation in the application to the process for capturing CO₂.^{12–14} Semiclathrate hydrates such as TBAB or TBAC hydrate was also introduced as a heat transport material because of its higher phase change temperature and saving energy compared to ice production.^{15–18}

Tetra-*n*-butyl ammonium chloride can form three crystal structures of the semiclathrate hydrates (TBAC·24H₂O, TBAC·30H₂O, and TBAC·32H₂O) with different aqueous solution concentrations.¹⁹ TBAC hydrates have prospects for a medium for gas storage and separation similar to the TBAB hydrates.^{6,7,14} However, phase equilibrium data of TBAC + gas hydrate are not enough. In the present work, the results of TBAC + methane hydrate phase equilibrium data are reported in the TBAC mass fraction range of (0.05 to 0.30). The equilibrium pressures of hydrate formation of TBAC + methane are lower than those of methane in pure water.

EXPERIMENTAL APPARATUS AND PROCEDURE

Experimental Apparatus. The experimental apparatus is sketched in Figure 1, which was the same as the previous one.²⁰ A stainless steel cell is used for hydrate formation and dissociation. The stainless steel cell is a cylindrical high-pressure cell. Its available volume is about 300 cm³. The cell is designed to operate at pressures up to 20 MPa and temperatures in the range of (253 to 323) K. There are two Plexiglas windows in the wall of the cell. Hydrate formation and dissociation can be also viewed from the windows. A stainless-steel flange, which has appropriate ports for access to the interior, is used to seal

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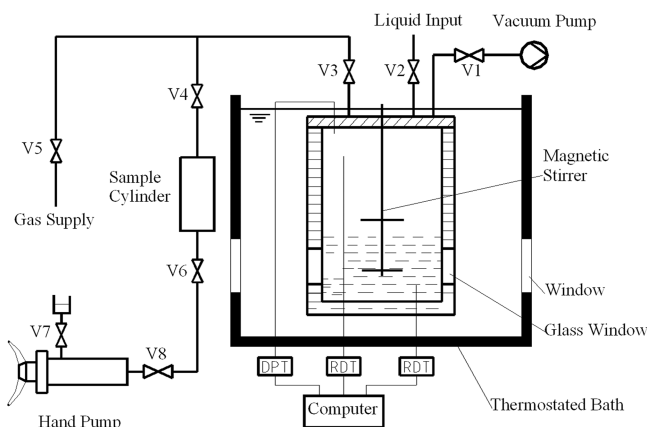


Figure 1. Schematic diagram of the experimental apparatus. DPT, differential pressure transducer; RTD, resistance temperature detector; V1–V8, valves.

the cell on the cell top. A magnetic stirrer is used to agitate the test fluids and hydrate crystals.

The cell was immersed in a temperature-controlled bath to maintain the temperature of the vessel T at a prescribed level. A platinum resistance thermometer (± 0.1 K) was placed inside the high-pressure cell to measure the temperature of the test fluids. A PTX7517 absolute pressure transducer ((0 to 10) MPa, ± 0.2 % of the full scale) was used to measure the test fluid pressure. A data acquisition system was used to collect data for temperature and pressure during the experiments.

Experimental Procedure. The test materials used in this work were described in Table 1. The methane gas was purchased

Table 1. Test Materials Used in This Work

component	purity	supplier
TBAC	≥ 99.0 %	Guangzhou Jinhua Chemical Reagent Co., Ltd.
methane	99.99 %	Fushan Kede Gas Co.
water	distilled	

from Kede Gas Co., which was research-grade pure gas (99.99 %). TBAC was also research-grade chemicals (≥ 99.0 % purity). Distilled water was used to dilute TBAC to the desired TBAC aqueous solution in the experiments. Appropriate quantities of TBAC and distilled water were weighed on an electronic balance with a readability of ± 0.1 mg (model CP225D, Sartorius Co., Ltd.).

Prior to each test, the cell was rinsed with distilled water two times, and then the cell and its loading lines were evacuated. The TBAC aqueous solution was introduced into the evacuated cell. Then methane was introduced into the cell to the desired experimental pressure from the sample cylindrical cell. In this work, an isochoric step-heating method (T -cycle method) was used for hydrate–liquid–vapor three-phase equilibrium measurements.^{3,4,21} After the test fluids were charged into the cell, the cell and the test fluids were cooled to form the hydrate. Once the temperature of the solution in the cell reached the desired temperature, the magnetic stirrer started to work. The presence of hydrates was determined visually from the windows of the cell. A large amount of hydrates were observed, while the temperatures of the test fluids increased to dissociate the hydrates. Then the temperature of test fluid lowered and reached the desired temperature again. A large amount of hydrates were observed again. The temperature of the thermostatted bath was

kept constant for (3 to 5) h, thereby keeping the temperature of the solution in the cell constant. Then the test fluids were heated very gradually and step by step (0.1 K each) until there was a negligibly small amount of hydrate left. Sufficient time (>5 h) was given to reach equilibrium state at each temperature step. When the last small hydrate dissociated completely during the heating in steps, this point was considered as the equilibrium point. More methane gas was introduced into the cell after each test up to the highest pressure of the test system. A different concentration solution of TBAC was subsequently selected, and the procedure was repeated to obtain the other hydrate equilibrium data.

RESULTS AND DISCUSSION

Phase equilibrium relations (pressure–temperature) for methane–TBAC semicathrate hydrates at various TBAC concentrations are summarized in Table 2. The data are also plotted

Table 2. Equilibrium Conditions for Methane and TBAC at Different TBAC Mass Fractions w in Water

w	T/K	P/MPa	w	T/K	P/MPa
0.3001	288.15	0.678	0.20	286.15	0.838
	288.85	1.324		287.05	1.358
	289.45	2.009		287.95	1.709
	290.05	2.523		288.55	2.014
	290.35	3.001		289.15	2.511
	290.95	3.545		289.75	3.086
	291.45	4.013		290.85	4.115
	292.05	5.017		291.65	5.168
	292.85	6.054		292.35	6.256
	292.85	6.054		292.35	6.256
0.0997	284.15	1.035	0.05	281.65	1.038
	285.15	1.617		282.75	1.577
	286.15	2.187		283.65	2.081
	286.85	2.706		283.95	2.570
	287.65	3.237		284.45	3.011
	288.55	4.010		285.75	4.022
	289.15	4.978		286.95	5.239
	290.15	6.411		287.95	6.593

in Figure 2. Figure 3 compares the hydrate formation conditions for methane + TBAC system with those for the methane

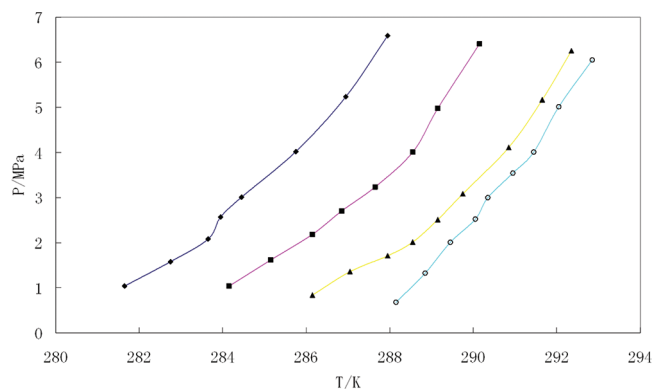


Figure 2. Hydrate formation conditions for methane + TBAC. \blacklozenge , $w = 0.05$; \blacksquare , $w = 0.0997$; \blacktriangle , $w = 0.20$; \circ , $w = 0.3001$.

system.^{6,22} As shown in Figure 2, the phase equilibrium pressure of methane + TBAC hydrates increases with the increase of temperature at a specified TBAC concentration while the hydrate equilibrium temperature reduces with the increase of

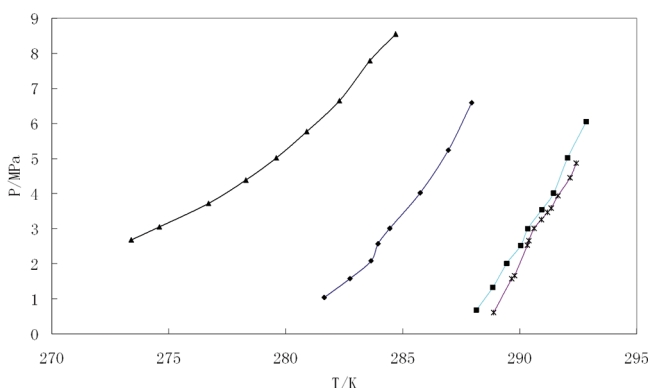


Figure 3. Comparison of hydrate equilibrium data for methane and methane + TBAC. ◆, $w = 0.05$; ■, $w = 0.3001$; *, $w = 0.3398$, ref 6; ▲, no TBAC, ref 22.

TBAC solution concentration at a specified pressure. Figure 2 also showed that data curves had inflection points. It might be hydrate structural phase transition. But it is necessary to confirm the structure transition by measurements using suitable physical techniques.

Figure 3 shows that when TBAC was present in the test system there was a drastic depression of the binary hydrate formation conditions by 5 MPa at a specified temperature in this work (for example, when T is (282.75 and 283.95) K, the hydrate equilibrium p is (1.577 and 2.570) MPa for methane + TBAC ($w = 0.05$) system, respectively, while when T is (282.3 and 283.6) K, the hydrate equilibrium p is (6.65 and 7.79) MPa for methane system, respectively). Figure 3 also shows that the shift phenomenon of equilibrium pressures for methane and TBAC solutions ($w = 0.3001$) system was similar to that of the methane and TBAC solutions ($w = 0.3398$) system by Makino et al.,⁶ but the shift of the hydrate phase boundary was smaller in this work. The results showed that methane was engaged into semiclathrate hydrates. The experimental results also showed that the binary hydrate formed with TBAC was more stable than methane hydrate in our experimental test region.

CONCLUSIONS

In this work, the phase boundaries of methane and TBAC binary hydrate are measured. The experimental TBAC mass fractions in the range of (0.05 to 0.30) and temperature range of (281.65 to 292.85) K have been investigated. The results show that the addition of TBAC reduces the formation pressures of methane hydrate by 5 MPa. Methane uptake into semiclathrate hydrates is confirmed by a shift in clathrate hydrate regions when TBAC is present. The effect of TBAC concentration on the stability of the binary hydrate is studied, and it is shown that hydrate stability increases with the increase of TBAC concentration in this work.

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Notes

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