Equilibrium Conditions of Semi-Clathrate Hydrate Dissociation for Methane + Tetra-*n*-butyl Ammonium Bromide

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The present work investigates hydrate equilibrium conditions for tetra-*n*-butyl ammonium bromide (TBAB) + methane + water mixtures. The experiments are carried out in the TBAB mass fraction range of (0.05 to 0.45) and in the pressure range of (0.5 to 7.0) MPa. The experimental results show that the presence of TBAB decreases the formation pressure of methane hydrate. Moreover, pressure reduction is dependent on the TBAB concentration.

Introduction

Gas hydrates are one of the clathrate inclusion compounds that are formed by the combination of water molecules (the host) and suitably sized gas molecules (the guest) under suitable conditions of pressure and temperature. These hydrate cages are composed of hydrogen-bonded water molecules. These hydrate structures are those of structure I, structure II, and structure H, depending on the size, shape, and physical properties of guest molecules.[1,2] Tetra-*n*-butyl ammonium bromide (TBAB) can form a semiclathrate hydrate. In TBAB semiclathrate hydrate, bromine forms a cage structure with water molecules in a structure of 10 dodecahedrons, 16 tetrakaideca-hedrons, and 4 pentakaidecahedrons at atmospheric pressure and room temperature.[3] Such a hydrate is called a semiclathrate hydrate as parts of some cages have a dangling bond for encaging the large tetra-*n*-butyl ammonium molecules. Tetra-*n*-butyl ammonium occupies those cages of tetrakaidecahedrons and pentakaidecahedrons in TBAB semiclathrate hydrate. TBAB semiclathrate hydrate has empty dodecahedral cages that can encage only small gas molecules. TBAB forms different hydrate crystal structures depending on the concentration of TBAB aqueous solutions.[3] Aladko et al. have reported the existence of crystals with various hydration numbers for TBAB hydrate: $TBAB \cdot 24H_2O$, $TBAB \cdot 26H_2O$, $TBAB \cdot 32H_2O$, and $TBAB \cdot 36H_2O$.[4] Oyama et al. identified two types of hydrate that can form simultaneously (type A $TBAB \cdot 26H_2O$ and type B $TBAB \cdot 38H_2O$).[5]

In recent years, TBAB semiclathrate hydrates have been investigated for different technologies by some researchers.[5−16] TBAB semiclathrate hydrate can be used for gas separation, gas storage, and transportation. Some studies have demonstrated that hydrogen can be stored in TBAB semiclathrate hydrates.[6,7] Shimada et al. confirmed that small molecules such as nitrogen and methane could be incorporated into TBAB semiclathrate hydrate, while the larger gas molecules such as ethane or propane were not incorporated into TBAB hydrates.[15] Kamata et al. reported that hydrogen sulfide was encaged during TBAB hydrate formation and separated successfully.[12] TBAB hydrate is also introduced as a heat transport material because of its

higher phase change temperature and saving energy compared to ice production.[5,9,10]

In the present work, the results of the TBAB + methane double hydrate dissociation equilibrium conditions are reported. The TBAB mass fraction is $w = 0.05$, 0.10, 0.20, 0.2818, and 0.45, respectively. The equilibrium pressures of hydrate forma-tion of TBAB + methane are lower than those of methane in pure water.

Table 1. Source and Purity of Compounds Used in This Work

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

Experimental Apparatus and Procedure

Experimental Apparatus. The experimental apparatus for hydrate phase equilibrium measurements was the same as the previous one.[16] A cylindrical high-pressure cell was used for equilibrium measurements. The high-pressure cell had an inner volume of about 300 cm³. There were two plexiglass windows, which could be used to view the phase behavior. A magnetic stirrer was used to agitate the test fluids and hydrate crystals. The maximum working pressure of the cell was 20 MPa.

The cell was immersed in a temperature-controlled bath to maintain the temperature of the vessel T at a prescribed level. Two platinum resistance thermometers (± 0.1 K) were placed inside the high-pressure cell. The cell pressure was measured using a PTX7517 absolute pressure transducer, (0 to 10) MPa, with uncertainties ± 0.2 % of full scale. A computer was used to collect data for temperature and pressure during the experiments.

Experimental Procedure. The test fluids used in this work were described in Table 1. Tetra-*n*-butyl ammonium bromide (TBAB) was research-grade (≥ 99.0 % purity). Distilled water was used to dilute TBAB to the desired TBAB aqueous solution in the experiments. An electronic balance CP225D (when the mass is less 80 g, its uncertainty is ± 0.01 mg, and when the mass is between (80 and 220) g, its uncertainty is ± 0.1 mg) was used to weigh the distilled water and TBAB.

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Table 2. Equilibrium Conditions for Methane and TBAB at Different TBAB Mass Fraction *w* in Water[a]

	T	*P*		*T*	*P*
w	K	MPa	*w*	K	MPa
	281.75	1.516		284.25	1.013
	282.75	2.224		285.35	1.540
	283.45	2.723		286.35	2.138
	285.25	3.265		287.25	2.684
0.05	286.25	3.809	0.10	287.85	3.195
	287.15	4.688		288.65	4.048
	287.85	5.735		289.55	5.060
	288.45	7.042		290.35	6.198
	286.05	0.797		285.85	0.508
	287.35	1.418		287.15	0.940
	287.85	1.708		288.25	1.483
	288.35	2.010		289.15	2.015
0.20	288.85	2.516		290.15	2.675
	289.65	3.191	0.2818	290.75	3.362
	290.65	4.243		291.25	3.953
	291.55	5.522		291.85	4.572
	286.25	0.708		292.35	5.234
	287.45	1.348		290.25	3.142
0.45	288.65	1.910	0.45	290.85	3.722
	289.35	2.458		291.25	4.126

[a] The uncertainty of TBAB solution mass fraction is less than 0.2 %, and the uncertainty of temperature measurements is ± 0.1 K.

Prior to each test, the cell was rinsed with distilled water two times, and then the cell and its loading lines were evacuated. The TBAB 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, the isochoric step-heating method (*T*-cycle method) was used for hydrate−liquid−vapor three-phase equilibrium measurement.[6,7] After the test fluids were charged into the cell, the cell and the test fluids were cooled and kept constant until the double hydrate formed (hydrate formation was confirmed through the window of the cell or the pressure reduction associated with gas consumption during hydrate formation). A large amount of hydrates were observed, while 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 the 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 studied system. A different concentration solution of TBAB 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−TBAB semiclathrate hydrate at various TBAB concentrations were summarized in Table 2. Figure 1 compared the hydrate formation conditions for the methane + TBAB system with those for the methane system.[1,17] As shown in Figure 1, when TBAB was present in the test system there was a drastic depression of the double hydrate formation conditions by 4 MPa at a specified temperature in this work. The results showed that methane was adsorbed into semiclathrate hydrates. The experimental results also showed that the double hydrate formed with TBAB was more stable than methane hydrate in our experimental test region.[7,14] It should be noted that the equilibrium points of TBAB, *w* = 0.05, 0.10, 0.20, 0.2818, and 0.45, semiclathrate hydrates were about (276.35, 278.25, 282.05, 284.25, and 285.65) K,
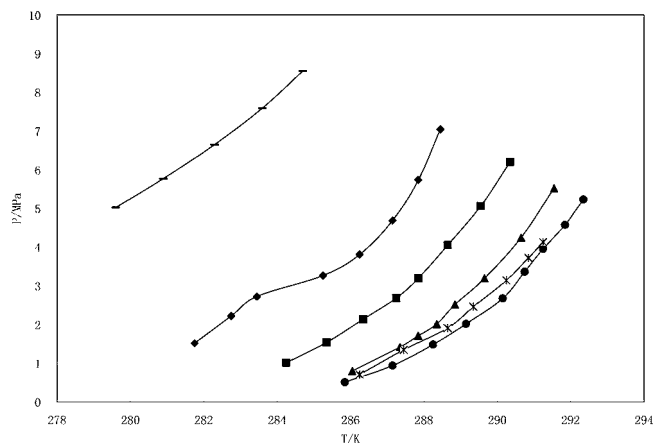
Figure 1. Hydrate formation conditions for methane with TBAB: ♦, *w* = 0.05; ■, *w* = 0.10; ▲, *w* = 0.20; ●, *w* = 0.2818; ∗, *w* = 0.45; −, no TBAB.

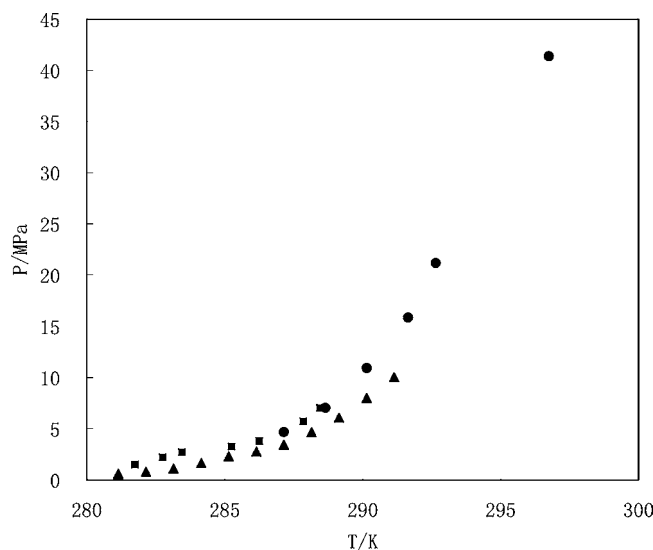**Figure 2.** Comparison of hydrate equilibrium data for methane with aqueous TBAB solutions (*w* = 0.05): ■, this work; ●, ref 7; ▲, ref 14.

respectively.[16] It was very interesting that the formation pressure condition of the double hydrate with TBAB was reduced with increasing TBAB mass fraction in the range of (0.05 to 0.2818), but the formation pressure condition for *w* = 0.45 TBAB solution + methane was higher than those for *w* = 0.2818 TBAB solution + methane at a specified temperature. The phase diagram of TBAB−H$_2$O binary systems by Oyama shows that there is a congruent melting compound corresponding to a maximum on the (*T*, *x*) curve.[5] The concentrations of TBAB aqueous solutions induce the change of double hydrate equilibrium conditions.

Figures 2, 3, 4, and 5 show the hydrate equilibrium data for the methane and TBAB system measured by Arimandi et al., Li et al., and in this work.[7,14] Figure 2 presents that hydrate equilibrium data for methane and TBAB solutions (*w* = 0.05) in this work are in agreement with the data by Arimandi et al., but there is a significant shift (about 1 MPa) in hydrate formation pressures to higher pressures compared with those by Li et al. Figure 3 shows that hydrate equilibrium data for methane and TBAB solutions (about *w* = 0.10) in this work are in agreement with the data by Arimandi et al. and also in agreement with the data reported by Li et al. in the pressure range of (4.8 to 6.8) MPa, but there is a shift in hydrate formation pressures to higher pressure compared with
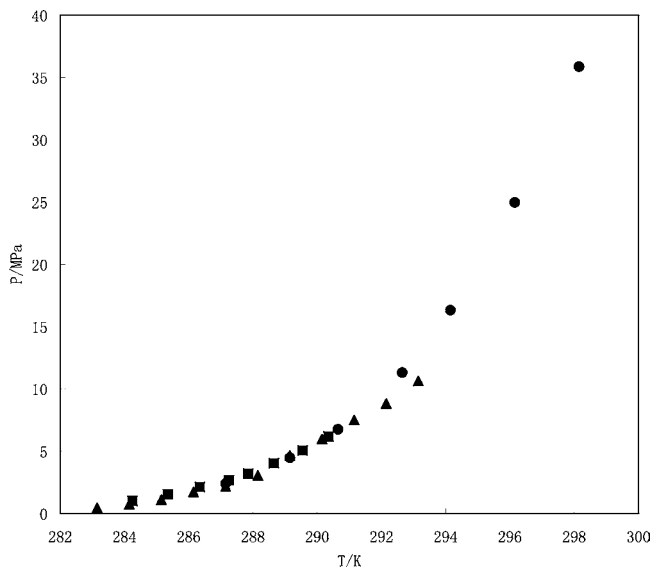
Figure 3. Comparison of hydrate equilibrium data for methane with aqueous TBAB solutions: ■, $w = 0.10$ (this work); ●, $w = 0.10$ (ref 7); ▲, $w = 0.099$ (ref 14).
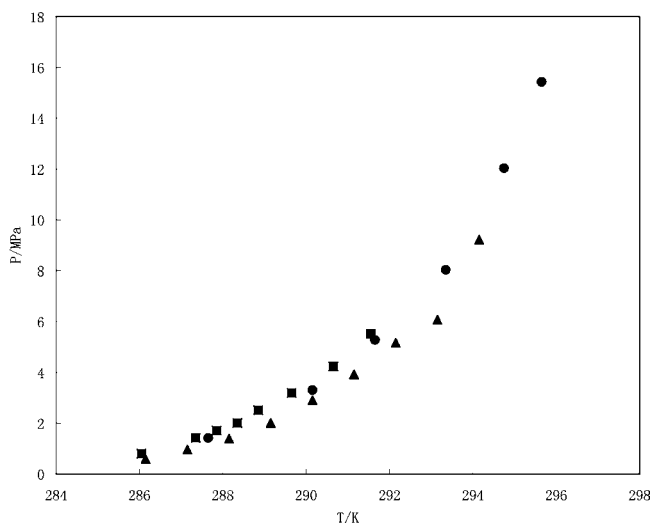

Figure 4. Comparison of hydrate equilibrium data for methane with aqueous TBAB solutions: ■, $w = 0.20$ (this work); ●, $w = 0.20$ (ref 7); ▲, $w = 0.197$ (ref 14).

those by Li et al. in other pressure ranges. Figure 4 shows that the shift phenomenon of equilibrium pressures for methane and TBAB solutions (about $w = 0.20$) system is similar to that of the methane and TBAB solutions ($w = 0.05$) system, but the shift of the hydrate phase boundary is smaller. Figure 5 compareS the hydrate equilibrium data for methane with aqueous TBAB solutions ($w = 0.45, 0.2818$, and 0.30). There was a little shift in the hydrate phase boundary in the three conditions. The concentrations of TBAB aqueous solutions induce the change of double hydrate equilibrium conditions.[5] Perhaps more TBAB inhibits hydrate formation.

Conclusions

In this work, the phase boundaries of methane and TBAB double hydrates are measured. The experimental TBAB mass fraction range of (0.05 to 0.45) and methane pressure range of (0.5 to 7.0) MPa have been investigated. The results show that the addition of TBAB reduces the formation pressures of
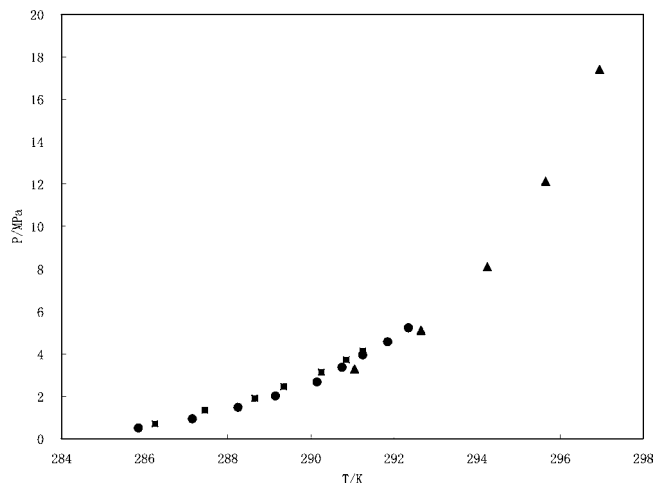

Figure 5. Comparison of hydrate equilibrium data for methane with aqueous TBAB solutions: ■, $w = 0.45$ (this work); ●, $w = 0.28$ (this work); ▲, $w = 0.30$ (ref 7).

methane hydrate by 4.0 MPa. Methane uptake into semiclathrate is confirmed by a shift in clathrate hydrate regions when TBAB is present. The effect of TBAB concentration on the stability of the double hydrates is studied, and it is shown that hydrate stability increases with TBAB concentration in the mass fraction range of (0.05 to 28.18); however, the hydrate of methane and $w = 0.2818$ TBAB solutions is more stable than that of methane and $w = 0.45$ TBAB solutions.

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