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Equilibrium Conditions for Semiclathrate Hydrates Formed in the $CH_4 + N_2 + O_2 +$ Tetra-*n*-butyl Ammonium Bromide Systems

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ABSTRACT: In the present work, phase equilibrium conditions for tetra-*n*-butyl ammonium bromide (TBAB) semiclathrate hydrates formed with the gas mixture (29.95 % CH_4 + 60.0 % N_2 + 10.05 % O_2 in mole fraction) were measured. The experimental temperature, pressure, and mass fraction of TBAB ranged from (282 to 290) K, from (0.99 to 6.56) MPa, and from (0.05 to 0.20), respectively. For the gas mixture used in this work, the experimental results showed that at a given temperature, the pressure required to form TBAB semiclathrate hydrates is significantly lower than that required for forming gas hydrates from the same gas mixture. The formation pressure of TBAB semiclathrates formed with the gas mixture is reduced as TBAB concentration is increased in the solution at a given temperature.

INTRODUCTION

Gas hydrates are icelike crystalline compounds composed of cavities formed by hydrogen-bonded water molecules that are stabilized by the presence of suitably sized gas molecules.[1] Gas hydrates have been intensively studied in the energy and environmental fields. The oil and gas industries are trying to inhibit hydrate formation in oil and gas transmission pipelines, because hydrates may result in the blockage of pipelines and a potential economic loss.[2−5] Natural gas hydrate deposits discovered in oceans or permafrost are considered as a potential energy resource for the future.[6] In addition, with the property of large gas storage capacity, gas hydrates have been regarded as a promising way to store and transport gases, such as hydrogen storage[7,8] and natural gas transportation.[1,9] Due to the difference between phase equilibrium conditions, gas hydrates have also been proposed for gas separation from gas mixtures, such as the capture of CO_2 from the combustion of fossil fuels[10,11] and the recovery of refrigerant R134a from air.[12]

In recent years, some researchers have focused on using the hydrate-based method to purify methane from the low-concentration coalbed methane (CBM) resource.[13,14] Ventilation air is usually used to dilute the coalbed methane remaining in underground coal mines to safe levels before coal mining.[15] In this way, the methane concentration is remarkably decreased, and the main components of CBM become CH_4, N_2, and O_2. Usually, the mole fraction of methane in the low-concentration CBM is less than 30 %; thus, the utilization of the low-concentration CBM resource is largely restricted. Moreover, once the mole fraction of methane is in the range of 5 to 16 %, explosions may occur when the low-concentration CBM is ignited by open flame sources. The direct emission of the low-concentration CBM to atmosphere not only wastes a huge amount of energy resource, but also causes a fatal damage to environment, because the greenhouse effect of methane is approximately 21 times stronger than that of CO_2.[16,17] Therefore, there is an urgent need to utilize the low-concentration CBM resource, and the key point is to separate methane from the low-concentration CBM.

The quaternary ammonium salt of tetra-*n*-butyl ammonium bromide (TBAB) forms semiclathrate hydrates with water molecules at atmospheric pressure.[18,19] In TBAB semiclathrates, anions Br^- form cage structures with water molecules and the tetra-*n*-butyl ammonium (TBA) cations occupy four cages.[20−22] Therefore, guest molecules can both form part of the host lattice and occupy cages after breaking part of the cage structure. Recently, TBAB semiclathrates have been applied for gas separation and gas storage,[23−25] because small gas molecules such as CH_4 and CO_2 can be captured in empty cages of TBAB semiclathrates at mild conditions. Arjmandi et al.[26] reported the equilibrium data for semiclathrates formed in H_2 + TBAB, CH_4 + TBAB, N_2 + TBAB, and natural gas + TBAB systems. Sun et al.[27] reported the equilibrium conditions for TBAB semiclathrate formed with methane and concluded that the formation pressure is dependent on the TBAB concentration. Lee et al.[28] measured the phase equilibria for TBAB semiclathrate hydrate formed with N_2, and showed that the addition of TBAB into the liquid solution could give a remarkable pressure reduction of hydrate formation. However, to the best of our knowledge, the equilibrium data for TBAB semiclathrates formed with the gas mixture of $CH_4 + N_2 + O_2$ have rarely been reported in the literature. Note that CH_4, N_2, and O_2 are the main components of the low-concentration CBM. In this work, the phase equilibrium data of semiclathrate hydrates formed in the $CH_4 + N_2 + O_2$ + TBAB + water system are measured. The effect of TBAB concentration on the formation pressure of TBAB semiclathrate hydrates formed with the gas mixture ($CH_4 + N_2 + O_2$) is discussed. Furthermore, the phase equilibrium data of TBAB semiclathrates formed from the low-concentration CBM are compared with the phase equilibrium data at other methane concentrations in the literature.

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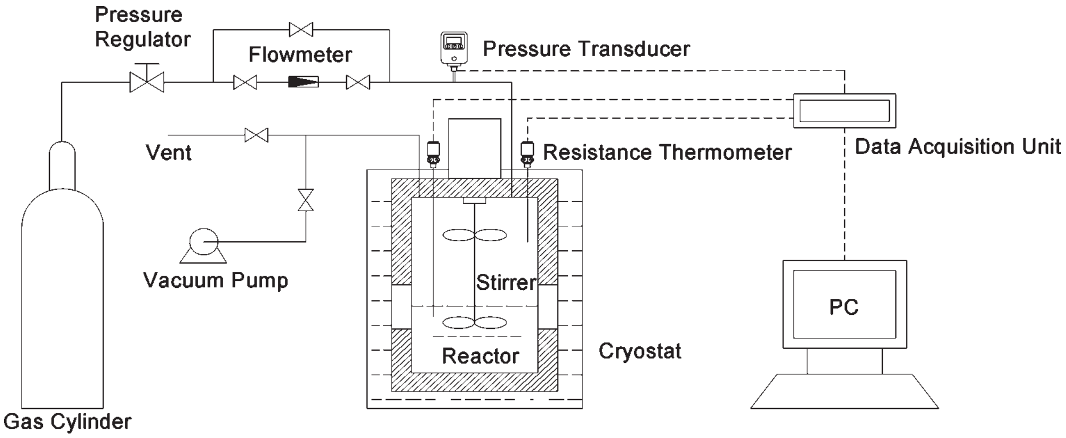

Figure 1. Schematic diagram of the experimental apparatus used to measure equilibrium conditions for TBAB semiclathrate hydrates formed with the low-concentration CBM.

EXPERIMENTAL SECTION

Materials. The gas mixture ($CH_4 + N_2 + O_2$) was supplied by Chongqing Rising Gas, China, with a supplier's reported uncertainty in composition of ± 0.05 %. To simulate the composition of most recovered low-concentration CBM in China, the gas mixture with the molar composition of (29.95 % CH_4 + 60.0 % N_2 + 10.05 % O_2) was chosen in this work. TBAB was purchased from Chongqing Oriental Chemical Co., Ltd. with a certified mass purity of 99.9 %. Deionized water was used in all experimental runs.

Apparatus. The schematic diagram of the experimental apparatus is shown in Figure 1, which was used for measuring the phase equilibrium data of semiclathrates formed in the $CH_4 + N_2 + O_2$ + TBAB + water system. The experimental apparatus consists of a 600 cm^3 high-pressure (20 MPa) vessel, which was immersed in a cryostat. The temperature in the vessel was controlled by circulating the $\varphi = 30.0$ % ethanol solution in the cryostat. Two quartz windows were equipped in the front and rear sides of the vessel, which allow a visual access to hydrate formation inside the vessel. An electromagnetic stirrer (0 to 1000 rpm) was used to agitate the vessel contents, ensuring quick hydrate formation in the vessel. All parts of the apparatus including the stirrer were made of stainless steel. Two WZPK-263 platinum resistance thermometers (Pt100, Shanghai Automation Instrumentation Co., Ltd., Shanghai, China) with the uncertainty of ± 0.1 K were inserted into the vessel at two different levels, used to measure temperatures of the gas and liquid phase, and connected to a data acquisition unit (Agilent 34970A). A PE80H−P250G12HP1A pressure transducer (Banna Electronics Inc., USA) with the uncertainty of ± 0.01 MPa was used to measure the pressure in the vessel and connected to the data acquisition unit. The Agilent online data acquisition unit communicated with a computer by means of the RS-232 interface. Therefore, the real time measurements of temperature and pressure were recorded and presented graphically on the computer screen. A D07−11C mass flowmeter (Beijing Sevenstar Electronics Co., Ltd., China) with the full sale of 33.3 $cm^3 \cdot s^{-1}$ was used to regulate the flow of low-concentration CBM, and connected to the computer. It can be operated on the computer screen. The uncertainty of the mass flowmeter is ± 1 % F. S. A vent valve used for venting the vessel or sampling the gas mixture was installed at the outlet of the vessel. A SC-2000 gas chromatograph (Chongqing Chuanyi Analyzer Co., Ltd., China) was used to analyze the composition of the gas released from the semiclathrate hydrates. The uncertainty in the gas composition measurement is ± 1.0 %.

Procedures. The method used in this work is similar to the *T*-cycle method,[29] which is reliable to determine equilibrium temperatures for semiclathrate hydrates.[30,31] Prior to the experiments, the vessel was cleaned using deionized water and dried. Then about 150 cm^3 TBAB aqueous solution was introduced into the vessel. Subsequently, the vessel was purged three times using the low-concentration CBM supplied by the gas cylinder, ensuring that the vessel chamber was free of air. Then the vessel was pressurized to the desired pressure by supplying the low-concentration CBM. The flow of the low-concentration CBM was regulated by the mass flowmeter. The pressure in the vessel was regulated by the pressure regulator that was equipped between the gas cylinder and the vessel. Then the vessel was separated from the gas cylinder by shutting off the valve after the mass flowmeter. The stirrer was adjusted to 200 rpm, and the vessel was cooled by decreasing the temperature of the cryostat. The data acquisition unit was initiated to record the temperatures in the gas and liquid phase and the pressure in the vessel and simultaneously transferred the data to the computer. When the formation of the semiclathrate hydrates at the gas/liquid interface or in the solution was observed through the quartz window, the temperature in the cryostat was kept constant for at least 4 h to establish an equilibrium state at which the temperatures in the gas and liquid solution and the pressure in the vessel were stabilized. Then the vessel was heated slowly by a step of 0.1 K until the solution became transparent and an infinitesimal amount of hydrate crystals were left. In each heating step, at least 4 h were remained for the vessel to achieve the equilibrium state. When the infinitesimal amount of hydrate crystals did not change the size after being kept at least 4 h, we continued heating the vessel by the step of 0.1 K. When the very small amount of hydrate crystals in the solution disappeared after the gradual heating, this point (the temperature of the solution and the pressure in the vessel) was determined as the equilibrium dissociation point. This procedure was repeated when the TBAB concentration in aqueous solution was changed. In addition, this procedure was also used to measure the phase equilibrium data of TBAB semiclathrate hydrates formed with methane.

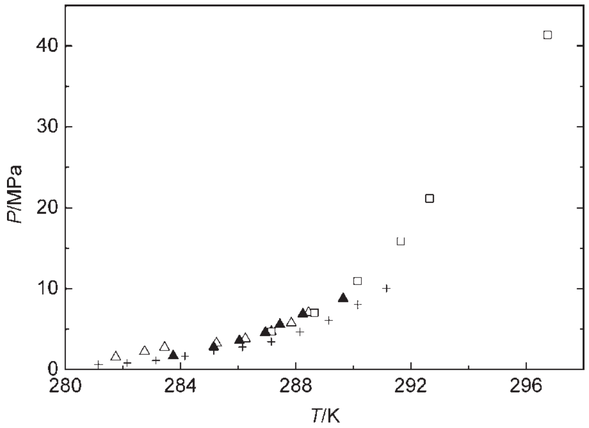

Figure 2. Comparison of phase equilibrium conditions for TBAB semiclathrate hydrates formed with CH_4 at the TBAB concentration $w = 0.05$. ▲, this work; □, Arjmandi et al.;[26] Δ, Sun et al.;[27] +, Li et al.[32]

Table 1. Phase Equilibrium Data of TBAB Semiclathrate Hydrates Formed with the Gas Mixture (29.95 % CH_4 + 60.0 % N_2 + 10.05 % O_2 in mole fraction) at Different TBAB Concentrations (w = 0.05, 0.10, and 0.20)

w = 0.05		w = 0.10		w = 0.20	
T/K	P/MPa	T/K	P/MPa	T/K	P/MPa
281.85	2.09	284.15	1.89	285.25	0.99
282.75	3.08	285.45	3.08	285.85	1.38
283.75	3.88	286.65	4.48	287.45	2.68
284.55	5.16	287.65	5.98	288.55	4.18
285.75	6.56			289.85	5.68

To confirm that CH_4 is captured in the TBAB semiclathrates that are formed with the low-concentration CBM, an additional step was conducted to analyze the composition of the gas released from the semiclathrates. When the formation of semiclathrate hydrates was observed in the $CH_4 + N_2 + O_2$ + TBAB + water system, the formation conditions were kept 24 h for the semiclathrates to grow sufficiently. Then the vessel was heated to dissociate the semiclathrates after the residual gas mixture was evacuated from the vessel. When the semiclathrate hydrates completely decomposed, the gas phase in the vessel was sampled and analyzed by the gas chromatograph.

■ RESULTS AND DISCUSSION

Validation of Apparatus. This was the first occasion that the experimental apparatus was used to measure the equilibrium conditions for semiclathrates. Therefore, an initial study was performed to establish the experimental methodology for semiclathrates. According to the experimental procedure mentioned above, the equilibrium conditions for TBAB semiclathrates formed with methane were measured at the TBAB mass fraction, $w = 0.05$. The results are shown in Figure 2, and compared with the data that were reported by Arjmandi et al.,[26] Sun et al.,[27] and Li et al.[32] As seen in Figure 2, the results obtained from our experimental setup are in excellent agreement with the data from the literature. This comparison suggests that the apparatus and procedure adopted in this work can produce reliable phase equilibrium data.

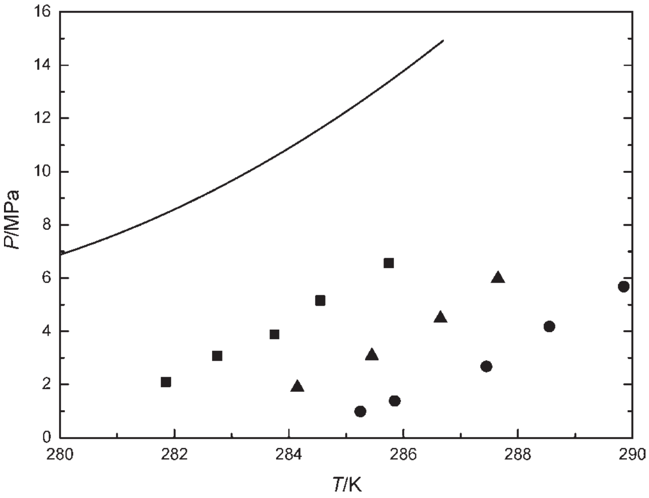

Figure 3. Phase equilibrium data of TBAB semiclathrate hydrates formed with the low-concentration CBM (29.95 % CH_4 + 60.0 % N_2 + 10.05 % O_2 in mole fraction) at different TBAB concentrations in the solution. ■, TBAB $w = 0.05$; ▲, TBAB $w = 0.10$; ●, TBAB $w = 0.20$; solid line, phase boundary for gas hydrates formed from the same low-concentration CBM, predicted using the Chen–Guo model.[33]

Table 2. Mole Fraction of Methane (x) in TBAB Semiclathrate Hydrates Formed with the Gas Mixture (29.95 % CH_4 + 60.0 % N_2 + 10.05 % O_2 in mole fraction) at the TBAB Concentration w = 0.10

	experimental conditions for semiclathrates formation		
w	T/K	P/MPa	x
0.10	277.25	2.68	0.3362
		3.58	0.3497
		4.28	0.3678

Experimental Results and Discussion. The phase equilibrium data of TBAB semiclathrates formed with the gas mixture (29.95 % CH_4 + 60.0 % N_2 + 10.05 % O_2 in mole fraction) were measured at three different concentrations of TBAB, w = 0.05, 0.10, and 0.20. These phase equilibrium data are indispensable to kinetic investigations on methane separation from the low-concentration CBM by hydrate formation. The experimental results are summarized in Table 1 and plotted in Figure 3. The solid line in Figure 3 is the phase equilibrium condition for gas hydrates formed from the same gas mixture used in this work, which is predicted using the Chen–Guo hydrate model.[33] As seen in Figure 3, the equilibrium conditions for TBAB semiclathrate hydrates formed with the gas mixture are quite lower than the solid line. This indicates that, at a given temperature, the pressure required to form TBAB semiclathrate hydrates is significantly lower than that required for forming gas hydrates from the same gas mixture. In addition, it can be seen in Figure 3 that, at a given temperature, the formation pressure of TBAB semiclathrates formed from the gas mixture (29.95 % CH_4 + 60.0 % N_2 + 10.05 % O_2 in mole fraction) is decreased as the TBAB concentration is increased.

Table 2 lists the mole fraction of CH_4 (x) captured in the TBAB semiclathrates, which were formed with the low-concentration CBM (29.95 % CH_4 + 60.0 % N_2 + 10.05 % O_2 in mole

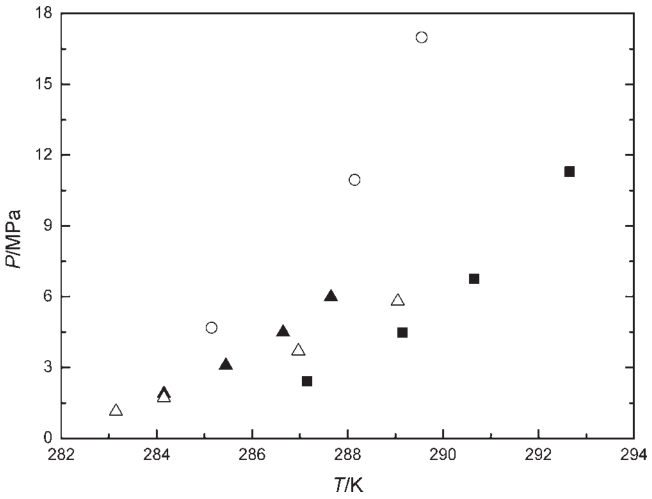

Figure 4. Phase equilibrium data of TBAB semiclathrate hydrates formed with different hydrate-forming gases at TBAB concentration $w = 0.10$. ○, nitrogen from Arjmandi et al.;[26] ▲, low-concentration CBM (this work); △, natural gas from Arjmandi et al.;[26] ■, methane from Arjmandi et al.[26] The mole fraction of methane in nitrogen, low-concentration CBM, natural gas and pure methane is 0, 29.95 %, 87.32 %, and 99.99 %, respectively.

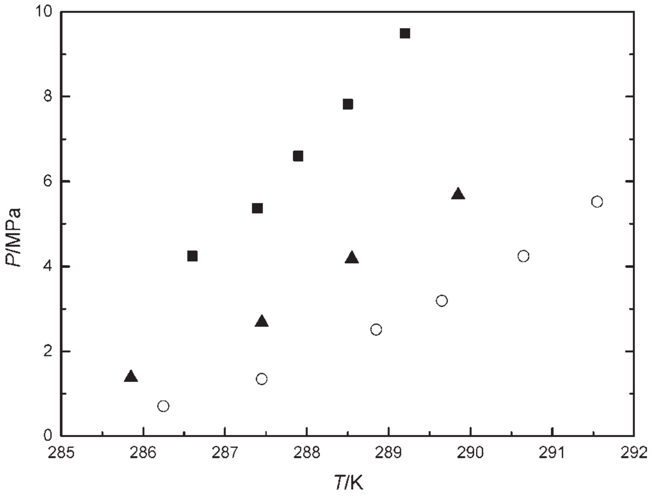

Figure 5. Phase equilibrium data of TBAB semiclathrate hydrates formed with different hydrate-forming gases at TBAB concentration $w = 0.20$. ○, methane from Sun et al.;[27] ▲, low-concentration CBM (this work); ■, nitrogen from Lee et al.[28] The mole fraction of methane in pure methane, low-concentration CBM, and nitrogen is 99.99 %, 29.95 %, and 0, respectively.

fraction) at the TBAB mass fraction $w = 0.10$. The mole fraction of CH_4 is obtained by measuring the composition of the gas released from the semiclathrates. It can be seen in Table 2 that the mole fraction of CH_4 encaged in TBAB semiclathrates is higher than that in the low-concentration CBM ($x = 0.2995$). Therefore, Figure 3 and Table 2 show that TBAB is a preferable promoter in the purification of methane from the low-concentration CBM. Lower pressures and higher temperatures are always desirable for future industrial applications of methane recovery from the low-concentration CBM.

Figure 4 illustrates the comparison of phase equilibria for TBAB semiclathrate hydrates formed with pure methane, natural gas, low-concentration CBM, and pure nitrogen at the TBAB mass fraction $w = 0.10$. It should be noted that the mole fraction of methane in pure methane, natural gas,[26] low-concentration CBM, and pure nitrogen is 99.99 %, 87.32 %, 29.95 %, and 0, respectively. As seen in Figure 4, for hydrate-forming gases with the main components such as CH_4, N_2 and O_2, the equilibrium boundary for TBAB semiclathrate hydrates is lowered as methane content in the hydrate-forming gases is increased. Figure 5 compares the phase equilibria for TBAB semiclathrates formed with pure methane, low-concentration CBM, and pure nitrogen at the TBAB mass fraction $w = 0.20$, and exhibits the same trend as that shown in Figure 4. Therefore, Figures 4 and 5 show that at a constant TBAB concentration and a given temperature, the formation pressure of TBAB semiclathrates formed with the hydrate-forming gases is reduced as methane content in the hydrate-forming gases is increased. In contrast to this result, the hydrate phase boundary for natural gas hydrate is much lower than that for methane hydrate without any additive in the solution.[34] The reason could be that natural gas contains ethane and/or propane gases. These gas species enter hydrate cages and lead phase boundary shift to milder pressure condition for natural gas hydrate, compared with methane hydrate. Nevertheless, cages in TBAB semiclathrate hydrates are too small to encage ethane and propane molecules,[35] so ethane and propane can not act the role of decreasing pressure condition at a given temperature in the gas + TBAB systems such as natural gas + TBAB system. Therefore, tendency of phase boundary for natural gas hydrate and methane hydrate would differ from that for TBAB semiclathrate hydrates formed with natural gas or low-concentration CBM.

■ CONCLUSIONS

In this work, equilibrium conditions for TBAB semiclathrate hydrates formed with the gas mixture (29.95 % CH_4 + 60.0 % N_2 + 10.05 % O_2 in mole fraction) were measured at three TBAB concentrations ($w = 0.05$, 0.10, and 0.20), and compared with the phase boundary for gas hydrates formed from the same gas mixture. It was shown that TBAB is a preferable promoter in purifying methane from the low-concentration CBM. At a given temperature, the formation pressure of TBAB semiclathrates formed with the low-concentration CBM is reduced as the TBAB concentration is increased. In addition, at a constant TBAB concentration and a given temperature, the formation pressure of TBAB semiclathrates formed with the hydrate-forming gases (methane, natural gas, low-concentration CBM, and nitrogen) is reduced as methane content in the hydrate-forming gases is increased.

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