Equilibrium Hydrate Formation Conditions for the Mixtures of $CO_2 + H_2 +$ Tetrabutyl Ammonium Bromide

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The equilibrium hydrate formation conditions for the gas mixture of CO_2 and H_2 with tetrabutyl ammonium bromide (TBAB) are measured. The data show that TBAB can reduce the gas hydrate formation pressure as an additive with the mole fraction of (0.14, 0.21, 0.29, 0.50, 1.00, and 2.67) %. The experiments were carried out in the temperature range of (274.05 to 288.55) K and the pressure range of (0.25 to 7.26) MPa. The equilibrium hydrate formation pressure of the $CO_2 + H_2 +$ TBAB mixture is remarkably lower than that of the $CO_2 + H_2$ mixture at the same temperature and decreases with the increase in the concentration of TBAB. In addition, to avoid the formation of pure TBAB hydrate, in which there are no CO_2 or H_2, for the above gas mixture, the formation conditions of the pure TBAB hydrate with TBAB mole fraction from (0.14 to 2.67) % were also measured.

Introduction

The emission of carbon dioxide from the burning of fossil fuels has been identified as the major contributor to the greenhouse gas emission and subsequent global warming and climate change. Particularly, fossil fuel electric power plants are producing about one-third of CO_2 emission worldwide.[1] Reducing or eliminating CO_2 emissions from the use of fossil fuels for power generation became an urgent and necessary task. Recently, integrated coal gasification cycle (IGCC) plants offered one of the most promising routes for CO_2 capture by converting the gas from the gasifier into a stream of H_2 and CO_2 via a shift reaction.[2] Then CO_2 can be removed for disposal, and the resultant H_2 here could be used in fuel cells or in gas turbines.[3] An essential element of this approach, in fact, is CO_2 separation from a $CO_2 + H_2$ mixture.

Separation of CO_2 from a gas mixture can be accomplished through a variety of methods, such as cryogenic fractionation, selective adsorption by solid adsorbents, gas absorption, and membrane separation. However, these methods have the individual issues of either high corrosion, large energy consumption, high cost, or low capacity, and so forth.[4] Hence, it is urgent to develop efficient and cost-effective capture/separation technologies for CO_2 separation.

A novel method for separating CO_2 is through gas hydrate formation.[5−9] The basis for the separation is the selective partition of the target component between the hydrate phase and the gaseous phase. Because the equilibrium hydrate formation pressure of CO_2 is much lower than that of H_2 at the same temperature, it is expected that CO_2 preferentially encaged into the hydrate crystal phase. The hydrate crystals are separated and subsequently decomposed to create the CO_2-rich stream, while the rest constitute the CO_2-lean one. The U.S. Department of Energy has proposed a high-pressure process for carbon dioxide separation where a shifted synthesis gas stream (CO_2, H_2, and other gases) is allowed to form a hydrate to obtain a CO_2 hydrate slurry and H_2-rich product gas.[3,10] A preliminary economic assessment shows that the cost of the hydrate technique for CO_2 separation from the IGCC power plant is about 10 U.S. dollars per ton of CO_2, which is much lower than that of other methods.[10] Hence, the hydrate separation technique is promising for separating CO_2 from IGCC syngas in the power plants.

For the hydrate separation process development for CO_2 capture in fuel gas, the first task is to determine the operating temperature and the minimum hydrate formation pressure of the $CO_2 + H_2$ mixture. Although there are many data for the $CO_2 + H_2$ mixture hydrate formation, the equilibrium hydrate formation pressure for this kind of mixture is relatively high in the pure water system. The higher pressure means more energy for compression work. Hence, it is necessary to find an effective and environmentally friendly promoter to decrease the equilibrium hydrate formation pressure, enhance the gas storage capacity, and accelerate the hydrate formation rate to reduce the cost for the hydrate-based gas separation process. Kumar et al.[11] studied the equilibrium hydrate-forming conditions for IGCC model gas with propane (C_3H_8) as an additive gas, and they concluded that the hydrate-forming pressure could be decreased by approximately 50 % with a mole fraction of 3.2 % C_3H_8. Hashimoto et al.[12] reported that the equilibrium pressure of $CO_2 + H_2 +$ tetrahydrofuran (THF) ternary hydrates was much lower than the equilibrium pressure of $CO_2 + H_2$ binary hydrates. Zhang et al.[13] found that the equilibrium pressure of $CO_2 + H_2 +$ cyclopentane (CP) hydrates was lower than that of $CO_2 + H_2 +$ THF hydrates. Lee et al.[14] determined the equilibrium data for the $CO_2 + H_2 +$ THF system containing the mole fraction of (0.5, 1, and 3) % of THF in the temperature range of (273.0 to 283.6) K. Tetrabutyl ammonium bromide (TBAB) is also an excellent hydrate promoter, which can form

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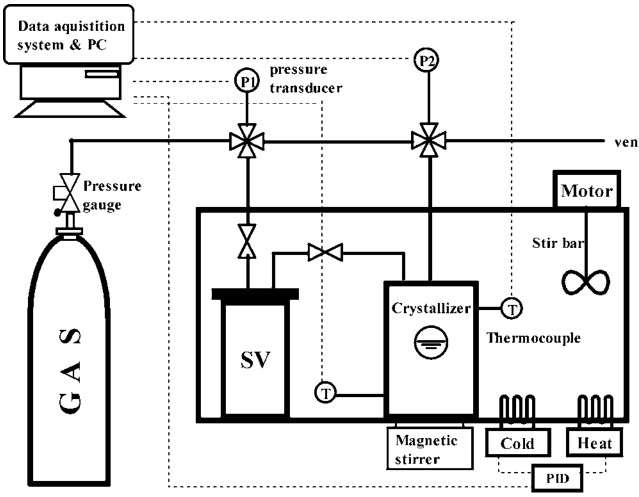

Figure 1. Schematic of experimental apparatus.

semiclathrate hydrates with water molecules and small gas molecules and moderate the hydrate formation condition significantly.[15] Studies[16,17] have shown that small molecules (CH_4, CO_2) can be encaged inside the dodecahedral cavities (S-cage, 5^{12}) of TBAB hydrate. Kamata et al.[18] conducted separation experiments to remove hydrogen sulfide from biogas including methane, carbon dioxide, and hydrogen sulfide using TBAB semiclathrate hydrate. To determine the temperature and pressure conditions for removing CO_2 from the $CO_2 + N_2$ mixture, Duc et al.[19] investigated equilibrium hydrate formation conditions of the $CO_2 + N_2$ mixture in the presence of TBAB of a mole fraction of 0.29 % with the CO_2 mole fraction of (15.5, 19.2, 23.4, and 21.5) %. The experimental results show that the presence of TBAB decreases considerably the formation pressure of $CO_2 + N_2$ hydrate, and the CO_2 selectivity in the hydrate phase is at least four times higher than that in the gas phase. However, no studies have reported the phase equilibrium data on the $CO_2 + H_2$ + TBAB hydrate system.

In this work, to determine the operating temperature and the minimum hydrate formation pressure for the CO_2 separation from the $CO_2 + H_2$ mixture via the hydrate crystallization, the equilibrium hydrate formation conditions of $CO_2 + H_2$ with the addition of TBAB were measured. The treated synthesis gas coming out of an IGCC power station consists of an approximate mole fraction of 40 % CO_2 and 60 % H_2 mixture,[3] and the residual gas of our first-stage separation process consists of an approximate mole fraction of 18 % CO_2 and 82 % H_2 mixture. Thus, the two $CO_2 + H_2$ mixture gases containing the mole fraction of (39.2 and 18.5) % CO_2 were used as the feed gases in the first and the second stage separation, respectively. The promotion effects of TBAB of the mole fraction of (0.14, 0.21, 0.29, 0.50, 1.00, and 2.67) %, respectively, on the equilibrium conditions in the pressure range of (0.25 to 7.26) MPa and the temperature range of (274.05 to 288.55) K were determined. The experimental data will be useful for verifying TBAB semiclathrate hydrate as a potential IGCC fuel gas ($CO_2 + H_2$) separation process.

Experimental Section

Apparatus. The schematic of the experimental apparatus is shown in Figure 1. It consists of a high-pressure hydrate crystallizer (CR) made of 316 stainless steel. The crystallizer contains two visible windows. Its effective maximum volume is 336 cm^3. The pressure in the cell of the crystallizer is measured using a MBS3000 absolute pressure transducer ((0 to 25) MPa) with the accuracy of ± 0.02 MPa. The temperatures in the cell is measured using a Pt1000 thermoprobe (JM6081) with the uncertainty of ± 0.05 K. The crystallizer is immersed in a constant temperature water bath. The signals of the pressure and temperature are acquired by a data acquisition system driven by a personal computer. The cell contents are agitated by a magnetic stirrer. Its stirring speed rate can be varied from (0 to 1000) rpm.

Materials and Preparation of Samples. The mixture gases ($CO_2 + H_2$) with precise composition were supplied by Guangdong South China Special Gases Technology Institute Ltd., China. TBAB with the purity of 99.9 % was supplied by Shanghai Sinopharm Chemical Reagent Co., Ltd., China. The deionized water was obtained by an ultrapure water system with a resistivity of 18.25 $m\Omega \cdot cm^{-1}$ made by Nanjing Ultrapure Water Technology Co., Ltd., China.

Experimental Procedure. In the work, our method is similar to the *T*-cycle method, which is reliable to determine the equilibrium hydrate formation temperatures.[20−23] Prior to the experiment, the crystallizer is cleaned using deionized water and allowed to dry. TBAB aqueous solution prepared at a desired concentration was introduced into the high-pressure hydrate crystallizer. Subsequently, the hydrate crystallizer with the solution was evacuated with a vacuum pump and flushed with the $CO_2 + H_2$ mixture gas at least four times to ensure that it was air-free. In the experiment, at first, the hydrate crystallizer was pressurized up to the desired pressure by supplying the mixture gas ($CO_2 + H_2$). Then, the system temperature was dropped and remained constant at the point of pressure depression which is caused by the $CO_2 + H_2$ + TBAB mixed gas hydrate formation. The system was heated quite gradually with each temperature step of 0.1 K until there was an infinitesimal amount of gas hydrate left. The interval time was taken at least for one day to determine the equilibrium state at each temperature step. When no particle of hydrates appeared during the gradual heating, we determined this point as the equilibrium point. In addition, the formation conditions for pure TBAB hydrate were also measured using the *T*-cycle method. The procedure followed in this work is described in detail elsewhere.[20−23]

Results and Discussion

Equilibrium Conditions for Pure TBAB. Before studying the $CO_2 + H_2$ + TBAB hydrate system, the equilibrium formation conditions of pure TBAB hydrate formed in the TBAB + H_2O system with TBAB mole fraction from (0.14 to 2.67) % under atmospheric conditions were measured and compared with the experimental values given by Oyama et al.[24] The results from our apparatus are in excellent agreement with the literature values[24] as shown in Figure 2. As reported by Hashimoto et al.[22] and Aladko et al.,[25] when the mole fraction of TBAB is less than 1.4 %, the type B TBAB hydrate forms preferentially. In addition, when the mole fraction of TBAB is more than 1.4 %, the type A TBAB hydrate is more thermodynamically stable. Our experimental data are plotted well on the thermodynamically stable curve given by Oyama et al.[24] It can be seen from Figure 2 that there are no pure TBAB hydrates in existence beyond the thermodynamically stable curve.[24] Thus, the main goal of the measurement for the above pure TBAB hydrate system is to provide identification to avoid the formation of pure TBAB hydrate, where there are no CO_2 or H_2, in the $CO_2 + H_2$ + TBAB system in the following work.

Equilibrium Conditions for $CO_2 + H_2$ + TBAB. Prior to the experiment for the $CO_2 + H_2$ + TBAB hydrate system, five equilibrium hydrate formation data for the $CO_2 + H_2$ gas

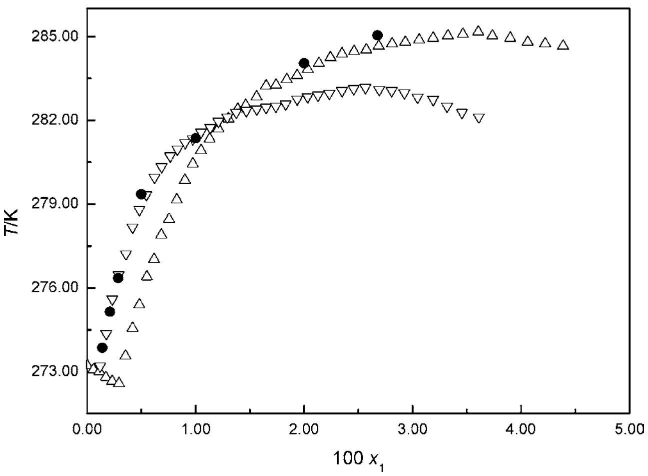

Figure 2. Hydrate phase equilibrium conditions for TBAB (1) + H_2O (2) mixtures. △, type A, Oyama et al.;[24] ▽, type B, Oyama et al.;[24] ●, this work.

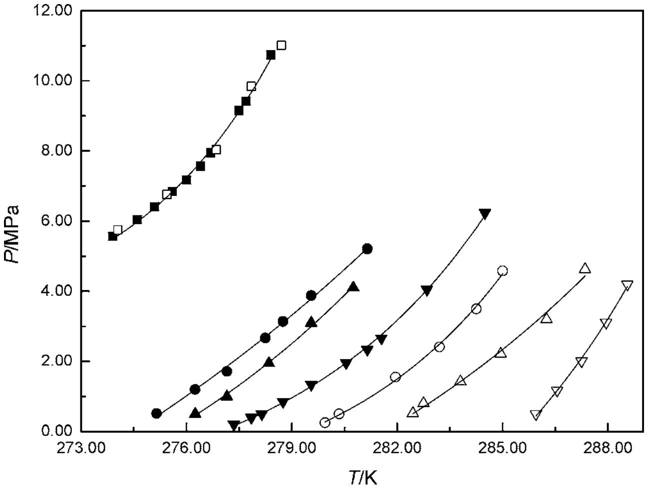

Figure 3. Equilibrium hydrate formation pressure for CO_2 (1) + H_2 (2) gas mixture with $x_1 = 39.2$ % and $x_2 = 60.8$ % in the presence of TBAB (3) + H_2O (4). ■, $x_3 = 0.00$, Kumar et al.;[11] □, $x_3 = 0.00$; ●, $x_3 = 0.14$ %; ▲, $x_3 = 0.21$ %; ▼, $x_3 = 0.29$ %; ○, $x_3 = 0.50$ %; △, $x_3 = 1.00$ %; ▽, $x_3 = 2.67$ %.

Table 1. Equilibrium Hydrate Formation Pressure for the CO_2 (1) + H_2 (2) Gas Mixture with $x_1 = 39.2$ % and $x_2 = 60.8$ % in the Presence of TBAB (3) + H_2O (4)

100 x_3	T/K	P/MPa
0.00	274.05	5.75
	275.45	6.75
	276.85	8.03
	277.85	9.84
	278.75	11.01
0.14	275.15	0.51
	276.25	1.20
	277.15	1.71
	278.25	2.67
	279.55	3.88
	281.15	5.21
0.21	276.25	0.50
	277.15	1.00
	278.35	1.95
	279.55	3.10
	280.65	4.19
0.29	277.35	0.25
	277.85	0.40
	278.15	0.50
	278.65	0.71
	279.55	1.34
	280.55	1.96
	281.15	2.34
	281.55	2.66
	282.85	4.05
	284.55	6.23
0.50	279.55	0.25
	280.35	0.50
	281.95	1.55
	283.25	2.41
	284.25	3.50
	285.05	4.58
1.00	282.45	0.52
	282.75	0.80
	283.80	1.42
	284.95	2.22
	286.25	3.20
	287.35	4.63
2.67	285.95	0.50
	286.55	1.17
	287.25	2.01
	287.95	3.11
	288.55	4.20

mixture of the mole fraction of 39.2 % CO_2 were measured in the temperature range of (274.05 to 278.75) K and compared with the values given by Kumar et al.[11] As shown in Figure 3, the results are in excellent agreement with the literature values.[11] To determine the operating temperature and the minimum hydrate formation pressure for CO_2 separation for the first stage IGCC fuel gas (CO_2 + H_2) with the addition of TBAB, the measurements of the equilibrium hydrate formation conditions for CO_2 + H_2 + TBAB hydrate system in the pressure range of (0.25 to 6.23) MPa and the temperatures in the range of (275.15 to 288.55) K were carried out. TBAB aqueous solutions containing the mole fraction of (0.14, 0.21, 0.29, 0.50, 1.00, and 2.67) % of TBAB and the CO_2 + H_2 gas mixture containing a mole fraction of 39.2 % CO_2 were used to form the hydrates. The phase equilibrium data are summarized in Table 1 and plotted in Figure 3. As shown in Figure 3, the addition of TBAB reduces considerably the pressure required to form the hydrate, and the equilibrium formation pressure decreases with the increase of the concentration of TBAB at the same temperature. For example, the equilibrium hydrate formation pressure for the gas hydrate compositions of a mole fraction of 39.2 % CO_2 and a mole fraction of 60.8 % H_2 is 11.01 MPa at 278.75 K. The pressure is reduced to 3.15 MPa at the same temperature in the presence of a mole fraction of 0.14 % TBAB in the liquid phase. As shown, there is an approximate 71.38 % reduction of the equilibrium pressure on account of the addition of only 0.14 % mole fraction of TBAB, and with the increase of the mole fraction of TBAB from (0.14 to 0.29) %, the pressure decreases to 0.85 MPa. In addition, at the same TBAB concentration, the equilibrium hydrate formation pressure increases with the increase of the equilibrium temperature.

After our first-stage separation, the residual gas contains an approximate mole fraction of 18 % CO_2. Thus, the residual gas requires further separation as the second-stage feed gas. Experimental measurements of equilibrium hydrate formation conditions were measured for the CO_2 + H_2 gas mixture of the mole fraction of 18.5 % CO_2 in the presence of TBAB with the mole fraction of (0.14, 0.21, 0.29, 0.50, and 1.00) %. The experiments were carried out in the pressure range of (0.48 to 7.26) MPa and the temperature range of (274.45 to 285.45) K. The experimental data are tabulated in Table 2 and plotted in Figure 4. As shown in Figure 4, the equilibrium hydrate formation conditions obtained have the similar characteristics with that for the CO_2 + H_2 gas mixture of a mole fraction of 39.2 % CO_2 with the different concentration of TBAB. The equilibrium formation pressure decreases with the increase of the concentration of TBAB at a certain temperature.

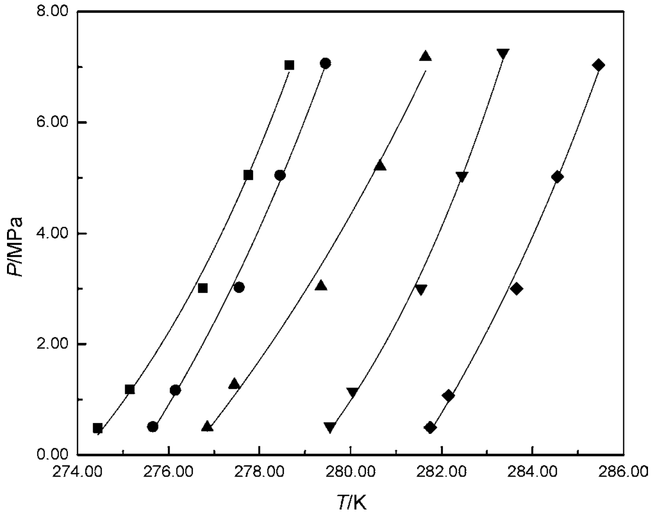

Figure 4. Equilibrium hydrate formation pressure for the CO_2 (1) + H_2 (2) gas mixture with $x_1 = 18.5$ % and $x_2 = 81.5$ % in the presence of TBAB (3) + H_2O (4). ■, $x_3 = 0.14$ %; ●, $x_3 = 0.21$ %; ▲, $x_3 = 0.29$ %; ▼, $x_3 = 0.50$ %; ◆, $x_3 = 1.00$ %.

Table 2. Equilibrium Hydrate Formation Pressure for the CO_2 (1) + H_2 (2) Gas Mixture with $x_1 = 18.5$ % and $x_2 = 81.5$ % in the Presence of TBAB (3) + H_2O (4)

100 x_3	*T*/K	*P*/MPa
0.14	274.45	0.48
	275.15	1.19
	276.75	3.01
	277.75	5.05
	278.65	7.04
0.21	275.65	0.51
	276.15	1.17
	277.55	3.03
	278.45	5.05
	279.45	7.07
0.29	276.85	0.50
	277.45	1.27
	279.35	3.04
	280.55	5.21
	281.65	7.18
0.50	279.55	0.52
	280.05	1.15
	281.55	2.97
	282.45	5.04
	283.35	7.26
1.00	281.75	0.51
	282.15	1.07
	283.65	3.00
	284.55	5.02
	285.45	7.04

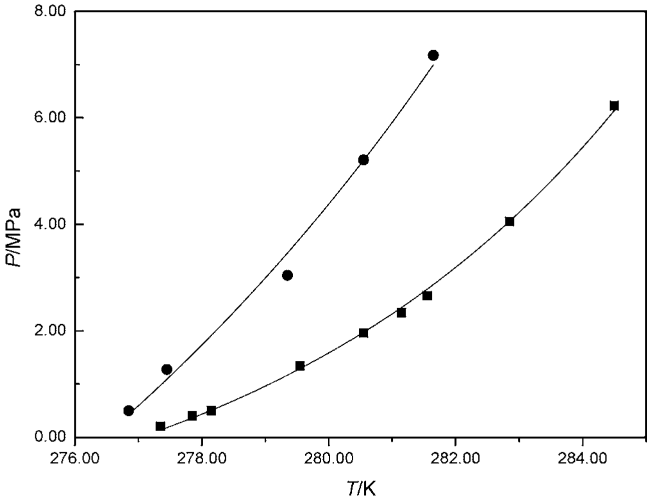

Figure 5. Equilibrium hydrate formation pressure for the CO_2 (1) + H_2 (2) gas mixture with different CO_2 concentration in the presence of TBAB (3) + H_2O (4) with $x_3 = 0.29$ %. ■, $x_1 = 39.2$ %; ●, $x_1 = 18.5$ %.

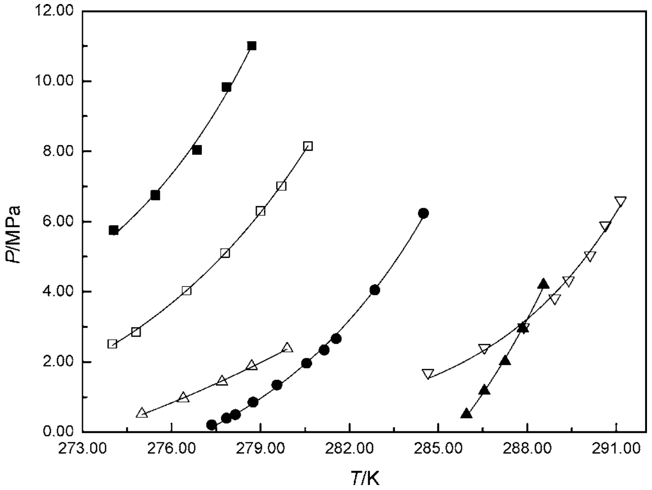

Figure 6. Effects of different additives on equilibrium hydrate formation pressure for the CO_2 + H_2 gas mixture. ■, pure water; □, a mole fraction of 3.2 % C_3H_8 (dry gas), Kumar et al.[11] ▲, a mole fraction of 1.0 % THF (liquid), Lee et al.;[14] ▲, CP (the volume ratio of CP to water = 1.5), Zhang et al.[13] ●, a mole fraction of 0.29 % TBAB (liquid); ▲, a mole fraction of 2.67 % TBAB (liquid).

Figure 5 gives the typical curve of the effect of the concentration of CO_2 on the equilibrium hydrate formation conditions for the CO_2 + H_2 gas mixture in the presence of TBAB with the same concentration. As shown in Figure 5, the equilibrium hydrate formation pressures for the two CO_2 + H_2 mixture containing a mole fraction of 60.8 % H_2 and a mole fraction of 81.5 % H_2 are (1.96 and 5.21) MPa, respectively, in the presence of a mole fraction of 0.29 % TBAB, at 280.55 K. The same behavior can be observed for the other given TBAB concentration and temperature. This illustrates that, as the relative amount of H_2 to CO_2 increases in the gas mixture, the equilibrium shifts to higher pressures at a given temperature with the addition of TBAB under the given concentration.

Figure 6 shows the hydrate formation conditions for CO_2 + H_2 mixtures containing a mole fraction of approximately (38.3 to 39.9) % CO_2 with the four different additives, propane (C_3H_8),[11] THF,[14] cyclopentane (CP),[13] and TBAB. With the effect of different additives, it can be found that the four additives all can effectively reduce the equilibrium hydrate formation pressure of the CO_2 + H_2 mixture, to the different degrees, compared with that of the pure CO_2 + H_2 mixture. For example, at 277.85 K, the phase equilibrium pressure of the CO_2 + H_2 mixture is 9.84 MPa without addition of any additive, 5.10 MPa[11] with the addition of a mole fraction of 3.20 % C_3H_8 in the vapor phase, 1.43 MPa[14] with the addition of a mole fraction of 1.00 % THF in the liquid phase, and 0.40 MPa with the addition of a mole fraction of 0.29 % TBAB in the liquid phase, respectively. That is, the presence of a mole fraction of 0.29 % TBAB, a mole fraction of 1.0 % THF, and a mole fraction of 3.2 % C_3H_8 can make the hydrate formation pressure of the CO_2 + H_2 mixture decrease by (95.93, 85.46, and 48.17) %, respectively, at 277.85 K.

In addition, we have a comparison with the effects of a mole fraction of 2.67 % TBAB and CP on the phase equilibrium pressure of CO_2 + H_2 mixture. As shown in Figure 6, when the temperature is less than 288.0 K, the addition of TBAB of a mole fraction of 2.67 % creates a larger decrease in the equilibrium pressure of CO_2 + H_2 mixture than the addition of

CP does. On the contrary, when the temperature is more than 288.0 K, the promotion effect of CP in the decrease of the equilibrium pressure is better.

Conclusions

The equilibrium hydrate formation conditions of $CO_2 + H_2 +$ TBAB hydrate have been investigated in this work. The results illustrate that TBAB can remarkably reduce the equilibrium hydrate formation pressure of $CO_2 + H_2$ hydrate. The equilibrium formation pressure decreases with the increase in concentration of the TBAB at a certain temperature. At any given concentration, the equilibrium formation pressure increases with the increase in equilibrium temperature. The equilibrium formation condition increases with the increase of the composition of H_2 in the mixture gas. In the certain concentration range for the additives, TBAB, THF, C_3H_8, and CP, the promotion of TBAB makes a bigger reduction of the equilibrium hydrate formation pressure of $CO_2 + H_2$ hydrate, compared with the effect of other additives except for the promotion effect of CP at a temperature of more than 288.0 K.

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