Thermodynamic Equilibrium Conditions for Simulated Landfill Gas Hydrate Formation in Aqueous Solutions of Additives

Zhi-Ming Xia,[†,‡] Zhao-Yang Chen,[†,‡] Xiao-Sen Li,[*,†,‡] Yu Zhang,[†,‡] Ke-Feng Yan,[†,‡] Qiu-Nan Lv,[†,‡] Chun-Gang Xu[†,‡] and Jing Cai[†,‡]

[†]Key Laboratory of Renewable Energy and Gas Hydrate, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, People's Republic of China

[‡]Guangzhou Center for Gas Hydrate Research, Chinese Academy of Sciences, Guangzhou 510640, People's Republic of China

ABSTRACT: This work presents the thermodynamic study of separating CH_4 and CO_2 from the simulated landfill gas (LFG) $[CO_2\ (0.45) + CH_4\ (0.55)]$ based on hydrate crystallization in the presence of tetra-*n*-butyl ammonium bromide (TBAB), tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), and their mixtures. The mole fractions of TBAB, THF, and DMSO aqueous solutions were fixed at 0.0234, 0.0556, and 0.0165, respectively. The equilibrium hydrate formation conditions were measured by *T*-cycle method in the temperature range of (274.15 to 294.95) K and the pressure ranges up to 6.72 MPa. The gas phase in the crystallizer at the equilibrium points was also sampled and analyzed. For the additives with the fixed concentrations studied in this work, it was found that both TBAB and THF can remarkably reduce the equilibrium hydrate formation pressure of LFG mixture gas, but the effect of THF is better than that of TBAB in the high temperature region, while DMSO have no obvious pressure drop effect on the equilibrium hydrate formation conditions but can promote the solubility of CO_2 in the solution. However, the mixture additives of TBAB + DMSO and THF + DMSO can not only remarkably promote the solubility of CO_2 but also remarkably reduce the equilibrium hydrate formation pressure of $CO_2 + CH_4 + H_2O$ hydrate. Moreover, the pressure drop effect of THF + DMSO is better than that of TBAB + DMSO on the $CO_2 + CH_4 + H_2O$ equilibrium hydrate formation in the high temperature region.
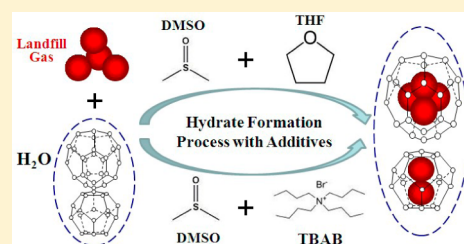
INTRODUCTION

Landfill gas (LFG) is currently generated through biological degradation of the biodegradable organic faction of waste in landfill sites and mainly consists of methane (CH_4) (0.50 to 0.60 mole fraction) and carbon dioxide (CO_2) (0.40 to 0.50 mole fraction).[1] It is acknowledged that both CH_4 and CO_2 are the major greenhouse gases (GHG), and reducing CH_4 and CO_2 emissions from landfills will have an important role in stabilizing GHG concentration in the atmosphere and preventing serious anthropogenic climate change.[2,3] On the other hand, LFG can be used as a kind of renewable bioenergy resource due to its high calorific value. According to Wang et al., the calorific values vary between (15 and 20) $MJ \cdot m^{-3}$ when the CH_4 components in the LFG range from 45 % to 60 %.[4] However, the removal of CO_2 from the landfill gas is very important in this case since it is the prerequisite process to enhance its calorific values and reduce the greenhouse effect. Numerous ways can achieve this goal,[5] such as absorption,[6,7] adsorption,[7] cryogenic fractionation,[8] and membrane separation.[9] These processes prove successful for the selective removal of CO_2, but their major drawback is the large energy cost.

Removing CO_2 selectively from a gas mixture by clathrate hydrate crystallization has been proposed by several groups.[10−21] Clathrate hydrates are nonstoichiometric crystal-line inclusion compounds consisting of a network of hydrogen-bonded water molecules,[22] in which different types of low molecular weight compounds can be enclathrated when the appropriate conditions of moderately low temperature (a few degrees above 273.15 K) and high pressure (in the range of a few MPa) are met. When the mixture gas formed hydrate with water aqueous solution, the component possessing a milder condition of hydrate formation will enrich in the hydrate phase.[23] For this reason, gas hydrate crystallization can be used as a potential separation process for CO_2 capture. It is well-known that CO_2 can form the hydrates under the milder conditions than CH_4.[22] Hence, the high selectivity can be expected for separating CO_2 from its mixtures accompanied with CH_4. On the other hand, the hydrate formation processes will consume considerable energy for pressuring the feed gas and cooling the solution due to the rigorous operating conditions.[23] Therefore, thermodynamic additives such as tetrahydrofuran (THF), tetrabutylammonium bromide (TBAB), and cyclopentane (CP) are encouraged to reduce the financial impact of such a phenomenon. Kang and Lee reported the equilibrium hydrate formation conditions of the mixture gas of $CO_2\ (0.17) + N_2\ (0.83)$ in the presence of mole fraction of 0.01 THF[24] and found that THF can remarkably reduce the equilibrium hydrate formation pressure. Three independent groups reported the thermodynamic studies of

TBAB semiclathrates formed from CO_2 mixture gases for potential applications for CO_2 capture from flue gas and fuel gas.[12,19−21] Our previous work also studied the TBAB hydrate process for removing CO_2 from fuel gas in terms of thermodynamic, kinetic, and separation efficiency.[15,16,18]

While in the case of recovering CO_2 from the LFG by hydrate process, it should be noted that only a limited amount of thermodynamic data currently available reported by Acosta et al. in the open literature.[17] They reported the thermodynamic data of TBAB semiclathrates formed from simulated LFG when the experimental temperature, pressure, mass fraction of TBAB, and mole fraction of CO_2 in the mixture gas ranged from (286 to 293) K, from (3 to 6.5) MPa, (0.05, 0.10 and 0.20), and (0.4 and 0.6), respectively. However, to our best knowledge, there is no research on the thermodynamic study of the hydrate process from simulated LFG (CO_2 (0.45) + CH_4 (0.55)) with TBAB, THF, dimethyl sulfoxide (DMSO), and the mixture of them. DMSO has been reported as an important industrial gas solvent due to its properties in water solutions.[25,26] With the expectation that DMSO can promote the solubility of CO_2 in water and promote the CO_2 hydrate formation, and TBAB and THF can reduce the equilibrium hydrate formation pressure of landfill gas, it is significant to study the thermodynamic properties of the hydrate formation from landfill gas with the mixture of the traditional hydrate promoters and a gas solubility promoter.

In this work, the equilibrium hydrate formation conditions of CO_2 (0.45) + CH_4 (0.55) mixture with DMSO, TBAB, THF, THF + DMSO, and TBAB + DMSO aqueous solutions and with pure water were measured. The mole fraction of TBAB, THF, and DMSO aqueous solutions were fixed at 0.0234, 0.0556, and 0.0165, respectively. The gas phase in the crystallizer was also sampled and analyzed at the equilibrium points. The CO_2 (0.45) + CH_4 (0.55) was simulated as the LFG due to that LFG is a mixture of CO_2 (0.50 to 0.60 mole fraction) and CH_4 (0.40 to 0.50 mole fraction) along with trace amounts of nitrogen (N_2) in practice.[1,27] However, relative to CO_2, the equilibrium hydrate formation pressure of N_2 is close to that of CH_4. Thus, for means of simplification, the ternary systems containing N_2 can be simulated as a binary system of CO_2 and CH_4 in this study.

■ EXPERIMENTAL SECTION

Materials. The chemicals including their suppliers and purities used in this work are listed in Table 1. The chemicals were used without any further purification.

Apparatus. Briefly, the main part of the experimental apparatus is a cylindrical high-pressure stainless steel crystallizer (CR); its inner volume and the maximum working pressure are 336 mL and 25 MPa, respectively. The crystallizer has two circular viewing windows on the front and the back. A magnetic stirrer (450 r·min^{-1}) that is driven by an electric motor (Shanghai Meiyinpu Instrument, Ltd., China) is installed in the crystallizer to agitate the fluids and hydrate crystals. Two Pt1000 thermoprobes (JM6081) with a ± 0.1 K accuracy are inserted into the crystallizer to measure the temperatures in the gas phase and in the hydrate slurry phase, respectively. All pressures are measured by Setra smart pressure transducers (model 552, Boxborough, MA, USA) with the pressures ranging up to 25 MPa and the accuracy of ± 0.02 MPa. All of the temperature and pressure data from the acquisition system are saved at preset sampling intervals on a personal computer (PC). The temperature of the crystallizer is controlled by a

Table 1. Experimental Materials Used in This Work[a]

material	mole fraction purity	supplier
methane	0.99	South China Special Gases Institute Co., Ltd. China
carbon dioxide	0.99	South China Special Gases Institute Co., Ltd. China
tetra-n-butyl ammonium bromide	0.9999	Shanghai Sinopharm Chemical Reagent Co., Ltd., China
tetrahydrofuran	0.9999	Shanghai Sinopharm Chemical Reagent Co., Ltd., China
dimethyl sulfoxide	0.9999	Shanghai Sinopharm Chemical Reagent Co., Ltd., China
water	0.9999	

[a]Aqueous solutions were prepared following the gravimetric method, using an accurate analytical balance. Consequently, uncertainties on the basis of mole fraction are estimated to be <0.01.

thermostatic water bath. The gas samples in the crystallizer at the phase equilibrium points are analyzed by a Wufeng GC522 gas chromatography (GC) (Shanghai Wufeng Scientific Instrument Co., Ltd., China.) immediately. A schematic diagram of the experimental apparatus is shown in Figure 1.
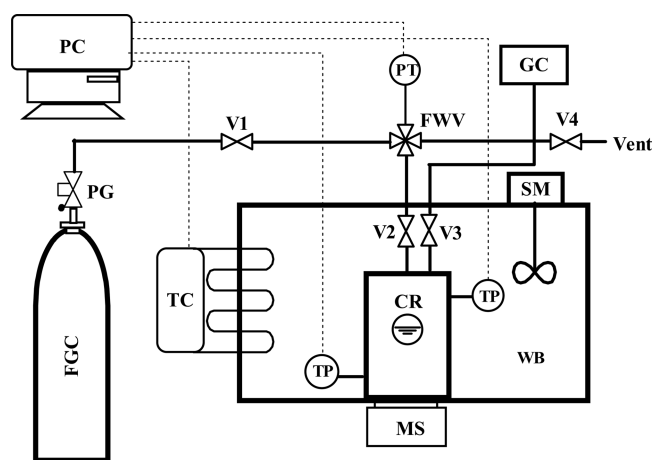

Figure 1. Schematic diagram of the experimental apparatus. FGC, feed gas cylinder; PG, pressure regulator; PC, personal computer; V1 to V4, valve; PT, pressure transducer; GC, gas chromatographer; FWV, four-way valve; SM, stirring motor; TC, temperature controller; TP, thermoprobe; CR, crystallizer; WB, water bath; MS, magnetic stirrer.

Experimental Procedure. The experimental procedure employed in this work was T-cycle method, which almost identical to that used by Ohgaki et al., Hashimoto et al., and Li et al.,[15,28,29] except for an additional step for sampling and analyzing the gas phase in the crystallizer at the equilibrium conditions. After cleaning with deionized water and drying, the high-pressure hydrate crystallizer was initially charged with approximately 180 mL of additive aqueous solution which was prepared at the desired concentration. Subsequently, the hydrate crystallizer filled with the additive aqueous solution was evacuated with a vacuum pump and purged with the CO_2 + CH_4 mixture gas four to five times to ensure the absence of any remnant gas. The CO_2 + CH_4 mixture gas was supplied from the feed gas cylinder through a pressure regulate valve into the hydrate crystallizer. Once the hydrate crystallizer was pressurized up to the desired pressure, the system was cooled and agitated to form the mixed gas hydrate. The hydrate

formation phenomenon can be integrative determined by observing through the circular viewing windows and the pressure depression caused by the hydrate formation. Subsequently, 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 for determining the equilibrium state at each temperature step. Until no particle of hydrates appeared during the gradual heating, we determined this point as the equilibrium point.[15,29,30] Once the equilibrium point was determined, the sampling line was flushed with inert argon, and the gas phase in the hydrate crystallizer was subsequently sampled and then analyzed with GC.[17]

■ RESULTS AND DISCUSSION

Equilibrium Conditions for CO_2 + CH_4 + H_2O Mixture Hydrate. Prior to the experiment for CO_2 + CH_4 + H_2O + TBAB hydrate system, four equilibrium hydrate formation points of the CO_2 (0.45) + CH_4 (0.55) mixture gas were measured in the temperature range of (274.15 to 278.75) K and compared with the equilibrium hydrate formation data of the CO_2 (0.50) + CH_4 (0.50) gas mixture given by Gaudette[30] and Servio et al.[31] As shown in Figure 2, at any certain temperature,
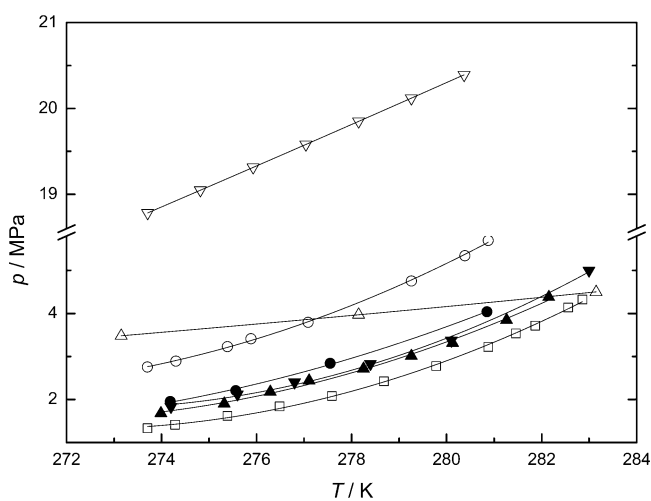

Figure 2. Equilibrium hydrate formation pressure for CH_4 (1) + CO_2 (2) mixture hydrate: ○, $y_1 = 1.00$, $y'_2 = 0.00$, Deaton and Frost;[32] ●, $y_1 = 0.55$, $y_2 = 0.45$, this work; ▲, $y_1 = 0.50$, $y_2 = 0.50$, Gaudette;[30] ▼, $y_1 = 0.50$, $y_2 = 0.50$, Servio et al.;[31] □, $y_1 = 0.00$, $y_2 = 1.00$, Deaton and Frost;[32] △, vapor pressure of pure CO_2, Matvienko and Yarym-Agaev;[35] ▽, vapor pressure of CH_4, Lu et al.[36]

the equilibrium pressure of the CO_2 + CH_4 mixture hydrate is between that of the unitary CO_2 hydrate and CH_4 hydrate.[32] Furthermore, the equilibrium hydrate formation pressure of CO_2 (0.45) + CH_4 (0.55) mixture gas is slightly higher than that of CO_2 (0.50) + CH_4 (0.50) gas due to the composition difference. It also demonstrates that the equilibrium hydrate formation pressure of the CO_2 + CH_4 + H_2O hydrate decreases with the increase of the composition of CO_2 in the mixture gas.

Equilibrium Conditions of Pure Additive Aqueous Solutions. Before studying the equilibrium hydrate formation conditions of the simulated LFG gas in the aqueous solution with additives, the equilibrium formation conditions of pure TBAB, THF, TBAB + DMSO, and THF + DMSO aqueous solutions hydrate were measured and are listed in Table 1. The mole fractions of TBAB, THF, and DMSO aqueous solutions

were fixed at 0.0234, 0.0556, and 0.0165, respectively. Figure 3 shows the equilibrium hydrate formation condition of pure
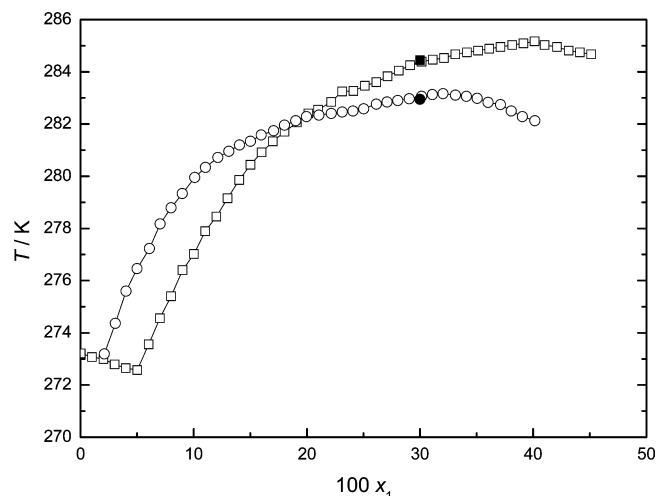

Figure 3. Hydrate phase equilibrium conditions for TBAB (3) + DMSO (5) + H_2O (6) aqueous solutions. □, Type-A TBAB hydrate, Oyama et al.;[33] ○, Type-B TBAB hydrate, Oyama et al.;[33] ■, $x_3 = 0.0234$, $x_5 = 0.0$, this work; ●, $x_3 = 0.0234$, $x_5 = 0.0156$, this work.

TBAB and TBAB + DMSO mixture aqueous solutions in this work and the experimental values of pure TBAB aqueous solution given by Oyama et al.[33] It can be seen from Figure 3 that the hydrate forms from 0.0234 mole fraction of TBAB aqueous solution are thermodynamically stable at the Type-A TBAB hydrate curve, and our experimental data of pure TBAB hydrate are in excellent agreement with the literature data.[33] Furthermore, it is interesting to find that the hydrate decomposition temperature of 0.0234 mole fraction TBAB aqueous solution without DMSO is 284.45 K, while that of 0.0234 mole fraction TBAB with 0.0165 mole fraction DMSO is 282.95 K, which is close to the decomposition temperature of the Type-A TBAB hydrate curve and is obviously lower than that of the Type-A TBAB hydrate curve. It indicates that the addition of DMSO may be lower the decomposition temperature of TBAB pure hydrate; in other words, the addition of DMSO reduces the stability of TBAB hydrate from Type A to Type B. Figure 4 shows the equilibrium formation condition of pure THF and THF + DMSO mixture aqueous solutions in this work and the experimental values of pure THF aqueous solution given by Delahaye et al.[34] The similar phenomenon also can be seen in the case of THF with DMSO. As shown in Figure 4, the hydrate decomposition temperature of THF + DMSO + H_2O mixture hydrate is 276.15 K, which is obviously lower than that of the 0.0556 mole fraction THF aqueous solution without DMSO.

Equilibrium Conditions for CO_2 + CH_4 + H_2O Mixture Hydrate Formation with Different Additives. The measurements of equilibrium hydrate formation conditions for the CO_2 (0.45) + CH_4 (0.55) mixture gas with TBAB, THF, DMSO, TBAB + DMSO, and THF + DMSO aqueous solutions in the pressure range of (0.44 to 4.3) MPa and temperatures in the range of (274.25 to 294.95) K were carried out. For all of the experiments, the mole concentrations of TBAB, THF, and DMSO aqueous solutions were fixed at 0.0234, 0.0556, and 0.0165, respectively. The equilibrium temperatures, pressures, and compositions were summarized in Table 2 and plotted in Figures 5 and 6. As shown in Figure 5,
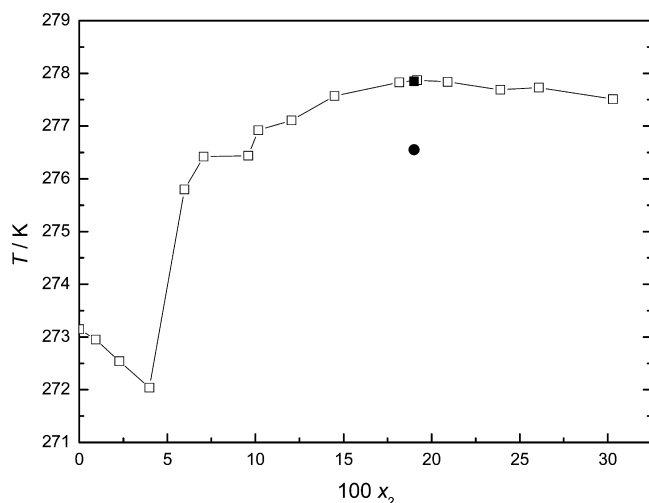
Figure 4. Hydrate phase equilibrium conditions for THF (4) + DMSO (5) + H_2O (6) aqueous solutions. □, x_4 = 0.0 to 0.3, x_5 = 0.0, Delahaye et al.;[34] ■, x_4 = 0.0556, x_5 = 0.0, this work; ●, x_4 = 0.0556, x_5 = 0.0156, this work.

Table 2. Hydrate−Liquid−Vapor Equilibrium Temperature T, Pressure p with Standard Uncertainty $u(p)$, and Equilibrium Vapor-Phase Mole Fraction of CO_2 y'_2 for CH_4 (1) + CO_2 (2) + TBAB (3) + THF (4) + DMSO (5) + H_2O (6) Mixture Hydrate[a]

x_3	x_4	x_5	T/K	p/MPa	$u(p)$/MPa	$10^2 y'_2$
			274.15	1.90	0.04	42.85
			275.55	2.18	0.03	42.62
			277.55	2.96	0.03	42.65
			280.85	4.34	0.04	42.58
0.0234			284.45	0.00		
			285.65	0.44	0.04	39.35
			287.85	1.40	0.05	38.82
			289.75	2.34	0.03	38.66
			291.55	3.83	0.02	39.25
	0.0556		277.85	0.00		
			284.65	0.50	0.04	38.62
			287.55	0.84	0.03	38.55
			290.95	1.52	0.05	38.37
			293.25	2.30	0.04	38.32
			294.95	3.08	0.05	38.28
		0.0165	274.25	1.83	0.05	33.32
			276.25	2.92	0.04	33.45
			278.95	4.03	0.02	31.06
			279.55	4.30	0.03	33.28
	0.0556	0.0165	276.15	0.00		
			283.35	0.60	0.03	37.37
			285.25	1.06	0.02	37.61
			288.15	1.69	0.02	
			291.45	2.37	0.03	37.86
			292.35	2.72	0.04	40.22
			293.85	3.07	0.03	38.59
0.0234		0.0165	283.15	0.00		
			284.75	0.77	0.03	37.24
			286.05	1.33	0.04	37.56
			286.85	1.63	0.05	37.26
			288.15	2.35	0.05	37.43

[a]Standard uncertainties u are $u(T)$ = 0.1 K, $u(x)$ = 0.0006, and $u(y'_2)$ = 0.0005; x_3, x_4, and x_5 denote the component concentration of TBAB, THF, and DMSO in the aqueous solutions, respectively; y_1 and y_2 denotes CH_4 and CO_2 composition in the feed gas, respectively; y'_2 denotes the gas phase composition of CO_2 at the equilibrium points.

the equilibrium hydrate formation pressure of the CO_2 + CH_4 + H_2O + DMSO mixture hydrate is almost close to that of the CO_2 + CH_4 + H_2O mixture hydrate, while the equilibrium hydrate formation pressure of the CO_2 + CH_4 + H_2O + TBAB and CO_2 + CH_4 + H_2O + TBAB + DMSO mixture hydrate is remarkably lower than that of the CO_2 + CH_4 + H_2O mixture hydrate. For example, for the certain (0.45) + CH_4 (0.55) gas mixture, the equilibrium hydrate formation pressure of the CO_2 + CH_4 + H_2O + DMSO hydrate is 1.83 MPa at 274.25 K, which is close to that of CO_2 + CH_4 + H_2O hydrate (1.90 MPa at 274.15 K); the equilibrium hydrate formation pressure of the CO_2 + CH_4 + H_2O mixture without any additives is 6.72 MPa at 285.95 K, while that of the CO_2 + CH_4 + H_2O mixture with TBAB and DMSO + TBAB aqueous solutions at the same temperature reduces to (0.67 and 1.25) MPa, respectively. It means that there is approximately 90 % reduction of the equilibrium pressure on account of the addition of only 0.0234 mole fraction of TBAB, but the addition of DMSO reduces the pressure drop effect of TBAB from 90 % to about 81 %. It demonstrates that the addition of TBAB can considerably reduces the pressure required to form the CO_2 + CH_4 + H_2O mixture hydrate, but DMSO will slightly lower the lower the pressure effect of TBAB on the CO_2 + CH_4 + H_2O hydrate when it is in conjunction with TBAB. Figure 6 shows the equilibrium hydrate formation pressure of the CO_2 + CH_4 + H_2O mixture hydrate with THF and THF + DMSO and also compares the results of that with pure water and pure DMSO aqueous solutions. As shown in Figure 6, it is obvious that THF can remarkably reduce the equilibrium hydrate formation pressure of CO_2 + CH_4 + H_2O mixture hydrate. For example, the equilibrium hydrate formation pressure of the mixture hydrate with THF is only 0.55 MPa at 285.95 K, which is about 91.8 % lower than that of the mixture hydrate without THF. On the other hand, even though the pure DMSO aqueous solution does not have the pressure drop effect on the CO_2 + CH_4 + H_2O + DMSO mixture hydrate formation conditions, and the equilibrium hydrate formation conditions of CO_2 + CH_4 + H_2O + DMSO mixture hydrate is almost close to that of the CO_2 + CH_4 + H_2O mixture hydrate, the THF + DMSO mixture additive still can remarkably reduce the equilibrium

hydrate formation pressure of the mixture hydrate. For example, the equilibrium hydrate formation pressure of CO_2 + CH_4 + H_2O mixture hydrate with THF + DMSO is only 1.16 MPa, which is about 82.73 % lower than that of the mixture hydrate without THF + DMSO.

The pressure drop effects of TBAB, DMSO, TBAB + DMSO, and TBAB + DMSO additives on the equilibrium hydrate formation of the CO_2 (0.45) + CH_4 (0.55) mixture gas were also compared each other and compared with that of CO_2 (0.5) + CH_4 (0.5) mixture gas with neohexane given by Servio et al.[31] in Figure 7. As shown in Figure 7, both TBAB and THF have the best pressure drop effect on the CO_2 + CH_4 + H_2O mixture hydrate formation among the investigated additives, but the effect of THF is better than that of TBAB in the high temperature region. For example, the equilibrium hydrate formation pressure of CO_2 + CH_4 + H_2O hydrate with TBAB is lower than that with THF at a certain temperature when the temperature below 286.45 K, while the equilibrium hydrate formation pressure of CO_2 + CH_4 + H_2O hydrate with TBAB is
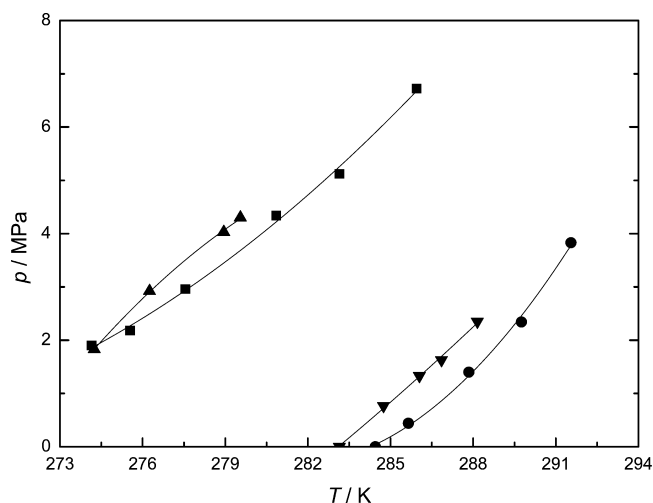
Figure 5. Effects of TBAB (3) + DMSO (5) + H_2O (6) aqueous solutions on equilibrium hydrate formation pressure of CH_4 (0.55) + CO_2 (0.45) mixture. ■, $x_6 = 1.0$; ●, $x_3 = 0.0234$, $x_5 = 0.0$; ▲, $x_3 = 0.0$, $x_5 = 0.0156$; ▼, $x_3 = 0.0234$, $x_5 = 0.0156$; all of the lines are drawn as fitting curves of the experimental data.
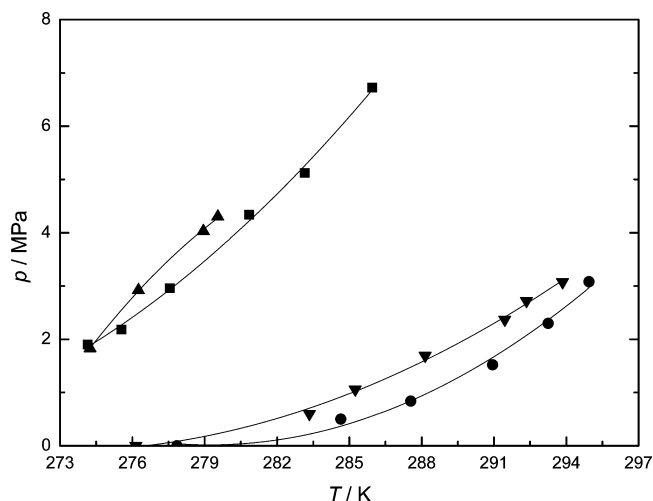

Figure 6. Effects of THF (4) + DMSO (5) + H_2O (6) aqueous solutions on equilibrium hydrate formation pressure of CH_4 (0.55) + CO_2 (0.45) mixture. ■, $x_6 = 1.0$; ●, $x_4 = 0.0556$, $x_5 = 0.0$; ▲, $x_4 = 0.0$, $x_5 = 0.0156$; ▼, $x_4 = 0.0556$, $x_5 = 0.0156$; all of the lines are drawn as fitting curves of the experimental data.

higher than that with THF at a certain temperature when the temperature above 286.45 K. Moreover, the pressure drop effect of TBAB + DMSO is better than that of THF + DMSO on the CO_2 + CH_4 + H_2O mixture hydrates form in the low-temperature region. For example, the pressure drop effect of TBAB + DMSO is better than that of THF + DMSO on the CO_2 + CH_4 + H_2O hydrate formation at a certain temperature when the temperature below 285.55 K, while the pressure drop effect of THF + DMSO is better than that of TBAB + DMSO on the CO_2 + CH_4 + H_2O hydrate formation at a certain temperature when the temperature above 285.55 K. On the other hand, although the pressure drop effect of both TBAB and THF on the CO_2 + CH_4 + H_2O mixture hydrate formation will be slightly lower when them mixing with DMSO, the pressure drop effects of both TBAB + DMSO and THF + DMSO are still remarkably better than that of neothexane.[31] It demonstrates that, among the investigated additives, TBAB and
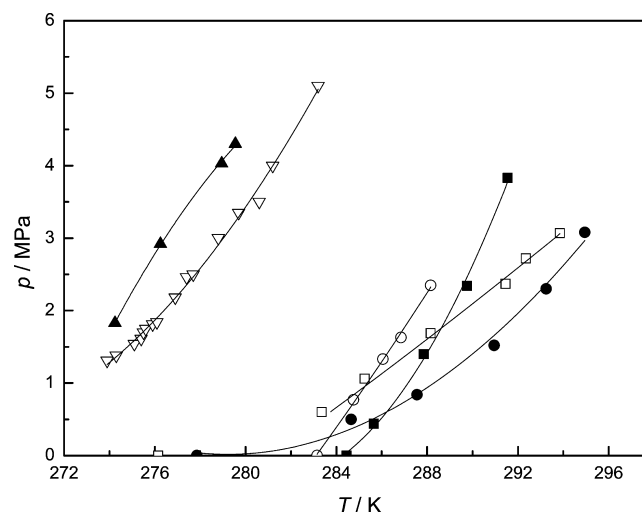

Figure 7. Comparison of the effects of different TBAB (3) + THF (4) + DMSO (5) + H_2O (6) aqueous solutions on equilibrium hydrate formation pressure of CH_4 (0.55) + CO_2 (0.45) mixture. ■, $x_3 = 0.0234$, $x_4 = x_5 = 0.0$; ●, $x_4 = 0.0556$, $x_3 = x_5 = 0.0$; ▲, $x_5 = 0.0156$, $x_3 = x_4 = 0.0$; □, $x_3 = 0.0$, $x_4 = 0.0556$, $x_5 = 0.0156$; ○, $x_3 = 0.0234$, $x_4 = 0.0$, $x_5 = 0.0156$; ▽, CO_2 (0.5) + CH_4 (0.5) mixture gas with 0.1036 mol fraction of neohexane, Servio et al.;[31] all of the lines are drawn as fitting curves of the experimental data.

THF have the best pressure drop effect on the CO_2 + CH_4 + H_2O hydrate formation, with TBAB + DMSO and THF + DMSO following, then neohexane, and finally DMSO.

For the above measurements of the equilibrium hydrate formation conditions, the gas phase compositions at the equilibrium points were also measured and listed in Table 2, which can be regarded as a token of the relative solubility of CO_2 + CH_4 in the different additive aqueous solutions. It can be seen from Table 2 that the mole fraction of CO_2 in the gas phase at the equilibrium points of the mixture hydrate systems without any additives and with DMSO, TBAB, THF, TBAB + DMSO, and THF + DMSO is approximately 0.42, 0.33, 0.38, 0.38, 0.37, and 0.37, respectively. It demonstrates that both DMSO and its mixture with TBAB or THF can considerably promote the solubility of CO_2 in the solution, but the effect of DMSO is remarkable. This proves the prominent promotion effect of DMSO as a CO_2 gas solvent in the water solution. Thus, DMSO may be a potential kinetic promoter for the CO_2 mixture hydrate formation, although this should be proved by the kinetic study in the following work.

■ CONCLUSION

The equilibrium hydrate formation conditions for simulated landfill gas (LFG) [CO_2 (0.45) + CH_4 (0.55)] with pure water and with TBAB, THF, DMSO, TBAB + DMSO, and THF + DMSO aqueous solutions have been experimentally investigated in this work. The gas phase compositions at the equilibrium points were also measured. The results illustrates that both TBAB and THF can remarkably reduce the equilibrium hydrate formation pressure of LFG mixture gas, while DMSO has no obvious pressure drop effect on the equilibrium hydrate formation conditions but has a considerable promoting effect on the solubility of CO_2 in the solution. However, the mixture additives of TBAB + DMSO and THF + DMSO can not only remarkably promote the solubility of CO_2 but also reduce the equilibrium hydrate formation pressure of

CO_2 + CH_4 + H_2O hydrate. Thus, DMSO may be a potential kinetic promoter for the CO_2 mixture hydrate formation. Moreover, for the investigated additives, the pressure drop effect of THF or THF + DMSO is better than that of TBAB or TBAB + DMSO on the CO_2 + CH_4 + H_2O equilibrium hydrate formation in the high temperature region.

■ AUTHOR INFORMATION

Corresponding Author
*Tel. and fax: +86-20-87057037. E-mail: lixs@ms.giec.ac.cn.

Notes
The authors declare no competing financial interest.

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