JOURNAL OF
CHEMICAL &
ENGINEERING
DATA

ARTICLE

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Measurements for the Dissociation Conditions of Methane Hydrate in the Presence of 1,3,5-Trioxane and Oxolan-2-ylmethanol

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ABSTRACT: The dissociation conditions for methane hydrates in the presence of (0.0104 to 0.0350) mole fraction ((0.05 to 0.15) mass fraction) 1,3,5-trioxane aqueous or brine solutions and (0.0192 to 0.0702) mole fraction ((0.10 to 0.30) mass fraction) oxolan-2-ylmethanol (tetrahydrofurfuryl alcohol, THFA) aqueous solutions were experimentally measured in this study. The hydrate phase dissociation conditions were measured with an apparatus which was operated at high pressure and low temperature conditions. The liquid water−hydrate−vapor (L_w-H-V) three-phase equilibrium dissociation temperatures and pressures for methane hydrate in the presence of these additives were determined by employing the isochoric method. New experimental data are reported within the pressure range from (4 to 10) MPa for the methane + water + 1,3,5-trioxane hydrate system and from (9 to 15) MPa for the methane + water + oxolan-2-ylmethanol hydrate system, respectively. It is demonstrated that the addition of 1,3,5-trioxane has a promotion effect on the formation of methane hydrate. In addition, the liquid−hydrate−vapor (L-H-V) three-phase equilibrium dissociation conditions for brine solution with water and 0.011 mole fraction (0.035 mass fraction) NaCl were also measured in this study with the addition of 1,3,5-trioxane. The promotion effect for methane hydrate formation in brine environments is also observed. On the other hand, the results of adding oxolan-2-ylmethanol show the inhibition effect on the formation of methane hydrate.

INTRODUCTION

Gas hydrates have drawn much attention in various fields. They are naturally found in deep seas and permafrost around the world, providing a large amount of methane energy. The amount of gas in known hydrate reserves is at least twice as much as the energy contained in the total fossil fuel. Gas hydrates are formed under low temperature and high pressure conditions. They are solid ice-like crystalline molecular complexes which are composed of water and suitably sized guest molecules. Water molecules build different arrangements of cages through hydrogen bonding where guest molecules are enclosed in those cages to stabilize the structure. Three different structures of sI, sII, and sH of gas hydrate are observed depending on the molecular size and shape of the guest molecules.[1] A detailed review of gas hydrate is described by Sloan and Koh.[2]

Gas hydrates may cause oil and gas pipeline blockage at particular temperature and pressure conditions. The oil and gas industry have introduced various thermodynamic inhibitors such as methanol,[3] glycols,[4,5] and electrolyte solutions[6] to maintain flow assurance in pipelines. On the contrary, gas hydrate formation is found to be favorable for other applications such as natural gas storage and transportation, refrigeration process, and CO_2 sequestration. Methane storage in sI hydrate structure usually exists at high formation pressures. Methane hydrate formation at a relatively lower pressure is preferred due to safety and economic concerns. Many previous studies have been devoted to adding promoters in methane hydrate to shift the dissociation temperature and pressure to milder conditions, leading to low energy consumption processes. Khokhar et al.[7] proposed that filling the second guest molecule in the cage would stabilize the hydrate structure, shift the hydrate dissociation to milder conditions, and achieve the promotion effect. Several investigations on the measurements of the dissociation data for methane hydrate with additives have been recently reported. The additives include cyclic organic compounds such as 1,4-dioxane,[8] tetrahydropyran (THP),[9] cyclobutanone (CB),[9] and tetrahydrofuran (THF),[10] all forming sII hydrate structures. Furthermore, sH hydrates formed when larger guest substances such as pinacolone,[11] pinacolyl alcohol,[11] and methylcyclohexane[12] were introduced. All of these compounds exhibit significant reduction of the methane hydrate dissociation pressure. Accordingly, these thermodynamic data provide useful information for natural gas storage and transportation. We have recently published our measurement results of methane hydrate dissociation conditions using 2-methyl-2-propanol as a promoter.[13]

In this study, a cyclic ether compound 1,3,5-trioxane ($C_3H_6O_3$) was selected as a possible promoter for methane hydrate formation. The concentration range for 1,3,5-trioxane in our measurements was from (0.0104 to 0.0341) mole fraction ((0.05 to 0.15) mass fraction) in aqueous solution by considering the solubility limit of 1,3,5-trioxane in water.[14] The pressure range in our experiments for measuring the methane hydrate conditions was from (4 to 10) MPa. To model the seawater conditions, the dissociation conditions of methane hydrates were also investigated for brine solution with water and 0.011 mole fraction (0.035 mass fraction) NaCl. A comparison of the promotion effects is reported in this study between the pure water and brine systems with the same mass fraction of additive of 1,3,5-trioxane. Another component oxolan-2-ylmethanol ($C_5H_{10}O_2$), a derivative of cyclic ether compound, was also selected to determine its effect on the dissociation conditions of methane hydrate. Oxolan-2-ylmethanol is a water-soluble compound, and its concentration

Received: April 23, 2011
Accepted: June 28, 2011
Published: July 08, 2011

range was set in this study from (0.0192 to 0.0702) mole fraction ((0.10 to 0.30) mass fraction) in aqueous solution. The motivation of this study is to obtain new thermodynamic equilibrium data of methane hydrate with additives. These data can be applied on the industrial design of gas hydrate exploitation, natural gas storage, and transportation.

■ EXPERIMENTAL SECTION

Materials. Methane was purchased from Air Products and Chemicals with a certified purity of 99.9 %. 1,3,5-Trioxane and oxolan-2-ylmethanol both with purities greater than 99.0 % and sodium chloride with a purity greater than 99.5 % were purchased from Sigma-Aldrich Company. All chemicals were used without further purification. Deionized water was used in all experiments.

Experimental Apparatus. The apparatus used in this study to measure the dissociation conditions of methane hydrates is the same as that described in our previous publication.[13] The main cylindrical equilibrium cell with a volume of 200 cm^3 was made of stainless steel that could endure pressure up to 30 MPa. The equilibrium cell had three sapphire windows on the top, front, and back sides, respectively. It was immersed in a water bath, and another water bath circulator with a programmable cooling and heating controller (Neslab, RTE 7 equipped with a remote programming controller) was used to control the temperature. The agitation of the solution and hydrate was made by employing a magnetic stirrer at 650 rpm that was equipped at the bottom of the equilibrium cell. The temperature and pressure inside the equilibrium cell were measured by a platinum resistance thermometer (Fluke, 1529) and a pressure gauge (Heise, type PM). The accuracies for the measurements of temperature and pressure in this study were ± 0.01 K and ± 0.001 MPa, respectively.

Experimental Methods. The isochoric method was employed in this investigation to measure the dissociation conditions of methane hydrate. The method was similar to those described by Sloan and Koh[2] and Tohidi et al.[15] The experimental procedures for measuring methane hydrate dissociation points were also similar to those reported in our previous work.[13] The equilibrium cell containing approximately 100 cm^3 solution of water and additive was first immersed into the temperature controlled water bath. Methane gas was delivered into the equilibrium cell from a high pressure gas cylinder through an ISCO pump. The cell was first repeatedly flushed with methane to degas air in the cell. Methane was finally introduced through the ISCO pump until the desired pressure was reached. The water bath circulator and magnetic stirrer were then switched on until a stable state in the equilibrium cell was observed. The temperature of the water bath was decreased afterward by a programmable controller. A rapid pressure drop was observed in the equilibrium cell where methane gas was captured into clathrate hydrate. At this stage, the temperature of the equilibrium cell was maintained for 2 h to keep the formation of methane hydrate. The temperature in the equilibrium cell was then increased to a value slightly below the dissociation temperature. Subsequently, the temperature was increased at a very slow heating rate of 0.05 $K\cdot h^{-1}$ to achieve a nearly thermodynamic equilibrium state. The increase of pressure was observed during these heating steps while hydrate still existed in the equilibrium cell. After the hydrate was totally dissociated, the plotted curve of pressure against temperature during the continuous heating process coincided with that of the initial cooling step. The dissociation condition was determined from the pressure–temperature plot by observing a sharp slope change during the final heating steps. The dissociation temperature and pressure data sets were measured with various initial pressures of the input methane and also with various concentrations of additives. The reproducibility of experimental data had been confirmed by repeated measurements conducted in this study.

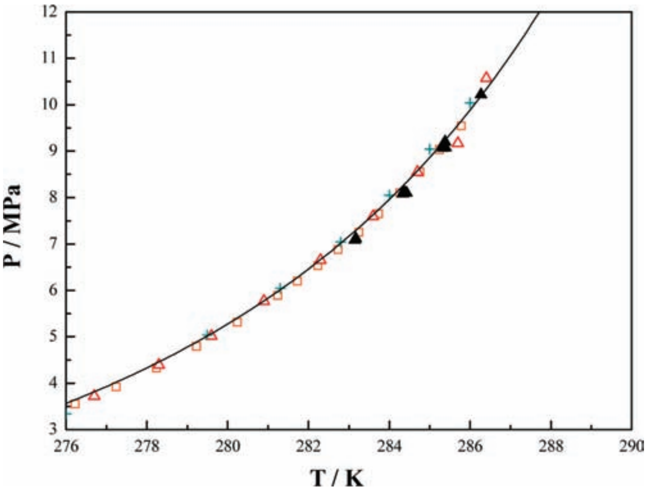

Figure 1. Comparison of methane hydrate dissociation conditions with literature data. ▲, this work; +, de Roo et al.;[16] △, Adisasmito et al.;[17] □, Nakamura et al.;[12] the solid line was predicted from the thermodynamic model, HW Hydrate Program.[18]

■ RESULTS AND DISCUSSION

The reliability and reproducibility of the experimental procedure were first investigated by comparing the measured L_w-H-V three-phase equilibrium methane hydrate dissociation data in this study with those in the literature.[12,16−18] The results are illustrated in Figure 1 where good consistency is demonstrated and the validity of experimental technique in this experiment is confirmed.

The dissociation pressures and temperatures for the equilibrium of L_w-H-V three phases of methane + water + 1,3,5-trioxane were experimentally determined in this study. The dissociation data are listed in Table 1 for various concentrations of the 1,3,5-trioxane additive. Considering the solubility limit of 1,3,5-trioxane in water,[14] the concentration range for 1,3,5-trioxane in our measurements was from (0.0104 to 0.0341) mole fraction ((0.05 to 0.15) mass fraction) in aqueous solution. The plot of those dissociation pressures against temperatures is shown in Figure 2 by solid symbols. As shown in Figure 2, the addition of 1,3,5-trioxane in methane hydrate system shifts the original methane hydrate phase boundaries to lower pressure and higher temperature ranges. The stability region of methane hydrate is broadened which illustrates a promotion effect. This result is consistent with the previous assumption that cyclic ether compounds could lower hydrate formation pressure. Furthermore, the promotion effect is enhanced with the increase of the concentration of 1,3,5-trioxane in hydrate system. For 0.0341 mole fraction (0.15 mass fraction) of 1,3,5-trioxane additive, the dissociation temperature increases about 13 K at a given pressure in comparison to that of methane + water system without an additive. No direct experimental evidence for the structure of methane hydrate with a 1,3,5-trioxane additive was investigated in this study. We determine the heat of dissociation for methane hydrate with a 1,3,5-trioxane additive through the experimentally measured

Table 1. Experimental Results for the Three-Phase (L_w-H-V) Dissociation Points in the System Containing Methane + Water + 1,3,5-Trioxane[a]

system	P/MPa	T/K
methane + water + 1,3,5-trioxane (x = 0.0104)	10.11	294.58
	9.15	293.83
	8.14	293.04
	7.21	292.25
	6.22	291.08
	5.20	289.97
	4.24	288.51
methane + water + 1,3,5-trioxane (x = 0.0217)	10.13	296.61
	9.18	296.03
	8.20	295.22
	7.24	294.40
	6.26	293.47
	5.25	292.29
	4.27	290.94
methane + water + 1,3,5-trioxane (x = 0.0341)	10.15	297.38
	9.18	296.76
	8.17	295.99
	7.20	295.12
	6.23	294.18
	5.25	293.11
	4.27	291.79

[a] x = mole fraction of 1,3,5-trioxane in aqueous solution.

Table 2. Experimental Results for the Three-Phase (L-H-V) Dissociation Points in the System Containing Methane + Brine + 1,3,5-Trioxane[a]

system	P/MPa	T/K
methane + brine + 1,3,5-trioxane (x = 0.0107)	10.15	293.42
	9.14	292.68
	8.19	291.98
	7.18	291.03
	6.22	290.18
	5.24	288.98
	4.25	287.60
methane + brine + 1,3,5-trioxane (x = 0.0223)	10.08	295.24
	9.18	294.63
	8.17	293.91
	7.22	293.08
	6.23	292.11
	5.23	290.92
	4.23	289.61
methane + brine + 1,3,5-trioxane (x = 0.0350)	10.10	295.81
	9.16	295.19
	8.18	294.44
	7.22	293.64
	6.25	292.66
	5.23	291.55
	4.26	290.11

[a] x = mole fraction of 1,3,5-trioxane in brine solution.

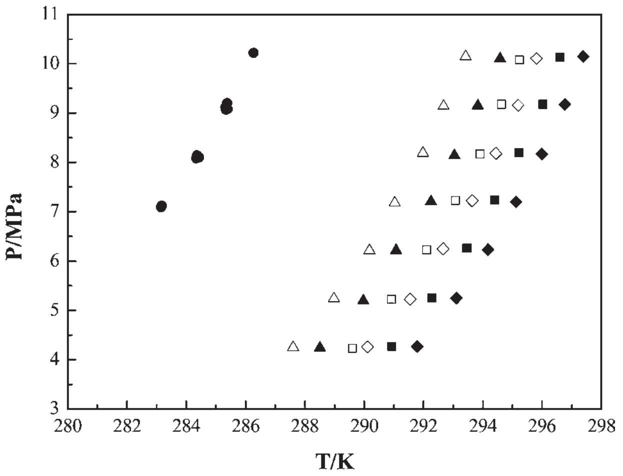

Figure 2. Comparison of dissociation conditions for the methane + water, methane + water + 1,3,5-trioxane, and methane + brine + 1,3,5-trioxane systems. ●, pure water; ▲, 1,3,5-trioxane in water (x = 0.0104); ■, 1,3,5-trioxane in water (x = 0.0217); ◆, 1,3,5-trioxane in water (x = 0.0341); △, 1,3,5-trioxane in brine (x = 0.0107); □, 1,3,5-trioxane in brine (x = 0.0223); ◇, 1,3,5-trioxane in brine (x = 0.0350); x = mole fraction of 1,3,5-trioxane in aqueous or brine solution.

pressure—temperature phase equilibrium data using the Clausius—Clapeyron equation. Following the previous literature of Sloan and Fleyfel,[19] we estimate that the structure of methane + 1,3,5-trioxane hydrate is sII.

The investigation of the methane hydrate promotion effect in the presence of an additive under the seawater conditions was also investigated in this study. To simulate the salinity of the seawater environment, the brine solution was synthesized with water and 0.011 mole fraction (0.035 mass fraction) NaCl. In the brine systems, the dissociation conditions of methane hydrate were measured with (0.0107 to 0.0350) mole fraction (0.05 to 0.15 mass fraction) of 1,3,5-trioxane in brine solution. The dissociation pressures and temperatures for the L-H-V three-phase equilibrium of methane + brine + 1,3,5-trioxane systems are presented in Table 2. A graphical comparison of the dissociation conditions of pure water, water with 1,3,5-trioxane additive, and brine with the 1,3,5-trioxane additive is also illustrated in Figure 2. The experimental results show that the 1,3,5-trioxane additive still exhibits the promotion effect on hydrate formation in the brine system. Similar to the pure water system, the promotion effect in the brine system also increases with the concentration of 1,3,5-trioxane. For the concentration of 0.0350 mole fraction (0.15 mass fraction) of 1,3,5-trioxane additive in brine system, the dissociation temperature increases about 12 K at a given pressure in comparison to that of methane + water system. The promotion effect of 1,3,5-trioxane in brine system, however, is less than that in pure water system. This result is consistent with the statement of Sloan and Koh[2] that the stronger bonding of water with ionized salt and the salting out effect inhibit methane hydrate formation. For various 1,3,5-trioxane concentrations of brine system in our study, the promotion effect for methane hydrate formation is also relatively smaller than that in pure water system.

Another additive of oxolan-2-ylmethanol, a derivative of cyclic ether compound, was also selected to examine its effect on dissociation conditions of methane hydrate. Oxolan-2-ylmethanol is a water-soluble and biodegradable compound that reduces the pollution to the environment. The concentration range of

Table 3. Experimental Results for the Three-Phase (L_w-H-V) Dissociation Points in the System Containing Methane + Water + Oxolan-2-ylmethanol[a]

system	P/MPa	T/K
methane + water + oxolan-2-ylmethanol ($x = 0.0192$)	14.94	287.80
	13.99	287.32
	13.03	286.85
	12.05	286.13
	11.08	285.43
	10.09	284.64
	9.12	283.82
methane + water + oxolan-2-ylmethanol ($x = 0.0422$)	14.93	286.10
	13.95	285.59
	13.01	284.96
	11.99	284.25
	11.06	283.61
	10.06	282.85
	9.13	282.15
methane + water + oxolan-2-ylmethanol ($x = 0.0702$)	14.96	283.93
	13.92	283.33
	12.99	282.78
	12.03	282.18
	11.05	281.46
	10.05	280.60
	9.14	279.81

[a] x = mole fraction of oxolan-2-ylmethanol in aqueous solution.

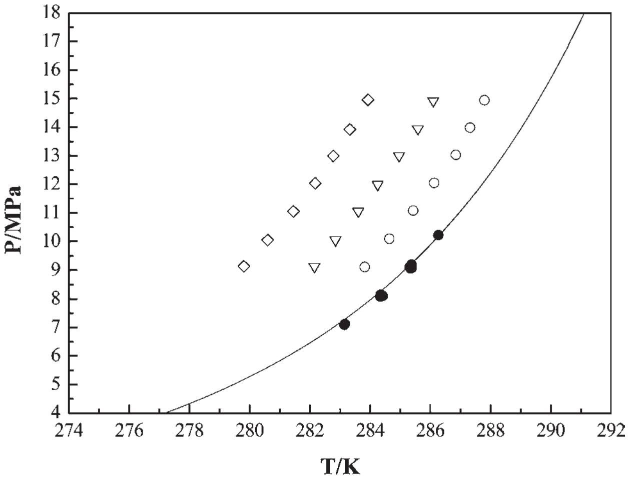

Figure 3. Hydrate dissociation conditions for the methane + water + oxolan-2-ylmethanol system. ●, pure water; oxolan-2-ylmethanol concentration: ○, $x = 0.0192$; ▽, $x = 0.0422$; ◇, $x = 0.0702$; solid line was predicted methane hydrate boundary from thermodynamic model, HW Hydrate Program;[18] x = mole fraction of oxolan-2-ylmethanol in aqueous solution.

oxolan-2-ylmethanol was set from (0.0192 to 0.0702) mole fraction ((0.10 to 0.30) mass fraction) in the aqueous system. The dissociation results for various concentrations of the oxolan-2-ylmethanol additive are listed in Table 3. A graphical expression of the dissociation pressures against temperatures is shown in Figure 3. As shown in Figure 3, the addition of oxolan-2-ylmethanol additive shifts the original methane hydrate phase boundary to a lower temperature and higher pressure region. The oxolan-2-ylmethanol additive thus has the inhibition effect on the formation of methane hydrate. This inhibition behavior might be due to molecular size, shape, and chemical nature of guest molecules that determine the occupation of hydrate cavities. The most significant inhibition effect was observed at 0.0702 mole fraction (0.30 mass fraction) of oxolan-2-ylmethanol in aqueous solution. With this concentration, the dissociation temperature decreases about 5 K at a given pressure in comparison to that of the methane + water system.

CONCLUSION

This study reports new experimental data of the dissociation temperatures and pressures for the L_w-H-V three-phase equilibrium of hydrate systems with additives by employing the isochoric method. The hydrate systems include methane + water + 1,3,5-trioxane and methane + water + oxolan-2-ylmethanol. To simulate the seawater conditions, the L-H-V three-phase equilibrium data for methane + brine + 1,3,5-trioxane are also determined. The experimental results show that the addition of 1,3,5-trioxane in the methane hydrate system shifts hydrate phase boundaries to lower pressures and higher temperatures. The maximum promotion effect on methane hydrate formation for the pure water system occurs at the concentration of 0.0341 mole fraction (0.15 mass fraction) of the 1,3,5-trioxane additive in aqueous solution. The methane hydrate formation temperature at a given pressure increases by 13 K in comparison to that of pure water system. The addition of 1,3,5-trioxane also shows the promotion effect on methane hydrate formation for brine system. The promotion of methane hydrate formation temperature of brine system is 12 K for an isobar. On the other hand, the addition of oxolan-2-ylmethanol additive exhibits the inhibition effect on methane hydrate formation. With the concentration of 0.0702 mole fraction (0.30 mass fraction) of the oxolan-2-ylmethanol additive in an aqueous system, the dissociation temperature decreases about 5 K at a given pressure in comparison to that of the pure water system.

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Funding Sources

The authors are grateful to the financial support from Grants 97-5226903000-02-04, 98-5226904000-04-04, and 99-5226904000-04-04 by the Ministry of Economic Affairs of Taiwan.

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