Measurements for the Dissociation Conditions of Methane Hydrate in the Presence of 2-Methyl-2-propanol

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The dissociation conditions for methane hydrates in the presence of (0.1 to 0.5) mass fraction 2-methyl-2-propanol aqueous solutions were experimentally measured in this study. The liquid water−hydrate−vapor (Lw−H−V) three-phase dissociation temperatures and pressures were determined using the isochoric method. New experimental data were reported within the pressure range from (4 to 10) MPa. It is demonstrated that the addition of 2-methyl-2-propanol had a promotion effect on the formation of methane hydrate. The liquid−hydrate−vapor (L−H−V) three-phase dissociation conditions for brine systems with methane + 0.035 mass fraction NaCl aqueous solution were also measured in this study with the addition of 2-methyl-2-propanol. The promotion effect for methane hydrate formation in brine environments was also observed with a 2-methyl-2-propanol additive.

Introduction

Gas hydrates are formed under low temperature and high pressure conditions. They are solid ice-like crystalline compounds consisting of water and suitably sized guest molecules. Guest molecules are held within cages formed by water through hydrogen bonding. Gas hydrates are known with structures I, II, and H that differ in cage sizes and shapes. The detailed review of gas hydrate is referred to by Sloan and Koh.[1] Thermodynamic studies on gas hydrates are important for oil and gas industries. Gas hydrates can be formed in the pipelines and transmission lines that cause blockage and lead to serious problems. Thermodynamic inhibitors, such as alcohols, glycols, and electrolytes, have generally been applied for the prevention of hydrate formation. The presence of inhibitors shifts the hydrate formation conditions to a region of higher pressure and lower temperature. The dissociation conditions of gas hydrate in the presence of various inhibitors have been presented in the literature.[2−6] On the other hand, gas hydrates have been proposed for technological applications such as the storage and transportation of natural gas, separation of gas mixtures, and carbon dioxide sequestration. For these purposes, gas hydrate formation is preferred at a lower pressure and higher temperature. Khokhar et al.[7] suggested that the filling of a large cage in the hydrate structure with the second guest molecule would improve the strictly stable condition. The addition of the second guest molecule would cause the shift of hydrate dissociation to milder conditions and the achievement of the promotion effect. Measurements of the dissociation data for gas hydrate with several additives as promoters have also been reported in the literature.[8−11]

2-Methyl-2-propanol was selected in this study as a possible promoter for methane hydrate formation. The dissociation conditions for methane hydrates were experimentally measured with 2-methyl-2-propanol additive. The concentration range for 2-methyl-2-propanol in our measurements was from (0.1 to 0.5) mass fraction in aqueous solution, and the pressure range was from (4 to 10) MPa. To model the seawater conditions, the dissociation conditions of methane hydrates were also measured for brine systems with methane + 0.035 mass fraction NaCl + 2-methyl-2-propanol aqueous solution. Comparison of the promotion effects was reported between the pure water and brine systems with the additive of 2-methyl-2-propanol.

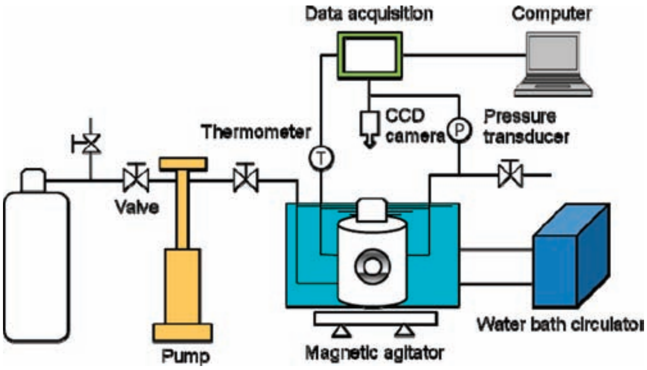

Figure 1. Experimental apparatus for methane hydrate dissociation point measurements.

Experimental Section

Materials. Methane was purchased from Air Products and Chemicals with 99.9 % certified purity. 2-Methyl-2-propanol and sodium chloride were purchased from Sigma-Aldrich Company with purity greater than 99.5 %. Deionized water was used in all experiments.

Experimental Apparatus. The apparatus used in this study to measure the dissociation conditions of methane hydrates is shown in Figure 1. The main part was a cylindrical stainless steel cell with volume of 200 cm^3 which could endure pressures up to 30 MPa. The cell was equipped with three sapphire windows on the top, front, and back sides, respectively. It was immersed in a water bath where temperature was controlled by another water bath circulator with a programmable cooling and heating controller (Neslab, RTE 7 equipped with remote programming controller). A magnetic stirrer at 650 rpm was

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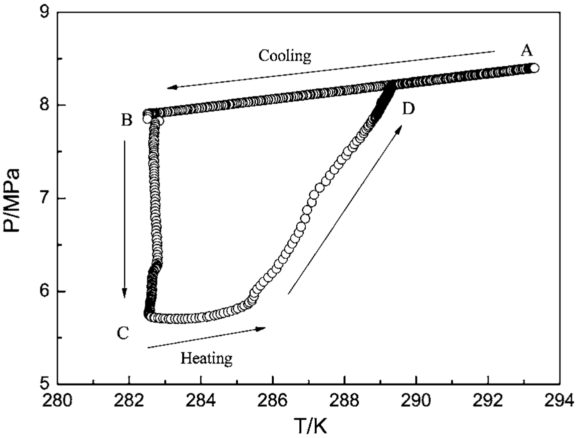

Figure 2. Typical temperature cycling curve in our experiments to determine the dissociation points.

equipped at the bottom of the cell to agitate the solution and hydrates. The temperature and pressure inside the cell were measured by a platinum resistance thermometer (Fluke, 1529) and a pressure gauge (Heise, type PM). The accuracies for the temperature and pressure measurements in this study were ± 0.01 K and ± 0.001 MPa, respectively.

Experimental Method. This study employed the isochoric method to measure the dissociation conditions of methane hydrate. The method was similar to those described by Sloan and Koh[1] and Tohidi et al.[12] A schematic illustration of a typical temperature cycling curve of our experiments is shown in Figure 2. The cell containing approximately 100 cm^3 solution of water and 2-methyl-2-propanol additive was immersed into the temperature-controlled water bath. Methane gas was charged from a high-pressure gas cylinder through an ISCO pump into the equilibrium cell. The cell was first repeatedly flushed with methane to get rid of air in the cell. Methane was finally introduced by the ISCO pump until the desired pressure was reached (Point A in Figure 2). The water bath circulator and magnetic stirrer were then switched on to attain a stable state in the equilibrium cell. After the temperature and pressure in the cell were stabilized, the temperature of the water bath was decreased by a programmable controller where methane hydrate began to form (Point B in Figure 2). A rapid pressure drop was observed in the equilibrium cell upon hydrate formation where methane gas was captured into hydrate (Point C in Figure 2). At this time, the temperature of the equilibrium cell was maintained for 2 h to keep the formation of hydrate. The temperature was then increased to a value slightly below the dissociation temperature. Subsequently, temperature was increased slowly by using a very low heating rate of 0.05 $K \cdot h^{-1}$ to ensure the achievement of nearly thermodynamic equilibrium. During the heating steps, the increase of pressure was observed, while hydrate still existed in the cell. Once the hydrate was totally dissociated, the pressure−temperature plot during the continuous heating process coincided with that of the initial cooling step. The dissociation condition was determined from the pressure−temperature plot where the slope changed sharply during the final heating steps (Point D in Figure 2). The dissociation temperature and pressure data sets were measured with various initial pressures of the input methane and with various concentrations of 2-methyl-2-propanol additive. Repeated measurements had been conducted in this study to confirm the reproducibility of experimental data.

Table 1. Dissociation Conditions for the Methane + Water System

system	P / MPa	T / K
methane + water	7.11	283.21
	7.48	283.70
	7.96	284.24
	8.03	284.28
	9.03	285.36
	10.28	286.50

Results and Discussion

To examine the reliability and reproducibility of our experiments, the hydrate dissociation conditions of methane and pure water were first measured, and the experimental results are listed in Table 1. Comparison with literature data[1] is graphically shown in Figure 3. It is observed that our results are in satisfactory agreement with literature data, and the validity of the experimental method in this study is confirmed.

The dissociation pressures and temperatures for the equilibrium of the Lw−H−V three-phase methane + water + 2-methyl-2-propanol system were experimentally measured in this study. The dissociation data are listed in Table 2 for various concentrations of the 2-methyl-2-propanol additive. A graphical presentation for the plot of dissociation pressures against temperatures is shown in Figure 4 with five concentrations of 2-methyl-2-propanol additive in the original aqueous solution. It is clearly depicted that the addition of 2-methyl-2-propanol in the methane hydrate system yielded a significant promotion effect. With the 0.1 mass fraction 2-methyl-2-propanol aqueous solution, the dissociation temperature increased about 5 K at a given pressure in comparison to that of the pure water system. As the concentration of the 2-methyl-2-propanol additive was increased from (0.1 to 0.2) mass fraction in aqueous solution, the dissociation temperature demonstrated a further increase of 1 K at a given pressure. The promotion effects became weaker for the concentration of 2-methyl-2-propanol additive greater than 0.2 mass fraction. Figure 3 also shows the decrease of promotion effect with (0.3 to 0.5) mass fraction 2-methyl-2-propanol additives in the original aqueous solution. Park et al.[13] have measured the structure of methane hydrate with 2-methyl-2-propanol additive using spectroscopic analyses. They stated that 2-methyl-2-propanol by itself does not form clathrate hydrate. They reported that the methane was enclosed in structure II clathrate hydrate at 2-methyl-2-propanol concentra-

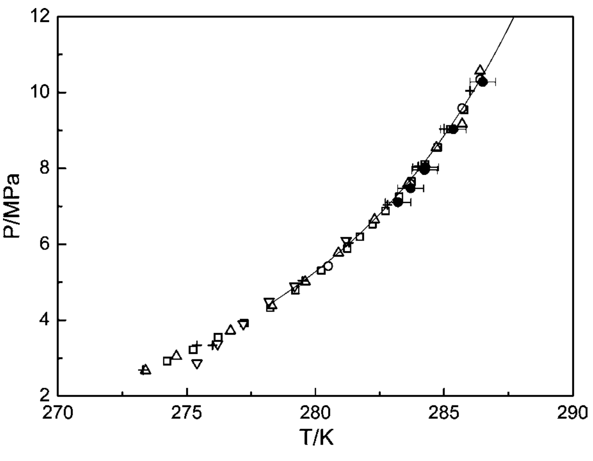

Figure 3. Dissociation conditions for methane + water systems. ●, this study; □, Nakamura et al.;[16] ○, Mohammadi et al.;[17] △, Adisasmito et al.;[18] ▽, Thakore and Holder;[19] +, De Roo et al.,[20] solid line was predicted from a thermodynamic model.[21]

Table 2. Dissociation Conditions for the Methane + Water + 2-Methyl-2-propanol System[a]

system	P/MPa	T/K
methane + water + 2-methyl-2-propanol (w = 0.1)	4.15	283.74
	5.11	285.34
	6.13	287.05
	7.18	288.26
	8.22	289.35
	9.06	290.11
	10.06	290.95
methane + water + 2-methyl-2-propanol (w = 0.2)	4.18	284.87
	5.15	286.52
	6.19	288.05
	7.20	289.24
	8.20	290.26
	9.27	291.24
	10.36	292.07
methane + water + 2-methyl-2-propanol (w = 0.3)	4.17	284.55
	5.16	286.27
	6.17	287.80
	7.17	288.97
	8.16	290.03
	9.21	290.97
	10.17	291.75
methane + water + 2-methyl-2-propanol (w = 0.4)	4.15	284.30
	5.11	286.05
	6.12	287.60
	7.23	288.90
	8.15	289.90
	9.17	290.82
	10.15	291.63
methane + water + 2-methyl-2-propanol (w = 0.5)	4.12	284.03
	5.10	285.85
	6.11	287.36
	7.09	288.55
	8.09	289.63
	9.10	290.60
	10.14	291.46

[a] w = mass fraction of 2-methyl-2-propanol in aqueous solution.

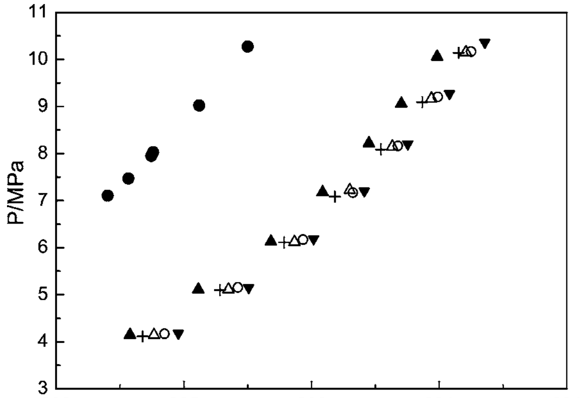

Figure 4. Dissociation conditions for methane + water + 2-methyl-2-propanol systems. ●, pure water; 2-methyl-2-propanol concentration: ▲, w = 0.1; ▼, w = 0.2; ○, w = 0.3; △, w = 0.4; +, w = 0.5) (w = mass fraction of 2-methyl-2-propanol in aqueous solution).

Table 3. Dissociation Conditions for the Methane + Brine + 2-Methyl-2-propanol System[a]

system	P/MPa	T/K
methane + brine + 2-methyl-2-propanol (w = 0.1)	4.13	282.55
	5.09	284.33
	6.11	285.78
	7.10	287.02
	8.08	288.06
	9.10	288.97
	10.13	289.83
methane + brine + 2-methyl-2-propanol (w = 0.2)	4.15	283.01
	5.13	284.76
	6.13	286.23
	7.11	287.42
	8.07	288.36
	9.11	289.33
	10.13	290.16

[a] w = mass fraction of 2-methyl-2-propanol in aqueous solution.

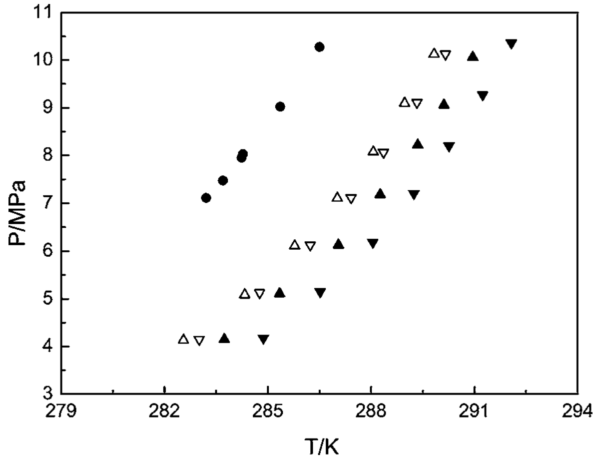

Figure 5. Comparison of dissociation conditions for methane + water, methane + water + 2-methyl-2-propanol, and methane + brine + 2-methyl-2-propanol systems. ●, pure water; ▲, 2-methyl-2-propanol in water (w = 0.1); ▼, 2-methyl-2-propanol in water (w = 0.2); △, 2-methyl-2-propanol in brine (w = 0.1); ▽, 2-methyl-2-propanol in brine (w = 0.2) (w = mass fraction of 2-methyl-2-propanol in aqueous solution.

tions below 0.7 mol fraction (or 0.906 mass fraction). Park et al.[13] have discussed the concentration effect on methane hydrate structure. On the basis of their spectroscopic analysis results, the methane hydrate was mainly with structure II in the concentration range of 2-methyl-2-propanol of this study. It is also shown by Park et al.[13] that at higher 2-methyl-2-propanol concentration the methane occupancy became weaker mainly because the ability of water to build the cage framework was lost. 2-Methyl-2-propanol was the second guest molecule to fill only large cages in forming structure II hydrates. The number ratio of large cages to water molecules under full occupancy in structure II hydrates is 1:17 which corresponds to 0.0588 mol fraction of 2-methyl-2-propanol additive.[14,15] The concentration of 0.2 mass fraction 2-methyl-2-propanol aqueous solution equals 0.0573 mol fraction which is similar to the ratio of large cages to water molecules. The maximum promotion effect was therefore exhibited at the concentration of 0.2 mass fraction 2-methyl-2-propanol aqueous solution.

The examination of methane hydrate promotion effect for the seawater condition was investigated in this study by adding NaCl into the aqueous phase. The salinity in seawater is 0.035 mass fraction, and the main composition is NaCl. To simulate the seawater environment, the brine solution in this study was taken as a 0.035 mass fraction NaCl aqueous solution. In the brine systems, the dissociation conditions were measured with (0.1 and 0.2) mass fraction 2-methyl-2-propanol in brine solution. The dissociation points for the L−H−V three-phase equilibrium for methane + brine + 2-methyl-2-propanol systems are presented in Table 3. Graphical comparison of the dissociation conditions of pure water, water with 2-methyl-2-propanol additive, and brine with 2-methyl-2-propanol additive is illustrated in Figure 5. The experimental results show that the 2-methyl-2-propanol additive still presented the promotion effect on hydrate formation in the brine solution. At given pressure, the dissociation temperatures for methane + brine + 2-methyl-2-propanol systems are higher by 3 K than those for the methane

+ water system. The promotion effect in the brine system was, however, less than that in the pure water system. This result is in agreement with the statement of Sloan and Koh[1] that the stronger bonding of water with ionized salt, as well as the salting out effect, inhibited methane hydrate formation. The promotion effect due to various 2-methyl-2-propanol concentrations for the brine system was also relatively smaller than that in pure water system.

Conclusions

This study reports the experimental data of the dissociation temperatures and pressures for the Lw−H−V three-phase equilibrium of the systems methane + water + 2-methyl-2-propanol, and the L−H−V three-phase equilibrium of the systems methane + brine + 2-methyl-2-propanol using an isochoric method. The experimental results show that the addition of 2-methyl-2-propanol exhibited the promotion effect on methane hydrate formation. The maximum promotion effect for the pure water system occurred at the concentration of 0.2 mass fraction 2-methyl-2-propanol additive. The methane hydrate formation temperature at a given pressure was increased by 6 K in comparison to that of the pure water system. This 0.2 mass fraction 2-methyl-2-propanol concentration was about the stoichiometric ratio of 1:17 for the large sII cages to water. The addition of 2-methyl-2-propanol also showed a methane hydrate promotion effect for the brine system. The promotion of methane hydrate formation temperature was 3 K for an isobar.

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