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Hydrate Formation Conditions of a Hydrogen + Methane Gas Mixture in Tetrahydrofuran + Water

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Hydrate formation conditions of ($H_2 + CH_4$) binary gas mixtures in the presence of tetrahydrofuran (THF) in water were measured in a sapphire cell using the "pressure search" method. The experimental temperature ranged from 277.7 K to 288.4 K, and pressure ranged from 0.12 MPa to 8.86 MPa. The hydrogen composition in the gas mixture varied from 0 mol % to 97.85 mol %. The THF content in the aqueous solution was fixed at 6 mol %.

Introduction

Hydrogen-containing gas mixtures are widely found in petroleum refining and petrochemical processes. Although it has been proven that hydrogen can form hydrates,[1] the formation pressure is much higher than that of light hydrocarbon components.[1,2] Hence, it is a promising method for separating hydrogen from hydrocarbon gas mixtures through forming and dissociating hydrates.[3] Methane is usually a main component in these gas mixtures besides hydrogen. Because methane forms hydrates at much higher pressure than other light hydrocarbons do,[2] it becomes a key component for the separation of these gas mixtures through hydrate formation. When the concentration of hydrogen in the mixture is high, the hydrate formation pressures will be so high[4] that hydrate-based separation methods become industrially impractical. To solve this problem, THF (tetrahydrofuran) has been considered to be a thermodynamic promoter to reduce the hydrate formation pressure.[3] There has been some work reported on hydrate formation in the presence of THF in water as an additive.[5−7] The most recent work was done by Florusse et al.,[7] in which the formation and dissociation of THF + the hydrogen binary hydrate was investigated and a promising hydrogen storage method at low pressure and near-ambient temperature was proposed.

The objective of this work is to measure the hydrate formation conditions of the ($H_2 + CH_4$) binary gas mixture in water with THF as a hydrate promoter.

Experimental Section

Experimental Apparatus. The apparatus used in this work has been described in detail in our previous papers.[8−10] The schematic diagram of the apparatus is given in Figure 1. The apparatus consists of a cylindrical transparent sapphire cell (2.54 cm in diameter, effective volume 60 cm^3) installed in the air bath and equipped with a magnetic stirrer for accelerating the equilibrium process. The formation and dissociation of hydrates in the cell can be observed directly through the transparent sapphire wall. The uncertainties of the temperature and pressure measurements are 0.2 K and 0.02 MPa, respectively.

Materials and Preparation of Samples. Analytical-grade methane (99.99%) and hydrogen (99.99%) supplied by Beifen Gas Industry Corporation were used in preparing the synthetic binary gas mixtures. The gas mixtures were prepared on the basis of the partial pressure law of ideal gas mixtures. The prepared gas mixtures were equilibrated for 1 day to allow for sufficient mixing. Afterward, they were sampled and analyzed by using a Hewlett-Packard gas chromatograph (HP 6890) at least three times. The average values were then taken as the compositions of the mixtures. THF (>99%) used for preparing the aqueous solution was supplied by Beijing Reagents Corporation. An electronic balance with a precision of ±0.1 mg was used to prepare aqueous solutions with the required concentration of THF. The uncertainties of the compositions of gas mixtures and the H_2O + THF solution were 0.01% and 0.005% respectively.

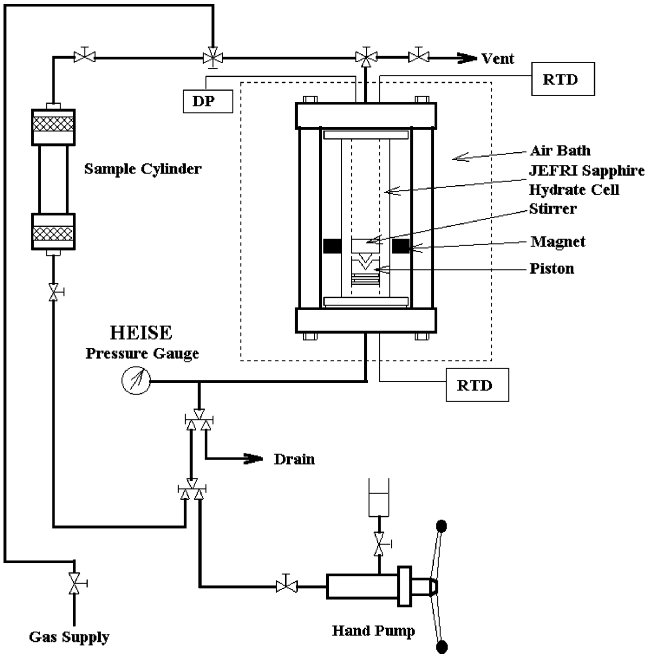

Figure 1. Schematic of the experimental apparatus: DP, differential pressure transducer; RTD, resistance thermocouple detector.

Experimental Procedure. First, the transparent cell was washed with deionized water and then rinsed three times with the prepared THF aqueous solution. After the

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cell was thoroughly cleaned, approximately 5 cm^3 of the prepared aqueous solution was added to the cell, and the cell was then installed in the air bath. The vapor space of the cell was then purged four times with the prepared gas mixture to ensure the absence of air. The temperature of the air bath was then adjusted to the desired value, and the cell was charged with the gas mixture.

To reduce the induction time, we first increased the pressure in the cell to a much higher value than the estimated hydrate formation pressure (using in-house software in which hydrogen was assumed to be a hydrate nonformer) via driving the piston upward by using the hand pump. When a large hydrate quantity was observed in the cell, the system pressure was decreased slowly by withdrawing the piston until the hydrate was decomposed thoroughly. This pretreatment was repeated two times for each experimental run to reduce or eliminate the induction time required for fresh aqueous solution to form a hydrate. After the pretreatment, the formation pressures of the system at different temperatures were measured using the "pressure search" method described below.

The system pressure was first set a little higher than the estimated initial formation pressure. When a trace of hydrate was observed, the pressure of the system was decreased slightly to let the hydrate decompose slowly. When all of the hydrate disappeared, the pressure of the system was then increased in steps of 0.05 MPa until the hydrate appeared again. When the temperature and pressure of the system could be maintained at constant values for 4 to 6 h with a trace amount of hydrate present, the system was assumed to achieve phase equilibrium, and the pressure was taken as the initial formation pressure at the temperature.

The above procedure was repeated for a series of temperatures. The uncertainties of the temperature and pressure measurements are 0.2 K and 0.02 MPa, respectively.

Experimental Results and Discussion

The hydrate formation conditions of pure methane and six synthetic (hydrogen + methane) gas mixtures in the presence of 6 mol % THF in water were measured systematically. The experimental temperature ranged from 277.7 K to 288.4 K, and the pressure ranged from 0.12 MPa to 8.86 MPa. The concentration of hydrogen in the gas mixture, x_1, varied from 0 mol % to 97.85 mol %. According to the results reported by Saito et al.,[6] the formation pressure of the methane + THF + water system at a fixed temperature achieves a minimum when the THF concentration is around 6 mol %. This concentration also provides the stoichiometric ratio for the THF hydrate (~17 water molecules per THF molecule); therefore, the THF concentration in aqueous solution can be kept essentially unchanged as hydrate formation proceeds, which is important for hydrate-based separation processes. On the basis of the above consideration, the THF concentration in the aqueous solution was fixed at 6 mol % in this work. The experimental data are tabulated in Table 1 and shown in Figure 2. As reported in the literature,[11] our experimental results show that hydrates can form in an aqueous solution of 6 mol % THF below 277.15 K at atmospheric pressure. Above this temperature, methane is required to form a hydrate. The hydrate formation pressures of methane in an aqueous solution of 6 mol % THF at 278.15 K and 283.15 K reported by Saito et al. were 0.2 MPa and 0.5 MPa, respectively.[6] Their result at 283.15 K was essentially equal to the value measured in this work, whereas that at 278.15 K was a little higher than ours.

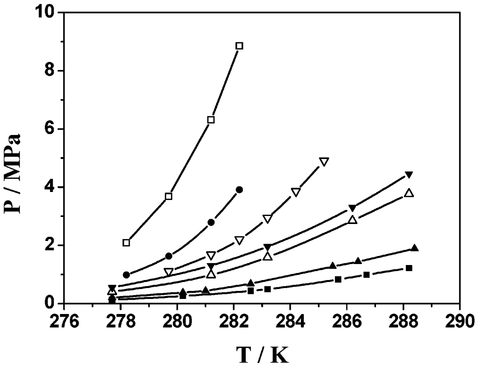

Figure 2. Hydrate formation conditions of hydrogen (1) + methane (2) gas mixtures in the presence of 6 mol % THF in aqueous solution: ■, $x_2 = 1.000$; ▲, $x_2 = 0.6526$; △, $x_2 = 0.3029$; ▼, $x_2 = 0.2124$; ▽, $x_2 = 0.1087$; ●, $x_2 = 0.0505$; □, $x_2 = 0.0215$.

Table 1. Hydrate Formation Conditions of Hydrogen (1) + Methane (2) Gas Mixtures in the Presence of 6 mol % THF in Aqueous Solution

x_2	T/K	P/MPa
1.000	277.7	0.13
	280.2	0.26
	282.6	0.44
	283.2	0.50
	285.7	0.83
	286.7	0.99
	288.2	1.22
0.6526	277.7	0.20
	280.2	0.38
	281.0	0.44
	282.6	0.68
	285.5	1.27
	286.4	1.44
	288.4	1.89
0.3029	277.7	0.41
	281.2	0.98
	283.2	1.59
	286.2	2.85
	288.2	3.77
0.2124	277.7	0.55
	281.2	1.31
	283.2	1.96
	286.2	3.31
	288.2	4.46
0.1087	279.7	1.11
	281.2	1.68
	282.2	2.20
	283.2	2.94
	284.2	3.86
	285.2	4.91
0.0505	278.2	0.98
	279.7	1.63
	281.2	2.79
	282.2	3.91
0.0215	278.2	2.09
	279.7	3.68
	281.2	6.31
	282.2	8.86

The results demonstrate that the presence of THF in water can drastically lower the hydrate formation pressure of pure methane or (hydrogen + methane) mixtures. Even when x_1 reaches 98 mol %, the gas mixture can still form hydrates at an industrially acceptable pressure and temperature in THF + water. Figure 3 depicts the comparison of formation pressures in cases with and without[2,4] the presence of THF in water.

Although the formation of a hydrogen hydrate has been demonstrated by Mao et al., it occurs at very high pressure (>180 MPa) and low temperature (<250 K)[1]. Therefore, it is still meaningful to ascertain whether hydrogen molecules

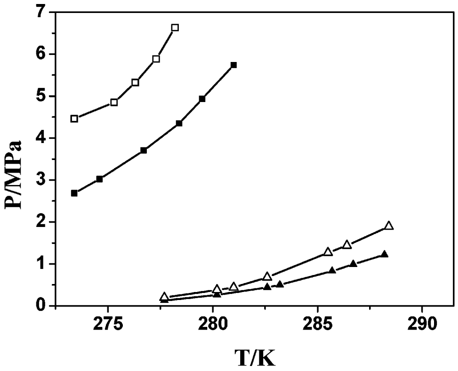

Figure 3. Comparison of formation conditions in cases with and without the presence of THF in aqueous solution: ■, pure CH_4 in pure water;[2] ▲, pure CH_4 in an aqueous solution of 6 mol % THF; □, 36.18 mol % H_2 + 63.82 mol % CH_4 in pure water;[4] △, 34.74 mol % H_2 + 65.26 mol % CH_4 in an aqueous solution of 6 mol % THF.

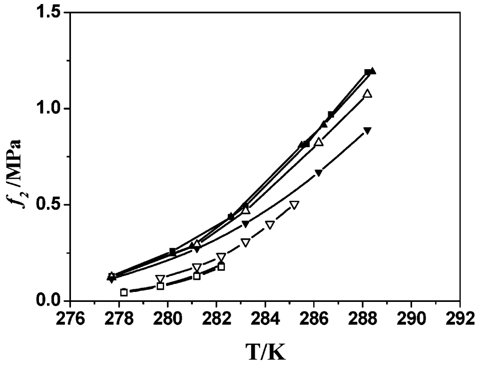

Figure 4. Calculated fugacity of methane in a gas mixture, f_2, with respect to the hydrate formation pressure and gas composition as tabulated in Table 1: ■, $x_2 = 1.000$; ▲, $x_2 = 0.6526$; △, $x_2 = 0.3029$; ▼, $x_2 = 0.2124$; ▽, $x_2 = 0.1087$; ●, $x_2 = 0.0505$; □, $x_2 = 0.0215$.

can occupy the cavities of hydrates when other guests form hydrates together with it at moderate pressures and temperatures such as in this work. To do this, the fugacity of methane in the gas mixture in equilibrium with a hydrate, f_2, was calculated using the Peng–Robinson equation of state[12] with respect to the pressures, temperatures, and gas compositions tabulated in Table 1. The results are shown in Figure 4. One can see that when $x_1 \leq$ 35 mol % f_2 is essentially equal to the fugacity of pure methane required to stabilize the hydrate at the same temperature. But when $x_1 > 35$ mol %, especially when it exceeds 70 mol %, f_2 is obviously smaller than the fugacity of pure methane and decreases with increasing x_1. It is well known that the stabilization of a hydrate is dependent on the fraction of cavities occupied by the guest molecules.[2] The smaller f_2 means that a smaller fraction of cavities are occupied by methane molecules.[2] If hydrogen had not occupied the cavities, then the total fraction of cavities occupied by guest molecules would be smaller than the value required to stabilize the hydrate, or in other words, the hydrate could not have been formed. Therefore, Figure 4 demonstrates that hydrogen can occupy the cavities of hydrates at moderate pressure and temperature. The occupancy percentage of hydrogen in small cavities has been evaluated by using the Chen–Guo hydrate model.[13] It is about 12% at 282.2 K and 3.9 MPa when x_1 is 95% and 14% at 282.2 K and 8.9 MPa when x_1 is 98%. These occupancy percentages are not large enough for hydrogen to stabilize a hydrate on its own, but they can affect the hydrate formation conditions of gas mixtures of hydrogen.

Conclusions

The hydrate formation data of pure methane gas and six synthetic hydrogen + methane gas mixtures were measured in the temperature range of 277.7 K to 288.4 K and the pressure range of 0.12 MPa to 8.86 MPa using the pressure search method. The experimental results demonstrated that the formation pressure of a hydrogen-containing gas mixture could be drastically lowered by adding 6 mol % of THF to water as a promoter. It was shown that hydrogen could occupy the cavities in the hydrate lattice and thus lower the fugacity of methane required to achieve an occupancy percentage of cavities to stabilize the hydrate. The obtained experimental data are valuable for developing or testing the existing hydrate models and designing an industrial process to separate hydrogen-containing gas mixtures by forming hydrates.

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