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Hydrate Formation Conditions of Methane + Ethylene + Tetrahydrofuran + Water Systems

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Hydrate formation conditions of (CH_4 + C_2H_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 288.2 K, and the pressure ranged from 0.16 MPa to 4.08 MPa. The mole fraction of ethylene in the gas mixtures varied from 6.28 % to 100 %. The mole fraction of THF in the aqueous solution ranged from 4 % to 20 %. The experimental results demonstrated that, in contrast with the case of pure water, the hydrate formation pressures increase with the increase of ethylene composition in the gas mixture in the presence of THF in water.

Introduction

Since methane and ethylene are two major components of various kinds of refinery gases or cracking gases in ethylene plants, the separation of them has been given special attention.[1] As methane and ethylene are both low-boiling components, it is expensive to separate them by the usual distillation methods because of the requirement of excessive cooling. Thus, it is of practical significance to develop new methods to separate them. Considering that the hydrate formation pressure of methane is much higher than ethylene,[2] it might be a promising method to separate them through forming and dissociating hydrate. There have been some works reported on the separation technology using the hydrate principles.[3−7]

Because it takes a much longer time to reach a vapor−hydrate−water equilibrium than to reach a vapor−liquid equilibrium, multi-stage separation like distillation is more difficult to realize for hydration separation technology. Thus, it is of more significance to increase the separation efficiency of a single equilibrium stage for hydration separation technology. In our previous work,[7] it has been shown that THF (tetrahydrofuran) can be used as a selective inhibitor that inhibits ethane or ethylene to form hydrate while promoting methane to form hydrate and therefore increases the single-stage separation efficiency of methane with ethane or ethylene.

There has been some work reported on hydrate formation in the presence of THF in water as a promoter.[8−10] The objective of this work was to measure the hydrate formation conditions of the (CH_4 + C_2H_4) binary gas mixture in the presence of THF in water as a selective inhibitor.

Experimental Section

Experimental Apparatus. The apparatus used in this work has been described in detail in our previous papers.[11−15] 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 of 60 cm^3) installed in the air bath and equipped with a magnetic stirrer for accelerating the equilibrium process. The formation and dissociation of hydrate in the cell can be observed directly through the transparent sapphire wall. The uncertainties of temperature and pressure measurements are 0.1 K and 0.02 MPa, respectively.

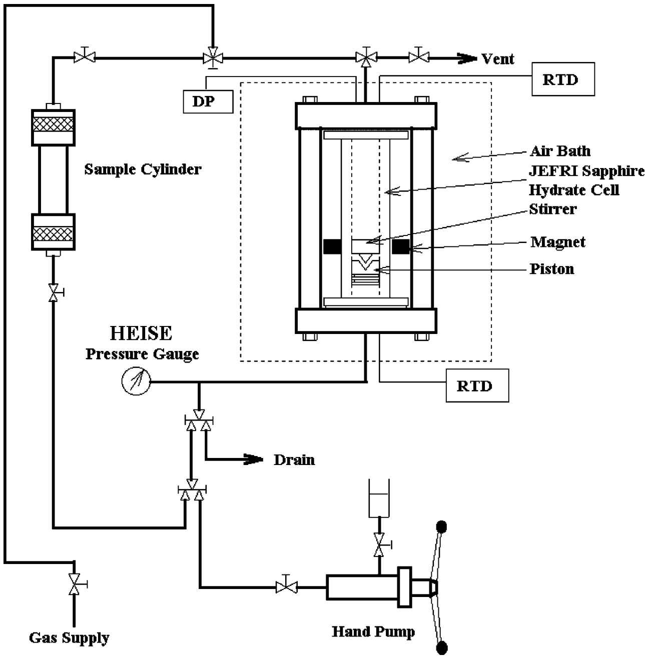

Figure 1. Schematic of the experimental apparatus: DP, differential pressure transducer; RTD, resistance thermocouple detector.

Materials and Preparation of Samples. Analytical grade methane (99.99 %) and ethylene (99.5 %) supplied by Beifen Gas Industry Corporation were used in preparing the synthetic binary gas mixtures. The gas mixtures were prepared based on the partial pressure law of ideal gas mixtures. The gas mixtures were prepared 1 day prior to use to allow them to mix. It has been proven that 1 day is long enough for the systems to reach equilibrium by continuing sampling and analyzing the composition of them. Afterward, they were sampled and analyzed 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 in

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preparing aqueous solution with the required composition of THF. The uncertainties in the compositions of the gas mixture and H_2O + THF solution were 0.01 % and 0.005 %, respectively.

Experimental Procedure. First, the transparent cell was washed with deionized water and then rinsed three times with the prepared THF aqueous solution. After the cell was thoroughly cleaned, approximately 10 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) by driving the piston upward using the hand pump. When a large quantity of hydrate 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. In our experience, this kind of pretreatment allows hydrates to form quicker than that from fresh aqueous solution due to the “memory effect”. 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 have achieved phase equilibrium, and the pressure was taken as the initial formation pressure at the temperature.

Results and Discussion

The hydrate formation conditions of pure ethylene (2) and six synthetic methane (1) + ethylene (2) gas mixtures in the presence of THF (3) in water (4) were measured systematically. As $x_3 = 6$ % corresponds to the stoichiometric mixture of THF + water whereby THF occupies all the large cages of sII hydrate, x_3 was held constant during the THF hydrate formation process if its initial value is 6 %. As an additive, it is important keep its concentration. Therefore, the measurements were first performed at fixed x_3 of 6 % in detail. The experimental temperature ranged from 277.7 K to 288.2 K, and the ethylene in the gas mixture varied from $y_2 = 6.28$ % to 100 %. The experimental data are tabulated in Table 1, shown in Figure 2, and compared with those[15] measured in the absence of THF in water in Figures 3 and 4. It can be seen that the hydrate formation pressure increases with the increase of ethylene composition in the gas mixture. As shown in Figure 3, this tendency is opposite to that observed in the absence of THF in water.[15] Our experimental results show that hydrates can form in an aqueous solution of $x_3 = 6$ % below 277.15 K at atmospheric pressure; this result is consistent with that reported in the literature.[16] Above this temperature, methane or ethylene is required for hydrate formation.

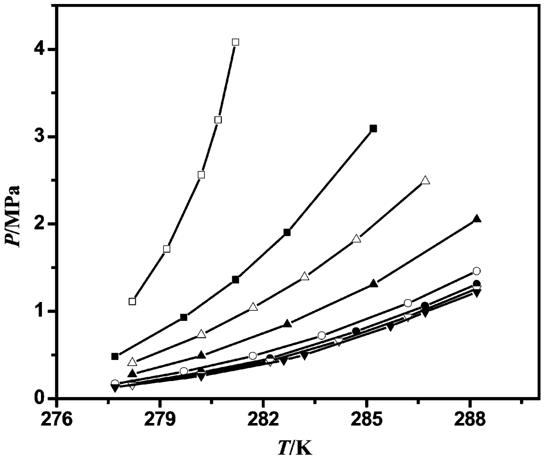

Figure 2. Hydrate formation conditions of methane (1) + ethylene (2) gas mixtures in the presence of 6 mol % THF in aqueous solution: □, $y_2 = 1.000$; ■, $y_2 = 0.8837$; △, $y_2 = 0.7615$; ▲, $y_2 = 0.5712$; ○, $y_2 = 0.2935$; ●, $y_2 = 0.1376$; ▽, $y_2 = 0.0628$; ▼, $y_2 = 0.0$.[14]

Table 1. Hydrate Formation Conditions of Methane (1) + Ethylene (2) Gas Mixtures in the Presence of Tetrahydrofuran (3) + Water (4) with $x_3 = 0.06$

y_2	T/K	P/MPa
1.000	278.2	1.11
	279.2	1.71
	280.2	2.56
	280.7	3.19
	281.2	4.08
0.8837	277.7	0.48
	279.7	0.93
	281.2	1.36
	282.7	1.9
	285.2	3.09
0.7615	278.2	0.41
	280.2	0.73
	281.7	1.04
	283.2	1.39
	284.7	1.82
	286.7	2.49
0.5712	278.2	0.28
	280.2	0.49
	282.7	0.85
	285.2	1.31
	288.2	2.05
0.2935	277.7	0.17
	279.7	0.31
	281.7	0.49
	283.7	0.72
	286.2	1.09
	288.2	1.46
0.1376	278.2	0.17
	280.2	0.3
	282.2	0.46
	284.7	0.77
	286.7	1.06
	288.2	1.31
0.0628	278.2	0.16
	280.2	0.28
	282.2	0.43
	284.2	0.66
	286.2	0.94
	288.2	1.26

Figures 3 and 4 show that the presence of THF in water can lower the hydrate formation pressure of (methane + ethylene) mixtures remarkably in most cases. But when the composition of ethylene is higher, especially for pure ethylene, it is more difficult to form the hydrates in the presence of THF in water than without THF. Therefore, THF inhibits ethylene hydrate formation, while it promotes methane hydrate formation. The reasons should be attributed to (i) an ethylene molecule cannot occupy the smaller cavity at moderate pressures while a methane molecule can, therefore ethylene is not a good help gas for THF

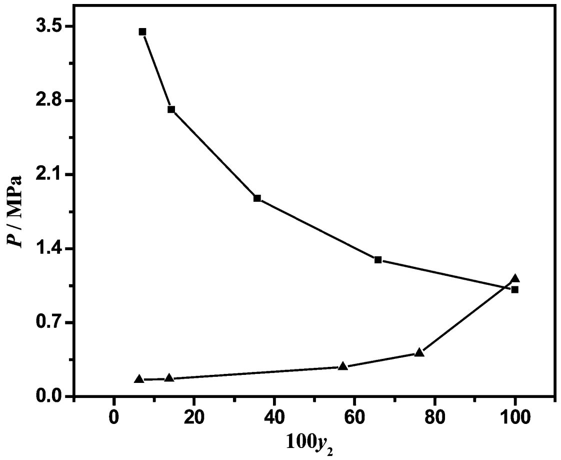

Figure 3. Comparison of hydrate formation conditions in cases with and without the presence of THF in water at 278.2 K: ▲, $x_3 = 6$ %; ■, $x_3 = 0$.[15]

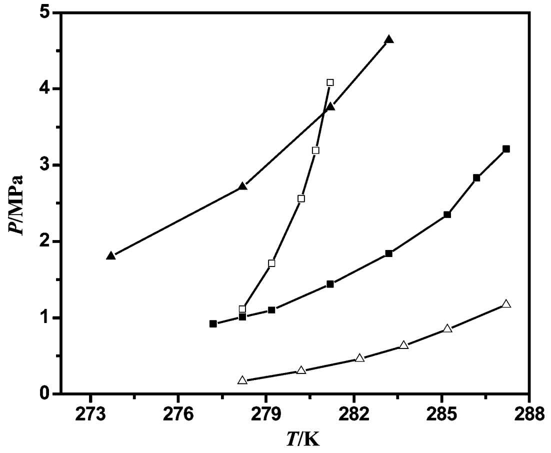

Figure 4. Comparison of formation conditions in cases with and without the presence of THF in water: ■, pure C_2H_4 in pure water;[15] □, pure C_2H_4 in THF aqueous solution (6 mol %); ▲, 85.69 mol % CH_4 + 14.31 mol % C_2H_4 in pure water;[15] △, 86.24 mol % CH_4 + 13.76 mol % C_2H_4 in THF aqueous solution (6 mol %).

to form hydrate while methane is; (ii) THF does not form a sI hydrate, therefore it plays the role of inhibitor when ethylene forms sI hydrate as the presence of THF in water will lower the chemical potential of water. As THF can form a sII hydrate very easily with the help of methane, guests CH_4, C_2H_4, and THF together will form a sII hydrate. Furthermore, as the methane composition increases in the gas mixture, the occupancy of methane molecules increases in the small cavities. Therefore, the hydrate formation pressures decrease with increasing methane composition in the gas mixture as shown in Figure 3. However, it is not possible to determine from the present phase equilibria measurements whether C_2H_4 and THF together will form the sII hydrate. The resulting hydrate structure may depend on the composition of THF or the partial pressure of ethylene.

Afterward, the hydrate formation conditions of a (methane + ethylene) gas mixture at different compositions of THF in water were measured systematically. The experimental temperature was specified as 282.2 K, the composition of ethylene in the gas mixture (y_2) was specified to be 61.08 %, and the compositions of THF in water (x_3) ranged from 4 % to 20 %. The experimental data are tabulated in Table 2 and shown in Figure 5. The results demonstrate that the hydrate formation pressure increases with an increase in the amount of THF in water. This phenomenon may be attributed to the decrease in the chemical potential of water with increasing amounts of THF in water. It is easy to understand that the decrease of water chemical potential makes it more difficult for ethylene to form hydrate (i.e., THF is not a promoter but an inhibitor for ethylene to form hydrate).

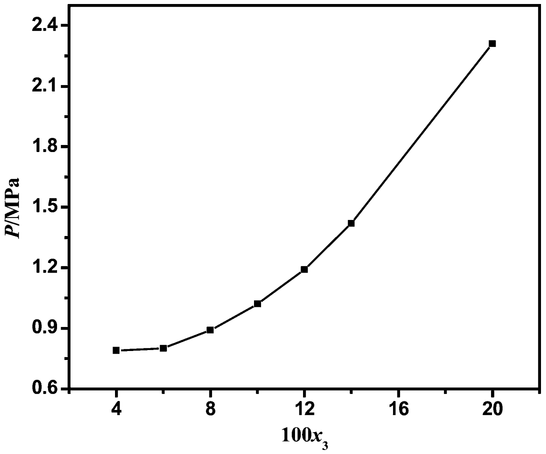

Figure 5. Hydrate formation pressures of methane (1) + ethylene (2) gas mixtures in the presence of different amount of THF in water at 282.2 K.

Table 2. Hydrate Formation Conditions of Methane (1) + Ethylene (2) Gas Mixtures in Tetrahydrofuran (3) + Water (4) Aqueous Solution at Fixed Temperature of 282.2 K

y_2	$100x_3$	P/MPa
0.6108	4.0	0.79
	6.0	0.80
	8.0	0.89
	10.0	1.02
	12.0	1.19
	14.0	1.42
	20.0	2.31

Summary and Conclusions

The hydrate formation condition data of pure ethylene gas and six synthetic methane + ethylene gas mixtures were measured in the temperature range of 277.7 K to 288.2 K, using the "pressure search" method. The experimental results demonstrated that the hydrate formation pressure of methane-containing gas mixtures could be remarkably lowered by adding THF to water while that of pure ethylene was increased by it. In contrast with the case of pure water, hydrate formation pressures decrease with increasing methane concentration in the gas mixture when THF is present in water.

Literature Cited

(1) Baronskaya, N. A.; Woldman, L. S.; Davydov, A. A.; Buyevskaya, O. V. Ethylene recovery from the gas product of methane oxidative coupling by temperature swing adsorption. *Gas. Sep. Purif.* **1996**, *10*, 85−88.

(2) Sloan, E. D. *Clathrate Hydrates of Natural Gases*, 2nd ed.; Marcel Dekker: New York, 1998.

(3) Ballard, A. L.; Sloan, E. D. Hydrate separation process for close-boiling compounds. In *Proceedings of the 4th International Conference on Gas Hydrates*, Japan. May 2002; pp 1007−1011.

(4) Yamamoto, Y.; Komai, T.; Kawamura, T.; Yoon, J. H.; Kang, S. P.; Okita, S. Studies on the separation and purification of guest component. In *Proceedings of the 4th International Conference on Gas Hydrates*, Japan. May 2002; pp 428−432.

(5) Kang, S. P.; Lee, H.; Lee, C. S.; Sung, W. M. Hydrate phase equilibria of the guest mixtures containing CO_2, N_2 and tetrahydrofuran. *Fluid Phase Equilib.* **2001**, *185*, 101−109.

(6) Chen, G. J.; Sun, C. Y.; Guo, T. M. A new technique for separating (hydrogen + methane) gas mixtures using hydrate technology. In *Proceedings of the 4th International Conference on Gas Hydrates*, Japan. May 2002; pp 1016−1020.

(7) Zhang, L. W.; Chen, G. J.; Guo, X. Q.; Sun, C. Y.; Yang, L. Y. The partition coefficients of ethane between vapor and hydrate phase for methane + ethane + water and methane + ethane + THF + water systems. *Fluid Phase Equilib.* **2004**, *225*, 141−144.

(8) Saito, Y.; Kawasaki, T.; Kondo, T.; Hiraoka, R. Methane storage in hydrate phase with water soluble guests. In *Proceedings of the 2nd International Conference on Gas Hydrates*, Toulouse, France, June 1996; pp 459−465.

(9) Florusse, L. J.; Peters, C. J.; Schoonman, J.; Hester, K. C.; Koh, C. A.; Dec, S. F.; Marsh, K. N.; Sloan, E. D. Stable low-pressure hydrogen clusters stored in a binary clathrate hydrate. *Science* **2004**, *306*, 469−471.

(10) Kang, S. P.; Lee, H. Recovery of CO_2 from flue gas using gas hydrate: thermodynamic verification through phase equilibrium measurements. *Environ. Sci. Technol.* **2000**, *34*, 4397−4400.

(11) Mei, D. H.; Liao, J.; Yang, J. T.; Guo, T. M. Hydrate formation of a synthetic natural gas mixture in aqueous solutions containing electrolyte, methanol and (electrolyte + methanol). *J. Chem. Eng. Data* **1998**, *43*, 178−182.

(12) Mei, D. H.; Liao, J.; Yang, J. T.; Guo, T. M. Experimental and modeling studies on the hydrate formation of a methane + nitrogen gas mixture in the presence of aqueous electrolyte solutions. *Ind. Eng. Chem. Res.* **1996**, *35*, 4342−4347.

(13) Fan, S. S.; Guo, T. M. Hydrate formation of CO_2-rich binary and quaternary gas mixtures in aqueous sodium chloride solutions. *J. Chem. Eng. Data* **1999**, *44*, 829−832.

(14) Zhang, Q.; Chen, G. J.; Huang, Q.; Guo, X. Q.; Ma, Q. L. Hydrate formation conditions of a hydrogen + methane gas mixture in tetrahydrofuran + water. *J. Chem. Eng. Data* **2005**, *50*, 234−236.

(15) Ma, C. F.; Chen, G. J.; Wang, F.; Sun, C. Y.; Guo, T. M. Hydrate formation of ($CH_4 + C_2H_4$) and ($CH_4 + C_3H_6$) gas mixtures. *Fluid Phase Equilib.* **2001**, *191*, 41−47.

(16) Larsen, R.; Knight, C. A.; Sloan, E. D. Clathrate hydrate growth and inhibition. *Fluid Phase Equilib.* **1998**, *150−151*, 353−360.

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