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Hydrate Formation Conditions of Sour Natural Gases

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Hydrate formation conditions of ($CH_4 + CO_2 + H_2S$) ternary sour natural gas mixtures in the presence of pure water were measured. The experimental temperature range was (274.2 to 299.7) K, and the pressure range was (0.58 to 8.68) MPa. The hydrogen sulfide and carbon dioxide contents in the gas mixtures varied from (4.9 to 26.6) mol % and from (6.8 to 10.8) mol %, respectively.

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1. Introduction

High hydrogen sulfide and carbon dioxide content sour natural gases are quite common in the world. One such natural gas field is located in southwest China, where hydrogen sulfide content up to 30 mol % has been found. As hydrogen sulfide is capable of forming hydrates under rather low pressure and rather high temperature in the presence of water, plugging of the production system could easily occur. To prevent the hydrate-plugging problem, it is important to know the hydrate formation conditions of high $H_2S + CO_2$ content sour natural gas mixtures.

Unfortunately, such experimental data are very scarce in the open literature. Adisasmito et al.[1] measured the hydrate formation conditions of (methane + carbon dioxide) binary systems in the presence of pure water systematically. Noaker and Katz[2] measured similar data for (methane + hydrogen sulfide) binary gas mixtures. The only available hydrate formation data of the (methane + carbon dioxide + hydrogen sulfide) ternary system was reported by Robinson and Hutton,[3] but the concentration range of H_2S covered in their work (5 to 16) mol % is not wide enough for industrial application and model developments. Hence, it is of significance to perform more systematical measurements on the hydrate formation conditions of this ternary system.

2. Experimental Section

2.1. Apparatus. The experimental apparatus used this work had been described in detail in the previous papers.[4−6] The apparatus consists of a cylindrical transparent sapphire cell (2.54 cm in diameter, working volume 60 cm^3) installed in an air bath with a view window and equipped with a magnetic stirrer for accelerating the equilibrium process. The formation and dissociation of the hydrate crystals in the solution can be observed directly. The accuracies of the temperature and pressure measurements are ±0.2 K and ±0.025 MPa, respectively.

2.2. Materials and Preparation of Samples. Analytical grade (99.99%) methane and carbon dioxide supplied by the Beifen Gas Industry Corporation were used in this work. Hydrogen sulfide (99.95%) was provided by the South-West Oil-Gas Corporation. The ternary gas mixtures were prepared in a gas sample cylinder with a volume of 1.2 L, where a balance with a precision of 1 g was used to weigh the mass of each component in the mixture (the pressure in the cylinder was about 40 MPa). The composition of each mixture presented in this paper was analyzed with a Hewlett-Packard gas chromatograph (HP 6890), which has been calibrated against a standard sample with known gas composition. The packing used in the column was Porapak QS.

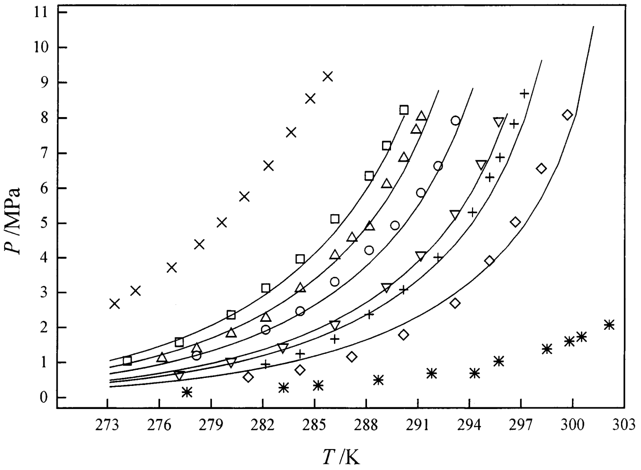

Figure 1. Hydrate formation conditions of studied ($CH_4 + CO_2 + H_2S$) ternary gas mixtures: (□) M1; (△) M2; (○) M3; (▽) M4; (+) M5; (◇) M6; (×) pure methane data (Adisasmito et al.[1]); (∗) pure hydrogen sulfide data (Selleck et al.[7]); (—) calculated by the Chen−Guo hydrate model.

2.3. Experimental Procedure. First, the sapphire cell was washed with distilled water and then rinsed three times with deionized water. After the cell was thoroughly cleaned, a small quantity (1 to 2 cm^3) of deionized water was added into the cell. The gas space of the cell was purged with the gas mixture four to five times to ensure the absence of air. The air bath temperature was then adjusted to the chosen temperature. Once the temperature was stabilized, the following “pressure search” method was used to determine the hydrate formation conditions.

The pressure in the cell was raised to ≈1 MPa higher than the estimated equilibrium pressure (using in house software) via the floating piston. When a trace of hydrate crystal was observed, the pressure was reduced gradually to allow the hydrate crystals to decompose slowly. When all the hydrate crystals disappeared, the pressure of the system was raised again with a small pressure step of 0.05 MPa until the hydrate crystal appears again (clinging to

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Table 1. Hydrate Formation Conditions of (CH_4 + CO_2 + H_2S) Ternary Natural Gas Mixtures

composition of gas mixture (mol %)	code no.	*T*/K	*P*/MPa
87.65% CH_4 + 7.40% CO_2 + 4.95% H_2S	M1	274.2	1.044
		277.2	1.580
		280.2	2.352
		282.2	3.126
		284.2	3.964
		286.2	5.121
		288.2	6.358
		289.2	7.212
		290.2	8.220
82.45% CH_4 + 10.77% CO_2 + 6.78% H_2S	M2	276.2	1.114
		278.2	1.385
		280.2	1.815
		282.2	2.265
		284.2	3.110
		286.2	4.065
		287.2	4.570
		288.2	4.890
		289.2	6.110
		290.2	6.862
		290.9	7.650
		291.2	8.024
82.91% CH_4 + 7.16% CO_2 + 9.93% H_2S	M3	278.2	1.192
		282.2	1.932
		284.2	2.460
		286.2	3.303
		288.2	4.212
		289.7	4.930
		291.2	5.868
		292.2	6.630
		293.2	7.916
77.71% CH_4 + 7.31% CO_2 + 14.98% H_2S	M4	277.2	0.646
		280.2	1.020
		283.2	1.428
		286.2	2.080
		289.2	3.164
		291.2	4.070
		293.2	5.270
		294.7	6.698
		295.7	7.910
75.48% CH_4 + 6.81% CO_2 + 17.71% H_2S	M5	282.2	0.950
		284.2	1.244
		286.2	1.670
		288.2	2.368
		290.2	3.080
		292.2	4.008
		294.2	5.314
		295.2	6.310
		295.8	6.880
		296.6	7.825
		297.2	8.680
66.38% CH_4 + 7.00% CO_2 + 26.62% H_2S	M6	281.2	0.582
		284.2	0.786
		287.2	1.160
		290.2	1.788
		293.2	2.688
		295.2	3.910
		296.7	5.030
		298.2	6.562
		299.7	8.080

the cell wall or suspended in the aqueous phase). The system temperature and pressure were maintained for 6 h, and if all the hydrate crystal disappeared during this period, the pressure of the system was raised slightly until a trace of hydrate crystals appeared again. When the hydrate crystals are retained in the cell after 6 h, the system pressure is taken as the equilibrium hydrate formation pressure at the given temperature. The above procedure was repeated for a series of assigned temperatures.

To eliminate the change of gas-phase composition resulting from the dissolution of sour gas components in water, in the course of the "pressure searching" process the gas phase was replaced with the gas sample in the gas cylinder three times.

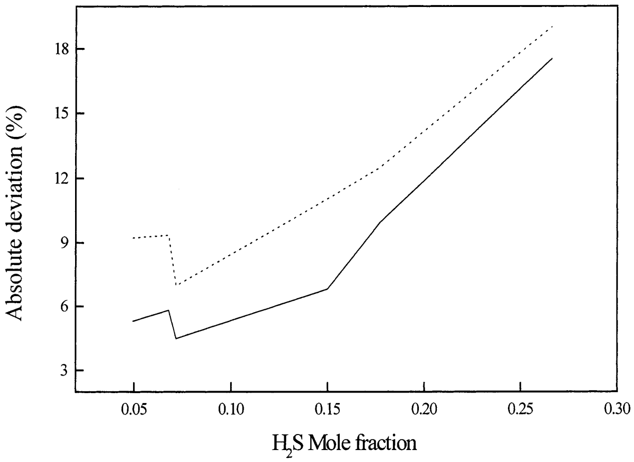

Figure 2. Absolute deviation of calculated results based on the Chen–Guo and CSMHYD hydrate models at various H_2S concentrations: (—) calculated by the Chen–Guo hydrate model; (···) calculated by CSMHYD.

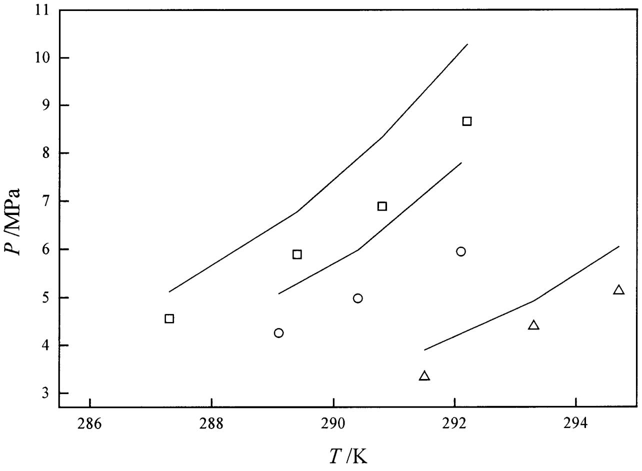

Figure 3. Comparison between the calculated hydrate formation conditions of three sour natural gas mixtures based on the Chen–Guo model and the experimental data reported by Robinson and Hutton:[3] (□) M7, 82.0% CH_4 + 12.6% CO_2 + 5.4% H_2S; (○) M8, 80.0% CH_4 + 12.0% CO_2 + 8.0% H_2S; (△) M9, 72.0% CH_4 + 12.0% CO_2 + 16.0% H_2S; (—) calculated by the Chen–Guo hydrate model.

2.4. Experimental Results. Following the above procedure, the initial hydrate formation data (in the presence of pure water) of six ternary (methane + carbon dioxide + hydrogen sulfide) gas mixtures have been measured. The compositions of the six ternary mixtures and the corresponding measured hydrate formation data are given in Table 1. Figure 1 shows the *P*–*T* plots of the experimental data. For comparison, the hydrate formation data of pure methane[1] and pure hydrogen sulfide[7] are also depicted in Figure 1. From Figure 1 and Table 1, increasing the H_2S content in a gas mixture causes the hydrate formation curve to move toward that of pure hydrogen sulfide. The solid line curves in Figure 1 are the calculated results based on the hydrate model developed by Chen and Guo.[8]

Figure 2 shows the comparison of the variation of the absolute deviation of the model calculation with H_2S concentration based on the Chen–Guo model and the CSMHYD model (Sloan[9]). The calculation deviation increases, in general, with increasing H_2S concentration in the gas mixture, and the Chen–Guo model gives better predictions. However, both models are subjected to further improvement for high H_2S content (e.g. >10 mol %) systems.

In addition, the Chen−Guo model has been applied to predict the hydrate formation conditions of the three sour natural gas mixtures reported by Robinson and Hutton.[3] The comparison of the prediction results with experimental data is presented in Figure 3. It should be noted that the deviations between experimental and predicted values are significantly larger than that based on the experimental data measured in this work (see Figure 1).

3. Conclusions

The hydrate formation data of six (methane + carbon dioxide + hydrogen sulfide) gas mixtures have been measured in the temperature range (274.2 to 299.7) K and the pressure range (0.58 to 8.68) MPa using the "pressure search" method. The reported data are valuable for sour natural gas production and hydrate model testing. The Chen−Guo hydrate model shows fairly good prediction results for the studied sour natural gas mixtures, but further improvement is required in the high H_2S concentration region.

Acknowledgment

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Literature Cited

(1) Adisasmito, S.; Frank, R. J.; Sloan, E. D. Hydrates of Carbon Dioxide and Methane Mixtures. *J. Chem. Eng. Data* **1991**, *36*, 68−71.
(2) Noaker, L. J.; Katz, D. L. Gas Hydrates of Hydrogen Sulfide−Methane Mixtures. *Trans. Am. Inst. Min., Metall. Pet. Eng.* **1954**, *201*, 237−239.
(3) Robinson, D. B.; Hutton, J. M. Hydrate Formation in Systems containing Methane, Hydrogen Sulphide and Carbon Dioxide. *J. Can. Pet. Technol.* **1967**, *6*, 6−9.
(4) 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.
(5) 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.
(6) Zhang, S. X.; Chen, G. J.; Ma, C. F.; Yang, L. Y.; Guo, T. M. Hydrate Formation of Hydrogen + Hydrocarbon Gas Mixture. *J. Chem. Eng. Data* **2000**, *45*, 908−911.
(7) Selleck, F. T.; Carmichael, L. T.; Sage, B. H. Phase Behavior in the Hydrogen Sulfide-Water System. *Ind. Eng. Chem.* **1952**, *44*, 2219−2226.
(8) Chen, G. J.; Guo, T. M. A New Approach to Gas Hydrate Modeling. *Chem. Eng. J.* **1998**, *71*, 145−151.
(9) Sloan, E. D. *Clathrate Hydrates of Natural Gases*; Marcel Dekker: New York, 1990.

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