Phase Equilibrium Data of Binary Hydrate in the System Hydrogen + Acetone + Water†

Jian-Wei Du, De-Qing Liang,* Dong-Liang Li, and Xin-Jun Li

Key Laboratory of Renewable Energy and Gas Hydrate, Guangzhou Institute of Energy Conversion,
CAS, Guangzhou 510640, China

In this work, we reported experimental equilibrium data for binary acetone−hydrogen clathrate hydrates with different initial molar concentrations of acetone [(0.030, 0.0556, and 0.0937) mol fraction]. Measurements were made using the isochoric pressure-search method. The hydrate dissociation data for the methane + acetone + water system at 0.0519 mol fraction of acetone were obtained in advance and compared with experimental data reported in the literature, and the acceptable agreements demonstrate the reliability of the experimental method and apparatus employed in this work. Hydrate equilibrium pressures in the ternary system hydrogen + acetone + water were investigated in the temperature range of (265.6 to 269.9) K and in the pressure range of (10.84 to 28.90) MPa, respectively. At 0.0556 mol fraction of acetone, the hydrate has the lowest phase equilibrium pressure. With the addition of acetone, a hydrogen molecule can be incorporated into hydrate cages more easily as the binary hydrate dissociation points shifted to a lower pressure and higher temperature region.

Introduction

Gas hydrates are a typical class of solid compounds that are crystallized mainly by water through the hydrogen bond and are stabilized by suitable size guest molecules under low temperature and elevated pressure conditions,[1] and this special structure allows gas hydrates to be used as a medium to accommodate methane or natural gas for practical applications in small and medium sized oil and natural gas fields. Previously, it was believed that H_2 could not form simple or mixed hydrates as its molecular diameter is too small to be fixed in water cavities.[2] However, since Mao et al.[3] reported that hydrogen could form a simple cubic structure II clathrate hydrate, especially Florusse et al.[4] found that H_2 could form binary clathrate hydrates with tetrahydrofuran (THF) at relatively low pressures and normal atmospheric temperatures close to ambient conditions (15 MPa and 283 K). The H_2 hydrate research has been prompted, and more hydrate formers such as cyclopentane,[5,6] tetrabutylammonium bromide (TBAB),[7] *tert*-butylamine,[8−10] *tert*-butyl methyl ether (TBME),[11] neohexane,[11] *n*-heptane,[11] methylcyclohexane (MCH),[11,12] and methyl tertiary butyl ether (MTBE)[10,11] are introduced to get much milder conditions in hydrogen storage and transportation.

Acetone had been investigated as the second guest molecule in the phase equilibrium of CH_4 and N_2 hydrates.[13,14] The addition of acetone caused the hydrate equilibrium pressure to be drastically lowered at a specified temperature and equivalently the hydrate equilibrium temperature to be greatly raised at a specified pressure.[14] However, the phase equilibrium condition for the binary acetone−hydrogen hydrate system has not been investigated in detail. It has been confirmed that, in a low and middle pressure region, the pure acetone formed sII hydrate, which is constructed from 16 small cages, 8 large cages, and 136 H_2O molecules in the unit cell, and its phase diagram is provided.[15] Because of its large molecular size, the acetone molecules can occupy the large cage only, leaving the small cage vacant. As the molecular hydrogen size is suitable to the hollow small cage, the molecular hydrogen should be able to be enclathrated in sII with cooperative assistance of acetone at mild pressure and temperature conditions. So, it is necessary to determine the phase equilibrium conditions for the binary hydrate of the hydrogen + acetone + water system in consideration of hydrogen storage using gas hydrate technology.

However, the information on the binary acetone−hydrogen hydrate is limited, and its phase equilibrium boundary has never been reported. Furthermore, the phase equilibrium relations for a mixed hydrate containing acetone should be clarified as they changed with the variation of the acetone concentration. To resolve these issues, traditional hydrate phase diagrams were the alternative solution by providing a convenient overview of the phase relations among the acetone aqueous solution, binary acetone−hydrogen hydrate, pure acetone hydrate, and hydrogen.

The purpose of the present study is to implement a traditional hydrate phase diagram to obtain the phase equilibrium conditions for the binary acetone−hydrogen hydrate system through measuring the hydrate equilibrium pressures at (0.030, 0.0556, and 0.0937) mol fraction of acetone in the temperature range of (265.6 to 269.9) K and in the pressure range of (10.84 to 28.90) MPa. The characteristic stable boundary curves of the binary acetone−hydrogen hydrate system are the subject of the present investigation. The experimental points were achieved using an isochoric pressure-search method.

Experimental Section

Materials Preparation. The chemicals used in the present study were listed in Table 1. Hydrogen, methane, and acetone were used without any further purification. Deionized water was used after careful degassing. In this work, the aqueous solutions used are mixtures of water and acetone. As acetone is a low boiling point and volatile liquid, the preparation of the aqueous

---

† Part of the "Sir John S. Rowlinson Festschrift".

* Corresponding author. E-mail: liangdq@ms.giec.ac.cn. Tel.: +(86)20-87057669. Fax: +(86)20-87057669.

10.1021/je100589u

Table 1. Experimental Materials Used in This Work

component	purity	supplier	phase
hydrogen	99.999 %	Fushan Kede Gas Co.	gas
methane	99.999 %	Fushan Kede Gas Co.	gas
acetone	>99.5 %	Tianjing Bodi Chemical Co., Ltd.	liquid
water	deionized		liquid

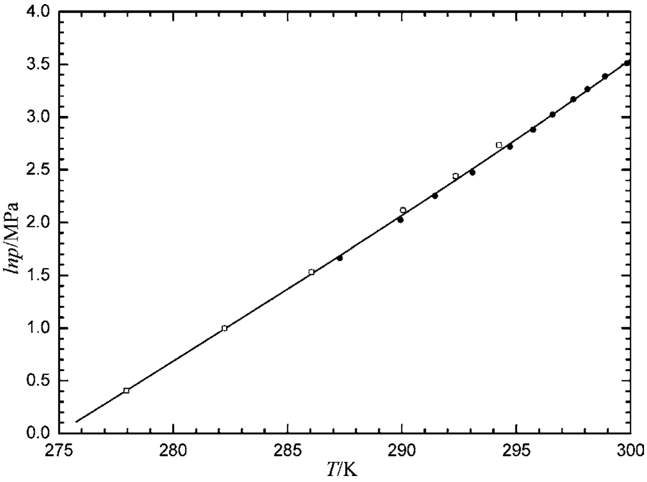

Figure 1. Hydrate equilibrium data of the methane + acetone + water system measured at 0.0519 mol fraction x of acetone. ●, this work; □, ref 13.

Table 2. Hydrate Equilibrium Data of the Methane + Acetone + Water System Measured at 0.0519 Mole Fraction x of Acetone

x	T/K	P/MPa
0.0519	287.3	5.27
	289.9	7.56
	291.5	9.51
	293.1	11.87
	294.7	15.16
	295.7	17.81
	296.6	20.57
	297.5	23.81
	298.1	26.17
	298.9	29.57
	299.8	33.41

solution is done by the following steps to reduce its volatilization. First, the required amounts of each component were predetermined. A predetermined amount of water was placed in a 50 mL flask. Then, acetone was added into the volumetric flask until the required amount was reached. Once the required mass of acetone was achieved, a stopper was placed on the volumetric flask. Throughout the process, the mass of the system was monitored by the mass balance. Finally, the overall concentration of the liquid solution was recalculated.

Experimental Apparatus. The apparatus used in the present study has been described by Liang et al.[9,16] and Sun et al.[17,18] The apparatus allows measurement of phase equilibrium conditions within pressure ranging from (0.1 to 40) MPa with an uncertainty of ± 0.024 MPa and temperature from (253 to 399) K with an uncertainty of ± 0.1 K. The equilibrium cell is a “full view” sapphire variable-volume cell with a movable piston. The cell consists of a sapphire tube sealed at the top end with a stainless steel flange. The test contents were mixed through a stirrer which was driven by a dc motor located at the end of the piston and a magnetic coupling mounted outside the cell. The cell volume was adjusted with the movable piston. The data from the acquisition system were saved at preset sampling intervals on a computer. A detailed schematic figure of the apparatus is depicted in ref 9.

Experimental Methods and Procedures. The experimental method employed in this work has been stated in detail by Liang et al.[9] For the ternary system hydrogen + acetone + water, clathrate dissociation $P-T$ conditions for various initial aqueous acetone concentrations [(0.030, 0.0556, and 0.0937) mol fraction] were determined by constant-volume cell isochoric equilibrium step-heating techniques. The acetone aqueous solution prepared at a desired mole fraction was introduced into the vacuum sapphire cell. The content was pressurized up to the desired pressure by supplying hydrogen or methane. Then the system temperature decreased until the hydrate formed, which can be confirmed through visual observation. Once the hydrate formed, the temperature increased gradually at about 0.1 K, and each interval takes at least 4 h to establish an adequate equilibrium state at each temperature step. The temperature and pressure were measured continuously, and the equilibrium data were plotted. The point at which the slope of the $P-T$ curve sharply changed was considered as the hydrate dissociation point at which all hydrate crystals have dissociated. This was also confirmed by visual observation. In this way, a pressure−temperature diagram was obtained for each experimental run, from which the hydrate dissociation point was determined.[19]

Results and Discussion

Measurements of the binary hydrate dissociation conditions for the methane + acetone + water system shown in Figure 1 were carried out not only in the existing pressure−temperature area reported but also in the higher pressure−temperature region. To check the reliability of the experimental apparatus and the procedure, 11 phase equilibrium points of binary hydrate formation in methane + acetone + water were compared with the experimental data reported in the literature.[13] The $P-T$ data obtained in this work were given in Table 2 and were plotted in Figure 2 together with previous data reported by Ng and Robinson[13] using the visual observation method. Figure 2 indicated the deviations of the experimental data in the present study and reported in the literature from the empirical correlation determined by all the experimental data sourced from the present study and Ng and Robinson[13] with a third-order polynomial. The definition of the deviation was $100(\ln p_{\text{exp}} - \ln p_{\text{calc}})/\ln$

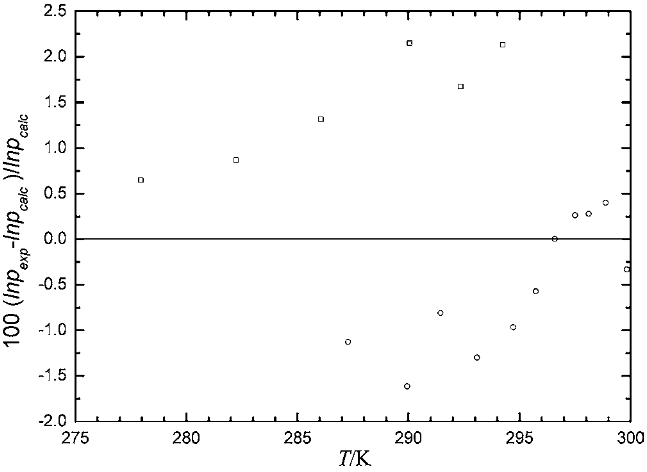

Figure 2. Deviations of the natural logarithm of experimental equilibrium pressures for binary hydrate in the methane + acetone + water system at 0.0519 mol fraction x of acetone from those calculated by the empirical correlation $\ln p = -354.818 + 3.55422T - 0.01227T^2 + 1.46814 \cdot 10^{-5}T^3$ determined on the basis of the experimental data obtained in the present study and the data from: ○, this work; □, ref 13.

Table 3. Hydrate Equilibrium Data of the Hydrogen + Acetone + Water System Measured at Three Different Mole Fractions *x* of Acetone

x	*T*/K	*P*/MPa
0.030	265.6	11.54
	266.7	14.73
	267.4	17.28
	267.8	19.26
	268.1	20.89
	268.7	23.64
	269.2	26.29
	269.7	28.90
0.0556	266.1	10.87
	266.7	12.61
	267.3	14.41
	268.1	17.03
	268.7	19.48
	269.5	23.22
	269.9	25.58
0.0937	265.9	10.84
	266.6	12.43
	267.7	16.21
	268.5	19.15
	269.4	23.56
	269.9	26.42

p_{calc}, where p_{exp} was the experimental equilibrium pressure and p_{calc} was the pressure calculated by the empirical third-order polynomial correlation mentioned above. The uncertainty of the measurements in the present study was also shown in Figure 2. As seen from Figure 2, the deviation of the data obtained in the present study was within the uncertainty of the measurements, and the absolute average deviation was within 2.5 % between the data obtained in the present study and the literature[13] with the data calculated. The difference may be caused by different measuring methods applied in the experiment.

The binary hydrate equilibrium data obtained from the ternary hydrogen + acetone + water system at (0.030, 0.0556, and 0.0937) mol fraction of acetone were reported in Table 3 and presented in Figure 3. The phase equilibrium relations for mixed hydrate containing acetone is displayed clearly through dotted lines of best-fit as they changed with the variation of the acetone concentration. Each three-phase equilibrium pressure increased continuously with the temperature increase at a similar slope. However, due to the various acetone contents in the system, the equilibrium lines rose at different slopes. It should be noted that among the three concentrations of acetone aqueous solutions the equilibrium pressure−temperature line at 0.0556 mol fraction of acetone was the lowest which was the stoichiometric concentration of the pure acetone hydrate,[15] while the line corresponding to 0.0937 mol fraction was slightly higher. This effect was the same as the equilibrium curve of binary THF + hydrogen hydrate which had the lowest curve at sII stoichiometry as well.[20−22]

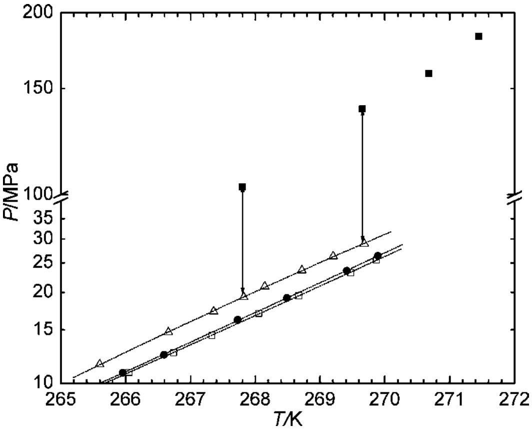

Figure 3. Hydrogen + acetone binary hydrate equilibrium data for Δ, 0.030 mol fraction; □, 0.0556 mol fraction; ●, 0.0937 mol fraction; dotted line, line of best-fit for the experimental points; ■, pure hydrogen hydrate equilibrium data from ref 23.

As shown in Figure 3, the comparison results with pure hydrogen hydrate phase equilibrium data demonstrated that the presence of acetone can allow the hydrogen molecule to be incorporated into hydrate cages more easily, which means shifting dissociation conditions of hydrogen hydrate due to the addition of acetone in the system to low pressures or high temperatures. In spite of the different acetone concentrations, the addition of acetone affected remarkably the decrease of the hydrate dissociation pressure in the hydrogen + water system at a given temperature. For example, at 0.030 mol fraction, the introduction of acetone resulted in approximately 84 MPa pressure reductions at 267.8 K. For the other two concentrations, the declines of equilibrium pressure were steeper. It was noteworthy that the increase of temperature would lead the pure hydrogen hydrate equilibrium pressure to a more significant reduction at the same mole fraction of acetone. This trend may be thought of as the expression of the stable effect caused by the acetone in the hydrogen and water system as the formation pressure range of pure hydrogen hydrate was narrowed. Acetone should be a noticeable hydrate former for reducing the hydrogen hydrate equilibrium pressure and hydrogen storage studies by gas hydrate technology.

Conclusions

In this work, the novel phase equilibrium behavior and data of methane + acetone + water and hydrogen + acetone + water system have been investigated and measured using a traditional hydrate phase diagram at (0.030, 0.0556, and 0.0937) mol fraction of acetone in the temperature range of (265.6 to 269.9) K and in the pressure range of (10.84 to 28.90) MPa. The three-phase diagram of binary hydrogen + acetone hydrate studies has been performed to gain a fundamental understanding of the phase equilibrium behavior of hydrogen encaged within hydrate. An isochoric pressure-search method was employed to fulfill the task. The results showed that the existence of acetone in aqueous solution made the binary hydrogen + acetone hydrate phase equilibrium pressure dramatically reduce compared with pure hydrogen hydrate phase equilibrium pressure, especially at 0.0556 mol fraction of acetone, and acetone would be helpful to reduce the hydrogen hydrate equilibrium pressure.

Literature Cited

(1) Sloan, E. D.; Koh, C. A. *Clathrate Hydrates of Natural Gases*, 3rd ed.; CRC Press, Taylor & Francis Group: Boca Raton, 2007.

(2) Holder, G. D.; Stephenson, J. L.; Joyce, J. J.; John, V. T.; Kamath, V. A.; Malekar, S. Formation of clathrate hydrates in hydrogen-rich gases. *Ind. Eng. Chem. Process. Des. Dev.* **1983**, *22* (1), 170–171.

(3) Mao, W. L.; Mao, H.; Goncharov, A. F.; Struzhkin, V. V.; Guo, Q.; Hu, J.; Shu, J.; Hemley, R. J.; Somayazulu, M.; Zhao, Y. Hydrogen clusters in clathrate hydrate. *Science* **2002**, *297*, 2247–2249.

(4) 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.

(5) Zhang, J. S.; Lee, J. W. Equilibrium of Hydrogen + Cyclopentane and Carbon Dioxide + Cyclopentane Binary Hydrates. *J. Chem. Eng. Data* **2009**, *54*, 659–661.

(6) Martin, A.; Peters, C. J. Thermodynamic Modeling of Promoted Structure II Clathrate Hydrates of Hydrogen. *J. Phys. Chem. B* **2009**, *113*, 7548–7557.

(7) Hashimoto, S.; Murayama, S.; Sugahara, T.; Sato, H.; Ohgaki, K. Thermodynamic and Raman Spectroscopic Studies on H_2 + Tetrahy-

drofuran + Water and H_2 + Tetra-n-butyl Ammonium Bromide + Water Mixtures Containing Gas Hydrates. *Chem. Eng. Sci.* **2006**, *61*, 7884–7888.

(8) Kim, D. Y.; Lee, J. W.; Seo, Y. T.; Seo, Y. T.; Ripmeester, J. A.; Lee, H. Structural transition and tuning of tert-Butylamine hydrate. *Angew. Chem., Int. Ed.* **2005**, *44*, 7749–7752.

(9) Liang, D. Q.; Du, J. W.; Li, D. L. Hydrate Equilibrium Data for Methane + *tert*-Butylamine + Water. *J. Chem. Eng. Data* **2010**, *55*, 1039–1041.

(10) Prasad, P. S. R.; Sugahara, T.; Sum, A. K.; Sloan, E. D.; Koh, C. A. Hydrogen storage in double clathrates with tert-Butylamine. *J. Phys. Chem. A* **2009**, *113*, 6540–6543.

(11) Susilo, R.; Lee, J. D.; Englezos, P. Liquid-liquid equilibrium data of water with neohexane, methylcyclohexane, tert-butyl methyl ether, n-heptane and vapor-liquid-liquid equilibrium with methane. *Fluid Phase Equilib.* **2005**, *231*, 20–26.

(12) Strobela, T. A.; Koh, C. A.; Sloan, E. D. Hydrogen storage properties of clathrate hydrate materials. *Fluid Phase Equilib.* **2007**, *261*, 382–389.

(13) Ng, H. J.; Robinson, D. B. New Developments in the Measurement and Prediction of Hydrate Formation for Processing Needs. *Ann. N.Y. Acad. Sci.* **1994**, *715*, 450–462.

(14) Seo, Y. T.; Kang, S. P.; Lee, H. Experimental determination and thermodynamic modeling of methane and nitrogen hydrates in the presence of THF, propylene oxide, 1,4-dioxane and acetone. *Fluid Phase Equilib.* **2001**, *189*, 99–110.

(15) Wilson, G. J.; Davidson, D. W. Dielectric evidence for acetone hydrate. *Can. J. Chem.* **1963**, *41*, 264–273.

(16) Liang, D. Q.; Guo, K. H.; Wang, R. Z.; Fan, S. S. Hydrate equilibrium data of 1,1,1,2-tetrafluoroethane (HFC-134a), 1,1-dichloro-1-fluoroethane (HCFC-141b) and 1,1-difluoroethane (HFC-152a). *Fluid Phase Equilib.* **2001**, *187−188*, 61–70.

(17) Sun, Z. G.; Fan, S. S.; Guo, K. H.; Shi, L.; Guo, Y. K.; Wang, R. Z. Gas Hydrate Phase Equilibrium Data of Cyclohexane and Cyclopentane. *J. Chem. Eng. Data* **2002**, *47*, 313–315.

(18) Sun, Z. G.; Fan, S. S.; Guo, K. H.; Shi, L.; Wang, R. Z. Equilibrium hydrate formation conditions for methylcyclohexane with methane and a ternary gas mixture. *Fluid Phase Equilib.* **2002**, *198*, 293–298.

(19) Tohidi, B.; Burgass, R. W.; Danesh, A.; Østergaard, K. K.; Todd, A. C. Improving the Accuracy of Gas Hydrate Dissociation Point Measurements. *Ann. N.Y. Acad. Sci.* **2000**, *912*, 924–931.

(20) Hashimoto, S.; Murayama, S.; Sugahara, T.; Sato, H.; Ohgaki, K. Thermodynamic and Raman Spectroscopic Studies on H_2 + Tetrahydrofuran + Water and H_2 + Tetra-n-butyl Ammonium Bromide + Water Mixtures Containing Gas Hydrates. *Chem. Eng. Sci.* **2006**, *61*, 7884–7888.

(21) Hashimoto, S.; Sugahara, T.; Sato, H.; Ohgaki, K. Thermodynamic Stability of H_2 + Tetrahydrofuran Mixed Gas Hydrate in Nonstoichiometric Aqueous Solutions. *J. Chem. Eng. Data* **2007**, *52*, 517–520.

(22) Anderson, R.; Chapoy, A.; Tohidi, B. Phase Relations and Binary Clathrate Hydrate Formation in the System H_2-THF-H_2O. *Langmuir* **2007**, *23*, 3440–3444.

(23) Dyadin, Y. A.; Larionov, E. G.; Manakov, A. Yu.; Zhurko, F. V.; Aladko, E. Ya.; Mikina, T. V.; Komarov, V. Yu. Clathrate Hydrate of Hydrogen and Neon. *Mendeleev Commun.* **1999**, *5*, 209–210.

Received for review May 29, 2010. Accepted September 6, 2010. This work was supported by the National Natural Science Foundation of China (50876107), National Basic Research Program of China (2009CB219504), NSFC-Guangdong Union Foundation (U0733003), and CAS Program (KGCX2-YW-805).

JE100589U