Clathrate Dissociation Conditions for Methane + Tetra-*n*-butyl Ammonium Bromide (TBAB) + Water

Dong-Liang Li,[†,‡,§] Jian-Wei Du,[†,‡,§] Shuan-Shi Fan,[†,‡] De-Qing Liang,*[†,‡] Xiao-Sen Li,[†,‡] and Ning-Sheng Huang[‡]

Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, China, Guangzhou Center for Gas Hydrate Research, Chinese Academy of Sciences, Guangzhou 510640, China, and Graduate University of Chinese Academy of Sciences, Beijing 100083, China

---

Hydrate equilibrium data of the CH_4 + tetra-*n*-butyl ammonium bromide (TBAB) + water have been measured by using the isothermal pressure search method for four components of TBAB aqueous solutions. The three-phase equilibrium lines obtained in the present study are shifted to the low-temperature or high-pressure side from that of the stoichiometric TBAB solution. Moreover, methane uptake into semi-clathrates is confirmed by a shift in the clathrate regions when methane is present. The experiments are carried out in the pressure range of (0.5 to11) MPa and in the temperature range of (281.15 to 295.15) K.

Introduction

Clathrate hydrates, or gas hydrates, are a group of icelike, crystalline inclusion compounds that form through the combination of water (the host) and suitably sized gas (the guest) molecules, typically at low temperature and elevated pressure conditions. These hydrates crystallize in three prominent structures, structures I, II, and H, depending on the nature and the size of the guest molecule.[1] Tetra-*n*-butyl ammonium bromide (TBAB) can also form a semi-clathrate hydrate crystal with water molecules even at atmospheric pressure and room temperature. In TBAB semi-clathrate hydrate, Br forms cage structures with water molecules and the tetra-*n*-butyl ammonium cation occupies four cages. Such a hydrate is called a semi-clathrate hydrate crystal because a part of the cage structure is broken to enclose the large tetra-*n*-butyl ammonium molecule. It is generally agreed that there are two main structures: one is type I, with a hydration number of 26, and another is type II, with a hydration number of 38. TBAB hydrate is often used as a heat transport medium, and it can save 40 % of energy in comparison with ice production.[2−4] Furthermore, TBAB hydrate has empty dodecahedral cages. Kamata et al. confirmed that H_2S can be incorporated into TBAB semi-clathrate hydrate, most likely by means of occupation of vacant dodecahedral cavities.[5,6] Hence, TBAB semi-clathrate hydrate can be used to separate or store some gases. Recently, some studies have demonstrated that hydrogen can be stored in semi-clathrates.[7,8] The formation condition of TBAB hydrate could be very important for industrial application of cool storage, gas separation, and gas storage. Phase equilibrium of pure TBAB hydrate has been determined by Oyama et al.[9] However, few experimental data are available in the literature, except the phase equilibrium data of H_2 in TBAB (w = 0.405) reported by Shunsuke[7] and Chapoy.[8]

Table 1. Test Fluids Used in This Work

component	purity/%	supplier
methane	99.99	Fushan Kede Gas Co.
TBAB	>99	Changzhou Xinhua Active Material Institute
water		distilled

Experimental Section

The experimental apparatus and procedures used in this work were described in detail by Sun et al.[10,12,13] 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 pressure was measured using a TF01 400A absolute pressure transducer (0 to 40 MPa) with uncertainties of about 0.06 % of full scale. The cell temperature was measured using platinum resistance thermometers with an accuracy of 0.1 K. The cell volume was adjusted with the movable piston. The data from the acquisition system were saved at preset sampling intervals on a computer.

The fluids used in this work are described in Table 1. The cell was washed with distilled water and the fluid three times, respectively. The cell was initially charged with approximately 15 mL of fluid by an injector. Next, the cell was vacuumed and methane was taken in subsequently. The hydrate equilibrium was established using the "pressure search" procedure at a fixed temperature.[11,12]

After the sample had been charged in the cell, the temperature was then lowered to form hydrates. The pressure was decreased by moving the cell piston to decompose the hydrates when a large amount of hydrates was observed. The temperature and pressure were considered as the equilibrium conditions when a small quantity of the hydrate crystals remained for (3 to 4) h. Once the equilibrium conditions were established, the pressure in the cell was lowered by 50 kPa to confirm that all of the hydrate decomposed. A different temperature was subsequently selected, and the procedure was repeated to obtain another hydrate equilibrium condition.

---

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

[†] Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences.

[‡] Guangzhou Center for Gas Hydrate Research, Chinese Academy of Sciences.

[§] Graduate University of Chinese Academy of Sciences.

10.1021/je700229e CCC: $37.00

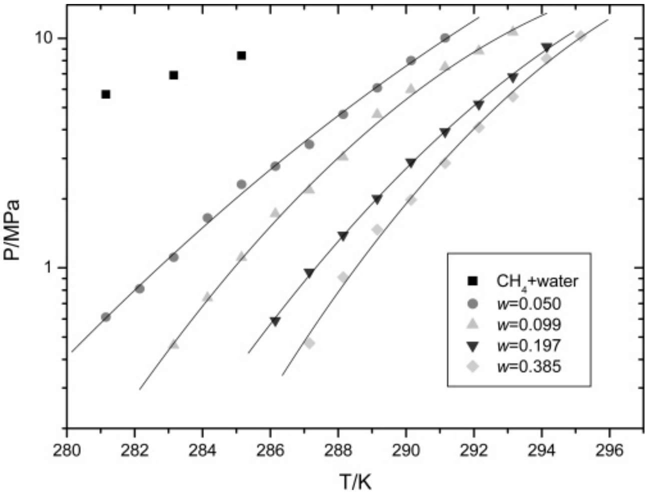

Figure 1. Hydrate dissociation condition for CH_4 (1) + TBAB (2) + water (3): ■, no TBAB; ▼, $w = 0.050$; ▲, $w = 0.099$; ▽, $w = 0.197$; △, $w = 0.385$.

Table 2. Hydrate Dissociation Pressure *P* for CH_4 (1) + TBAB (2) + Water (3) as a Function of Temperature *T* at TBAB Mass Fraction $w = (0.050, 0.099, 0.197, \text{and } 0.385)$

	P/MPa			
T/K	*w* = 5.0	*w* = 9.9	*w* = 19.7	*w* = 38.5
281.15	0.61			
282.15	0.81			
283.15	1.11	0.46		
284.15	1.65	0.74		
285.15	2.31	1.11		
286.15	2.77	1.72	0.59	
287.15	3.45	2.18	0.96	0.47
288.15	4.66	3.04	1.39	0.91
289.15	6.08	4.66	2.01	1.47
290.15	8.00	5.98	2.9	1.98
291.15	10.03	7.5	3.92	2.86
292.15		8.82	5.17	4.09
293.15		10.64	6.08	5.57
294.15			9.22	8.16
295.15				10.23

Results and Discussion

Measured formation conditions for CH_4–TBAB semi-clathrates are compared with those for simple CH_4 in Figure 1. Table 2 presents the hydrate formation data for methane in solutions of different TBAB concentrations. TBAB mass percent is 5, 9.9, 19.7, and 38.5, respectively. As Figure 1 shows, the addition of TBAB causes the hydrate equilibrium pressure to be drastically lowered by (52 to 96) % at a specified temperature and, equivalently, the hydrate equilibrium temperature to be raised by about (4 to 17) K at a specified pressure depending on the concentration of TBAB in water. Methane uptake into semi-clathrates is confirmed by a shift in the clathrate regions when TBAB is present. It is clear that the slope in pressures versus temperatures curve is not a constant and, actually, gradually decreases with increasing temperature.

TBAB hydrate formation conditions for different methane pressures are compared with the pure TBAB system in Figure 2. Measurements show that the hydrate equilibrium temperature curves of the mixture at the same pressure were the same as those of pure TBAB type I semi-hydrate at atmospheric pressure. There are at least five different structures in the system TBAB + water, with hydration numbers of 24, 26, 32, 36, and 38, but this has not been confirmed at this time. Type I with a hydration number of 26 is more stable; the structure of the mixture hydrate may be also type I in contrast to the equilibrium curves of the pure TBAB system. The increase of the pressure can enhance the hydrate equilibrium temperature at the same TBAB mass fraction.

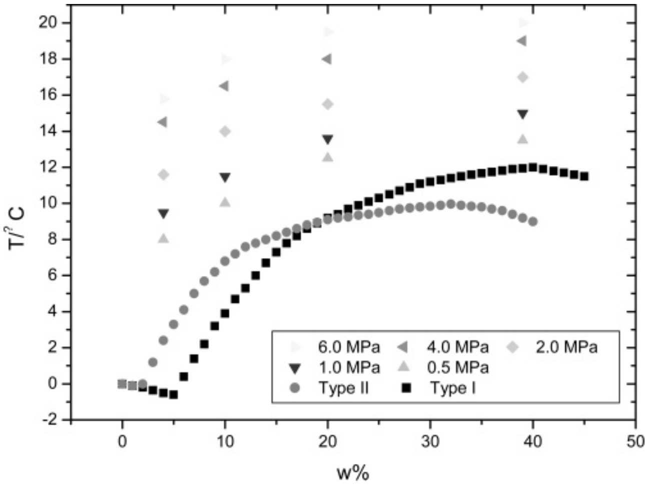

Figure 2. Hydrate dissociation conditions for methane with TBAB at various pressures: solid right-pointing triangle, 6.0 MPa; solid left-pointing triangle, 4.0 MPa; ■, 2.0 MPa; ▼, 1.0 MPa ▲, 0.5 MPa; ○, type I, Oyama et al.;[9] △, type II, Oyama et al.[9]

Conclusions

In the present work, the three- and four-phase hydrate equilibria of the ternary system of methane + TBAB + water are measured by using the isothermal pressure search method. The experimental temperature range from (281.15 to 295.15) K and pressure up (0.5 to 11) MPa have been investigated. Measurements show that the addition of TBAB causes the hydrate equilibrium pressure to be drastically lowered by (52 to 96) % at a specified temperature and, equivalently, the hydrate equilibrium temperature to be raised by about (4 to 17) K at a specified pressure depending on the component of TBAB in water. Methane uptake into semi-clathrates is confirmed by a shift in clathrate regions when TBAB is present. The curve of the temperatures versus TBAB component at different pressures shows that the structure of CH_4–TBAB semi-hydrate may be type I, but this needs further investigation.

Literature Cited

(1) Sloan, E. D. Fundamental Principles and Applications of Natural Gas Hydrates. *Nature* **2003**, *426*, 353–356.
(2) Ichiro, T.; Shingo, T. Clathrate hydrate slurry of tetran-butylammonium bromide as a cold-storage material. In *Proceedings of the 4th ICGH*, Yokohama, Japan, 2002.
(3) Oyama, H.; Shingo, T. Air-conditioning system using clathrate hydrate slurry. *JFE Tech. Rep.* **2004**, *3*, 1–5.
(4) Darbouret, M.; Cournil, M.; Herri, J. M. Rheological study of TBAB hydrate slurries as secondary two-phase refrigerants *Int. J. Refrig.* **2005**, *28* (5), 663–671.
(5) Kamata, Y.; Yamakoshi, Y.; Ebinuma, T., et al. Hydrogen sulfide separation using tetra-*n*-butyl ammonium bromide semi-clathrate (TBAB) hydrate. *Energy Fuels* **2005**, *19*, 1717–1722.
(6) Kamata, Y.; Oyama, H.; Shimada, W., et al. Gas separation method using tetra-*n*-butyl ammonium bromide semi-clathrate hydrate. *Jpn. J. Appl. Phys.* **2004**, *43* (1), 362–365.
(7) Shunsuke, H.; Shu, M.; Takeshi, S., et al. 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.
(8) Chapoy, A.; Anderson, R.; Tohidi, B. Low-pressure molecular hydrogen storage in semi-clathrate hydrates of quaternary ammonium compounds. *J. Am. Chem. Soc.* **2007**, *129*, 746–747.
(9) Oyama, H.; Shimada, W.; Ebinuma, T., et al. Phase diagram, latent heat, and specific heat of TBAB semiclathrate hydrate crystals. *Fluid Phase Equilibr.* **2005**, *234* (1), 131–135.

(10) Sun, Z. G.; Fan, S. S.; Shi, L., et al. Equilibrium conditions hydrate dissociation for a ternary mixture of methane, ethane, and propane in aqueous solutions of ethylene glycol and electrolytes. *J. Chem. Eng. Data* **2001**, *46*, 927−929.
(11) Liang, D. Q.; Guo, K. H.; 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 Equilibr*. **2001**, *187*, 61−70.
(12) Sun, Z. G.; Fan, S. S.; Guo, K. H., et al. Gas hydrate phase equilibrium data of cyclohexane and cyclopentane. *J. Chem. Eng. Data* **2002**, *47*, 313−315.
(13) Sun, Z. G.; Fan, S. S.; Guo, K. H., et al. Equilibrium hydrate formation conditions for methylcyclohexane with methane and a ternary gas mixture. *Fluid Phase Equilibr*. **2002**, *198* (2), 293−298.

Received for review April 28, 2007. Accepted July 3, 2007. The work was supported by the National Natural Science Foundation of China (50676097) and Hi-tech Research and Development Program of China (2006AA05Z204).

JE700229E