J. Chem. Eng. Data **2008,** *53,* 2375–2377

Hydrate Equilibrium Conditions for Tetra-*n*-butyl Ammonium Bromide

Zhi-Gao Sun,* Cheng-Ming Jiang, and Nuo-Lin Xie

School of Engineering, Sun Yat-Sen University, Guanggzhou 510275, People's Republic of China

Hydrate equilibrium conditions for tetra-*n*-butyl ammonium bromide (TBAB) aqueous solutions were experimentally studied and reported in the mole fraction from 0.003 to 0.047 and the temperature range of (276.35 to 285.65) K at atmospheric pressure. The phase change temperature of TBAB hydrate increases with the increase of the concentration of TBAB aqueous solution when the mole fraction of TBAB aqueous solution is less than 0.044.

Introduction

Clathrate hydrates are icelike crystalline inclusion compounds formed by hydrogen bonding of water molecules in the presence of molecules such as methane, ethane, or propane. The activity of water has an important effect on the hydrate equilibrium conditions. Water activity is a very important factor in hydrate study and is paid more attention.[1−5] The most well-known hydrate structures are those of structure I and structure II. Comprehensive treatises on hydrates have been reviewed by Sloan.[1] There are two opposite directions in the investigation on hydrates. Studies related to the problematic side of hydrates are those which attempt to find ways of hydrate inhibition, whereas some studies are focused on determining some means for the promotion of hydrate formation.[6−9]

Hydrates have been considered as phase change materials for cool storage for air-conditioning systems to decrease the power peak load of air conditioning. Concerning air-conditioning systems, a suitable phase change material should present a melting temperature from 6 °C to 12 °C. Some refrigerant hydrates (such as HFC-134a, HFC-152a, and HCFC-141b, etc.) meet this property and were studied.[10−12] These refrigerants usually are not soluble in water, and refrigerant hydrates do not easily form. Water-soluble hydrate materials were paid more attention recently. Quaternary ammonium salts, such as tetra-*n*-butyl ammonium bromide (TBAB), became subjects for phase change materials for cool storage as ammonium salt hydrates can form in the temperature range of air-conditioning water.[13,14] TBAB is soluble in water and can form semiclathrate hydrate at atmospheric pressure. Unlike clathrate hydrates, Br anions and water molecules build a clathrate framework (hydrophilic intercalation), and the TBA cation is embedded in framework cavities (hydrophobic intercalation) in the TBAB semiclathrate hydrate. As TBAB hydrate can form at atmospheric pressure, it was considered a good promoter to improve hydrate formation for hydrogen storage in hydrates.[15,16]

In the present work, hydrate formation data have been measured for TBAB aqueous solutions at atmospheric pressure. The measurements are performed in mole fraction from 0.003 to 0.047 and the temperature range of (276.35 to 285.65) K.

Experimental Apparatus and Procedure

Experimental Apparatus. The experimental apparatus is sketched in Figure 1. A cylindrical high-pressure cell, made of stainless steel, was used as a test section. A stainless-steel flange, which has appropriate ports for access to the interior, is used to seal the cell on the top. There are two plexiglass windows which can be used to view hydrate formation. The cell is equipped with a magnetic stirrer to agitate the fluids and hydrate crystals inside the vessel. The cell is designed to operate at pressures up to 20 MPa and temperatures in the range of (253 to 323) K, and its available volume is about 300 cm^3.

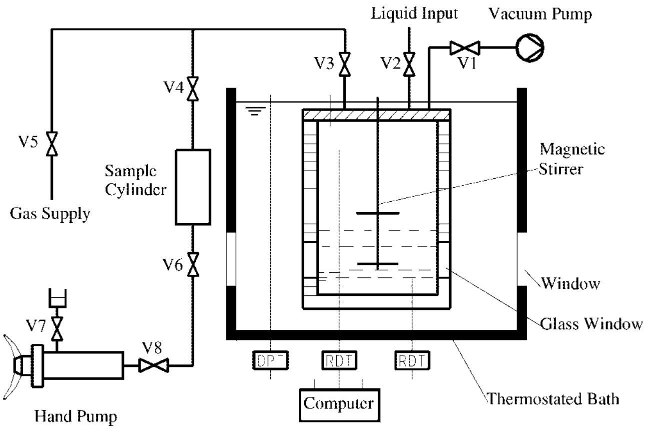

Figure 1. Schematic diagram of the experimental apparatus. DPT, differential pressure transducer; RTD, resistance temperature detector; V1 to V8, valves.

The vessel is immersed in a thermostated bath to maintain the temperature inside the vessel *T* at a prescribed level. The temperatures in the gas and liquid phases are measured with two platinum resistance thermometers with an accuracy of ± 0.1 K. The thermostated bath is made of glass which is enclosed by insulation. The cell pressure is measured using a PTX7517 absolute pressure transducer, (0 to 600) kPa, of accuracy about 0.2 % of the scale. The sample cylindrical cell is also made of stainless steel, whose volume is about 1000 cm^3. The working volume of the sample cell can be adjusted by the floating piston, which is driven by a positive displacement pump.

Experimental Procedure. The test fluids used in this work are described in Table 1. TBAB was a research-grade chemical. Appropriate quantities of TBAB and distilled water were weighed on an electronic balance with a readability of ± 0.1 mg (model CP225D, Sartorius Co., Ltd.). The mole fractions of TBAB aqueous solutions for this work are from 0.003 to 0.047.

---

* Corresponding author. E-mail: szg.yzu@163.com. Fax: +86-20-39332895.

10.1021/je8005612 CCC: $40.75

Table 1. Test Fluids Used in This Work

component	purity	supplier
TBAB	≥ 99.0 %	Guangzhou Jinhua Chemical Reagent Co. Ltd.
water		distilled

Table 2. Equilibrium Data of Aqueous TBAB Solutions

mole fraction	T/K	solution	T/K
0.003	276.35	0.021	284.25
0.006	278.25	0.023	284.45
0.010	279.95	0.029	284.85
0.012	281.15	0.036	285.25
0.014	282.05	0.042	285.55
0.015	282.85	0.044	285.65
0.018	283.75	0.047	284.75

The equilibrium experimental data were obtained using the batch, isochoric procedure.[10,17,18] The test procedure was the same as the following. Prior to the test, the cell was rinsed with distilled water two times and evacuated. Approximately 80 cm^3 of TBAB aqueous solution was inhaled into the cell for each experiment. Then, the valve 2 for liquid input was opened. After the aqueous solution was charged into the cell, the temperature was decreased to form hydrate. Once the solution in the cell reached the desired temperature, the sample solution was stirred by the magnetic stirrer. The presence of hydrates in the cell was determined visually in the equilibrium cell. A large amount of hydrates were observed, while the temperatures of the test fluids increased. The temperature of the thermostated bath was kept constant for (4 to 6) h, thereby keeping the temperature of the solution in the cell constant. Then, the temperature of the test solution was increased in steps of 0.1 K. The temperature of the test solution was kept constant for (4 to 6) h to achieve a steady equilibrium state in the cell at every temperature step. The equilibrium temperature was established using the batch, isochoric method. The temperature is considered the equilibrium condition when a small number of very tiny hydrate crystals in the cell remain stable for an extended period of time [(5 to 6) h]. The temperature in the cell was increased by 0.1 K to confirm that all hydrates decomposed. A different concentration solution of TBAB was subsequently selected, and the procedure was repeated to obtain the other hydrate equilibrium data.

Results and Discussion

The batch, isochoric procedure was used to determine the hydrate phase equilibrium conditions of aqueous TBAB solution. The experimental hydrate equilibrium conditions were tabulated in Table 2. The data were also plotted in Figure 2.

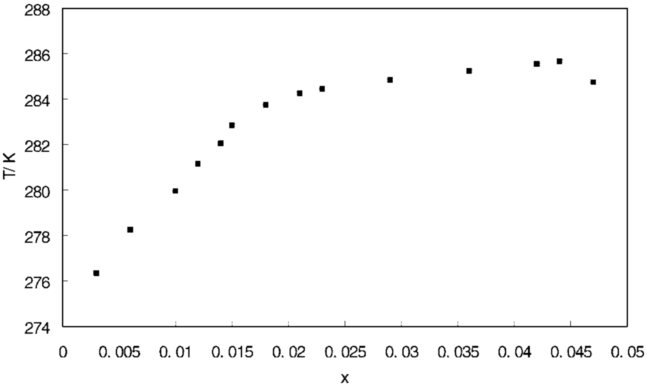

Figure 2. Hydrate phase equilibrium conditions ($T - x$) of aqueous TBAB solutions.

Figure 2 shows hydrate equilibrium conditions for TBAB solution mole fraction from 0.003 to 0.047. The temperature of hydrate equilibrium conditions increased with the increase of TBAB solution mole fraction when TBAB solution mole fraction was less than 0.044. When the TBAB solution mole fraction reached about 0.014, the temperature increment of hydrate equilibrium conditions decreased. Some researchers have pointed out that the pure TBAB hydrate has structural phase transition points. The structural phase transition points depend on the concentration.[16,19,20] The inflection point at the mole fraction of 0.014 may be the structural transition point of the TBAB hydrate. The maximum dissociation temperature of TBAB hydrate was about at 285.65 K when the mole fraction of TBAB solution was about 0.044. It is different from the data where the maximum equilibrium temperature is 285.35 K when the mole fraction of TBAB solution is about 0.037.[16] When the TBAB mole fraction reached 0.010, the temperature of hydrate equilibrium conditions was about 279.95 K (6.6 °C). The temperature is coincident with the temperature of chilled water of the air-conditioning system (input and output temperatures of chilled water are 12 °C and 7 °C in China, respectively). The experimental results show that the phase change temperature of TBAB solution is easily fit for the chilled water temperature of air-conditioning system by adjusting the mole fraction of TBAB solution.

Conclusions

One hydrate former, i.e., TBAB, which is soluble in water, has been studied in this work. The hydrate equilibrium data are obtained in the mole fraction from 0.003 to 0.047 and the temperature range (276.35 to 285.65) K. The experimental results show that the temperature of hydrate formation conditions increases with the increase of the TBAB solution mole fraction when the mole fraction of TBAB aqueous solution is less than 0.044, but the increment of temperature decreases when the TBAB solution mole fraction exceeds 0.014. The maximum equilibrium temperature of TBAB hydrate was about 285.65 K at a TBAB aqueous solution mole fraction of 0.044.

Literature Cited

(1) Sloan, E. D., Jr. *Clathrate Hydrate of Natural Gases*; Marcel Dekker Inc.: New York, 1998.
(2) Makogon, Y. F. *Hydrates of Hydrocarbons*; PennWell Publishing Company: OK, 1997.
(3) Patwardhan, V. S.; Kumar, A. A unified approach for prediction of thermodynamic properties of aqueous mixed - electrolyte solutions. *AIChE J.* **1986**, *32*, 1419–1428.
(4) Pitzer, K. S.; Mayorga, G. Thermodynamics of electrolytes. II. Activity and osmotic coefficients for strong electrolytes with one or both ions univalent. *J. Phys. Chem.* **1973**, *77*, 2300–2308.
(5) Stokes, R. H.; Robinson, R. A. Thermodynamic relation between activity coefficients of hydrated and unhydrated solute. *J. Phys. Chem.* **1957**, *61*, 1132.
(6) Sun, Z. G.; Fan, S. S.; Shi, L.; Guo, Y. K.; Guo, K. H. 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.
(7) Lee, D. J.; Englezos, P. Unusual kinetic inhibitor effects on gas hydrate formation. *Chem. Eng. Sci.* **2006**, *61*, 1368–1376.
(8) Sun, Z. G.; Ma, R. S.; Wang, R. Z.; Guo, K. H.; Fan, S. S. Experimental studying of additives effects on gas storage in hydrates. *Energy Fuels* **2003**, *17*, 1180–1185.
(9) Zhong, Y.; Rogers, R. E. Surfactant effects on gas hydrate formation. *Chem. Eng. Sci.* **2000**, *55*, 4175–4187.
(10) Liang, D. Q.; Guo, K. H.; Wang, R. Z.; Fan, S. S. Hydrate equilibrium data of 1,1,1,2-tetrafluoroethane (HFC-134a), 1,2-dichloro-1-fluoroethane (HCFC-141b) and 1,1-difluoroethane (HFC-152a). *Fluid Phase Equilib.* **2001**, *187–188*, 61–70.
(11) Watanabe, K.; Imai, S.; Mori, Y. H. Surfactant effects on hydrate formation in an unstirred gas/liquid system: An experimental study using HFC-32 and sodium dodecyl sulfate. *Chem. Eng. Sci.* **2005**, *60*, 4846–4857.

(12) Li, J. P.; Guo, K. H.; Liang, D. Q.; Wang, R. Z. Experiments on fast nucleation and growth of HCFC141b gas hydrate in static water columns. *Int. J. Refrig.* **2004**, *27*, 932–939.

(13) Shimada, W.; Wbinuma, T.; Oyama, H.; Takeya, S.; Uchida, T.; Nagao, J.; Narita, H. Growth mechanism of semiclathrate-hydrate single crystals. *Proceedings of the Forth International Conference on Gas Hydrates*, Yokohama, Japan, May 19−23, 2002; pp 57−560.

(14) Aladko, L. S.; Dyadin, Y. A. Clathrate hydrates of tetrabutylammonium dicarboxylates system tetrabutylammonium adipate-water. *Russian J. Gen. Chem.* **2004**, *74*, 214–216.

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

(16) Hashimoto, S.; Sugahara, T.; Moritoki, M.; Sato, H.; Ohgaki, K. Thermodynamic stability of hydrogen + tetra-n-butyl ammonium bromide mixed gas hydrate in nonstoichiometric aqueous solutions. *Chem. Eng. Sci.* **2008**, *63*, 1092–1097.

(17) Østergaard, K. K.; Tohidi, B.; Anderson, R.; Todd, A. C.; Danesh, A. Can 2-propanol from clathrate hydrates. *Ind. Eng. Chem. Res.* **2002**, *41*, 2064–2068.

(18) Ohmura, R.; Takeya, S.; Uchida, T.; Ebinuma, T. Clathrate hydrate formed with methane and 2-propanol: confirmation of structure II hydrate formation. *Ind. Eng. Chem. Res.* **2004**, *43*, 4964–4966.

(19) Aladko, L. S.; Dyadin, Y. A.; Rodionova, T. V.; Terekhova, I. S. Clathrate hydrates of tetrabutylammonium and tetraisoamylammonium halides. *J. Struct. Chem.* **2002**, *43*, 990–994.

(20) Oyama, H.; Shimada, W.; Ebinuma, T.; Kamata, Y.; Takeya, S.; Uchida, T.; Nagao, J.; Narita, H. Phase diagram, latent heat, and specific heat of TBAB semiclathrate hydrate crystals. *Fluid Phase Equilib.* **2005**, *234*, 131–135.

Received for review April 20, 2008. Accepted July 26, 2008. This work was supported by the Higher College Doctoral Subject Foundation of China (20070558059) and the Guangdong Province Natural Science Foundation of China (05300535).

JE8005612