Phase Equilibria of Semi-Clathrate Hydrates of Tetra-*n*-butylammonium Bromide + Hydrogen Sulfide and Tetra-*n*-butylammonium Bromide + Methane

Amir H. Mohammadi* and Dominique Richon

MINES ParisTech, CEP/TEP - Centre Énergétique et Procédés, 35 Rue Saint Honoré, 77305 Fontainebleau, France

---

In this work, experimental dissociation data for semi-clathrate hydrates of tetra-*n*-butylammonium bromide + hydrogen sulfide and tetra-*n*-butylammonium bromide + methane are reported in the temperature range of (290.9 to 295.7) K and (283.6 to 290.1) K, respectively at 0.05 mass fraction of tetra-*n*-butylammonium bromide in aqueous solution. The experimental data were generated using an isochoric pressure-search method. The hydrate dissociation data for the tetra-*n*-butylammonium bromide + methane system are compared with the corresponding experimental data reported in the literature, and the acceptable agreement demonstrates the reliability of the experimental method used in this work. The experimental data for both measured systems are finally compared with the corresponding experimental data in the absence of tetra-*n*-butylammonium bromide reported in the literature to study its hydrate promotion effect.

Introduction

Tetra-*n*-butylammonium bromide (TBAB) is a semi-clathrate hydrate former, which can be used as promoter in gas separation, storage, and transportation processes using hydrate technology. Unlike clathrate hydrates where water molecules form hydrate cages and small guest molecules like methane are trapped inside cages, in TBAB semi-clathrate hydrates, bromide forms cage structures with water molecules, and the tetra-*n*-butylammonium cation occupies four cages.[1,2] Like clathrate hydrates, TBAB semi-clathrate hydrates can engage small guest molecules.

Most of the equilibrium data for TBAB semi-clathrate hydrates have been reported for the TBAB + methane,[3,4] TBAB + carbon dioxide,[3,5,6] TBAB + hydrogen,[3] and TBAB + nitrogen.[3,6] To our knowledge, there is no equilibrium data for semi-clathrate hydrates of TBAB + hydrogen sulfide. On the other hand, no thermodynamic model or correlation has been developed to predict hydrate phase equilibria of TBAB containing systems.

The main aim of this communication is to report equilibrium data for semi-clathrate hydrates of TBAB + hydrogen sulfide at 0.05 mass fraction of TBAB in aqueous solution. The experimental dissociation data were generated using an isochoric pressure-search method.[7−10] As sufficient experimental dissociation data for the TBAB + methane semi-clathrate hydrates have been reported in the literature,[3,4] we first measured and report some experimental dissociation data for the latter system and compare them with the corresponding literature data to demonstrate the reliability of the experimental method used in our work. Then, we report dissociation data for the TBAB + hydrogen sulfide semi-clathrate hydrates, for which there is no experimental data in the literature. For both measured systems, the experimental dissociation data are compared with the corresponding literature data in the absence of TBAB to identify hydrate promotion effect of TBAB aqueous solution.

Experimental Section

Chemicals. Table 1 reports the purities and suppliers of the chemicals used in this work.

Table 1. Purities and Suppliers of Chemicals[a]

chemical	supplier	purity
hydrogen sulfide	Air Liquide	99.9 (volume %)
methane	Messer Griesheim	99.995 (volume %)
tetra-*n*-butylammonium bromide	Sigma-Aldrich	50 mass % aqueous solution

[a] Deionized water was used in all experiments.

Experimental Apparatus.[7−9] Briefly, the main part of the apparatus is a sapphire cylindrical vessel, which can withstand pressures higher than 10 MPa. The volume of the vessel is 33.1 cm^3. A stirrer was installed in the vessel to agitate the fluids and hydrate crystals inside it. The stirrer and all metallic parts of the apparatus (flanges, etc.) were made of stainless steel. Two platinum resistance thermometers (Pt100) inserted into the vessel were used to measure temperatures and check for equality of temperatures within temperature measurement uncertainties, which is estimated to be less than 0.1 K. This temperature uncertainty estimation comes from calibration against a 25 Ω reference platinum resistance thermometer. The pressure in the vessel was measured with two Druck pressure transducers (Druck, type PTX611 for pressure ranges up to (2.5 and 12) MPa, respectively). Pressure measurement uncertainties are estimated to be less than 5 kPa, as a result of calibration against a dead weight balance (Desgranges and Huot, model 520).

Experimental Method.[7−9] The dissociation conditions were measured with an isochoric pressure-search method.[7−10] The vessel containing aqueous solution (approximately 10 % by volume of the vessel was filled with aqueous solution) was immersed into the temperature-controlled bath, and the gas was supplied from the cylinder through a pressure-regulating valve into the vessel. Note that the vessel was evacuated before introducing any aqueous solution and gas. After obtaining temperature and pressure stability (far enough from the hydrate formation region), the valve in the line connecting the vessel and the cylinder was closed. Subsequently, temperature was slowly decreased to form the hydrate. Hydrate formation in the vessel was detected by pressure drop. The temperature was then increased with steps of 0.1 K. At every temperature step, the

---

* Corresponding author. E-mail: amir-hossein.mohammadi@ensmp.fr. Tel.: +(33) 1 64 69 49 70. Fax: +(33) 1 64 69 49 68.

10.1021/je9004257 CCC: $40.75

Table 2. Experimental Dissociation Conditions of the TBAB + Methane and TBAB + Hydrogen Sulfide Semi-Clathrate Hydrates[a]

T[b]	p[c]
K	MPa
TBAB + Methane Semi-Clathrate Hydrates	
283.6	1.31
284.7	1.94
285.9	2.93
286.4	3.46
287.3	4.60
288.0	5.87
288.5	6.92
289.1	8.33
289.7	9.92
290.1	11.08
TBAB + Hydrogen Sulfide Semi-Clathrate Hydrates	
290.9	0.17
291.3	0.19
292.0	0.24
292.1	0.27
293.3	0.33
293.9	0.40
294.6	0.49
295.1	0.58
295.3	0.63
295.7	0.68

[a] Concentration of TBAB in aqueous solution is equal to 0.05 mass fraction. [b] Uncertainty on temperatures through calibrated platinum resistance thermometers is estimated to be less than 0.1 K. [c] Uncertainty on pressures through calibrated pressure transducers is estimated to be less than 5 kPa.

temperature was kept constant for 4 h to achieve an equilibrium state in the vessel. In this way, a pressure−temperature diagram was obtained for each experimental run, from which we determined the hydrate dissociation point.[7−9,11] If the temperature is increased in the hydrate-forming region, hydrate crystals partially dissociate, thereby substantially increasing the pressure. If the temperature is increased outside the hydrate region, only a smaller increase in the pressure is observed as a result of the change in the phase equilibria of the fluids in the vessel.[7−9,11] Consequently, the point at which the slope of pressure−temperature data plots changes sharply is considered to be the point at which all hydrate crystals have dissociated and hence reported as the dissociation point.[7−9,11]

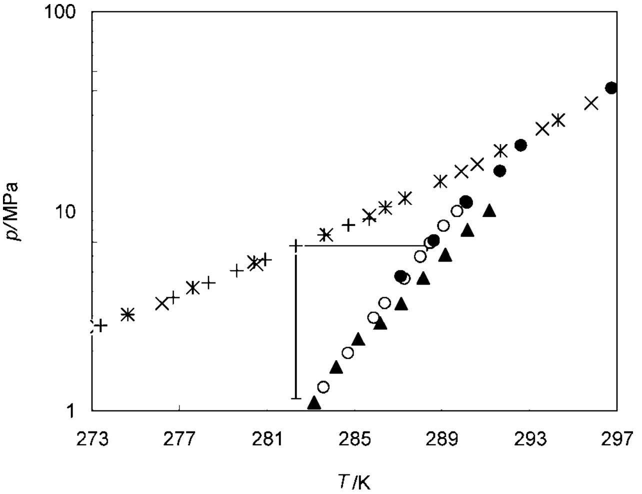

Figure 1. Experimental hydrate dissociation conditions for the methane + TBAB + water and methane + water systems. Symbols represent experimental data. Methane + water system: ×, ref 12; +, ref 13; *, ref 14. Methane + TBAB (0.05 mass fraction) + water system: ○, this work; ●, ref 3; ▲, ref 4. Pressure band: 5.5 MPa. Temperature band: 6 K.

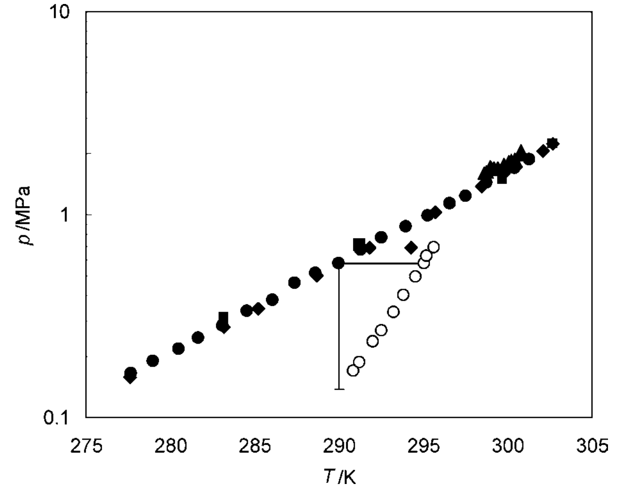

Figure 2. Experimental hydrate dissociation conditions for the hydrogen sulfide + TBAB + water and hydrogen sulfide + water systems. Symbols represent experimental data. Hydrogen sulfide + water system: ■, ref 18; ◆, ref 17; ▲, ref 16; ●, ref 15. Hydrogen sulfide + TBAB (0.05 mass fraction) + water system: ○, this work. Pressure band: 0.44 MPa. Temperature band: 5 K.

Experimental Results

All of the experimental data are reported in Table 2 and are plotted in Figures 1 and 2.

As mentioned earlier, we first measured the dissociation conditions of the TBAB + methane semi-clathrate hydrates at 0.05 mass fraction of TBAB in aqueous solution. As can be observed in Figure 1, the experimental data measured in this work for the latter system are in good agreement with the experimental data reported in ref 3 demonstrating the reliability of the experimental method[7−10] used in this work. The experimental data reported in ref 4, however, show some deviations at high temperatures. It should be mentioned that the addition of very high concentrations of TBAB in the aqueous solution can diminish its pressure-reducing effect, while small concentrations relative to water lower the equilibrium pressure at a given temperature significantly.[3−6]

In Figures 1 and 2, we have shown some selected experimental data from the literature for the methane + water[12−14] and hydrogen sulfide + water systems,[15−18] respectively, to study the hydrate promotion effect of TBAB aqueous solution. It should be mentioned that hydrate promotion effect means shifting dissociation conditions of methane or hydrogen sulfide hydrates due to the presence of TBAB in the system to low pressures or high temperatures.[19] As can be seen in Figure 1, the presence of 0.05 mass fraction of TBAB in aqueous solution can increase the hydrate dissociation temperature of the methane + water system at given pressures in the temperature ranges shown in this figure. However, this value depends on pressure and can vary for this system. In this figure, the decrease in hydrate dissociation pressure of the methane + water system due to the presence of 0.05 mass fraction of TBAB in aqueous solution is strong function of temperature. In Figure 2, it can be observed that the presence of 0.05 mass fraction of TBAB in aqueous solution can reduce the hydrate dissociation pressure of the hydrogen sulfide + water system at given temperatures. Again, this value depends on temperature and can vary. Similarly, it can increase the hydrate dissociation temperature at given pressures, and again, this value depends on pressure and can vary. This hydrate promotion effect has not been reported for the hydrogen sulfide + TBAB + water system and can be regarded in acid gas capture and sequestration studies by gas hydrate technology.

Conclusions

We reported experimental dissociation data for semi-clathrate hydrates of TBAB + methane and TBAB + hydrogen sulfide at 0.05 mass fraction of TBAB in aqueous solution (Table 2). An isochoric pressure-search method[7−10] was used to perform all of the measurements. The measurements were first performed for the TBAB + methane semi-clathrate hydrates, and the comparisons between the experimental data measured in this work and the experimental data reported in ref 3 showed acceptable agreement confirming the reliability of the isochoric pressure-search method[7−10] used in this work. The experimental data reported in ref 4 for the latter system, however, showed some deviations at high temperatures. We then reported novel experimental dissociation data for the TBAB + hydrogen sulfide semi-clathrate hydrates, for which there is no equilibrium data in the literature. The comparison of the dissociation data for both measured systems with the corresponding literature data in the absence of TBAB showed significant promotion effect of 0.05 mass fraction of TBAB aqueous solution (Figures 1 and 2).

Literature Cited

(1) Davidson, D. W. *Water - A Comprehensive Treatise*; Franks, F., Ed.; Plenum Press: New York and London, 1973; Vol. 2, pp 115−234.

(2) Shimada, W.; Shiro, M.; Kondo, H.; Takeya, S.; Oyama, H.; Ebinuma, T.; Narita, H. Tetra-n-butylammonium bromide - Water. *Acta Crystallogr., Sect. C* **2005**, *61*, 65–66.

(3) Arjmandi, M.; Chapoy, A.; Tohidi, B. Equilibrium Data of Hydrogen, Methane, Nitrogen, Carbon Dioxide, and Natural Gas in Semi-Clathrate Hydrates of Tetra-n-butylammonium bromide. *J. Chem. Eng. Data* **2007**, *52*, 2153–2158.

(4) Li, D. L.; Du, J. W.; Fan, S. S.; Liang, D. Q.; Li, X. S.; Huang, N. S. Clathrate Dissociation Conditions for Methane + Tetra-n-butyl Ammonium Bromide (TBAB) + Water. *J. Chem. Eng. Data* **2007**, *52*, 1916–1918.

(5) Lin, W.; Delahaye, A.; Fournaison, L. Phase equilibrium and dissociation enthalpy for semi-clathrate hydrate of CO_2 + TBAB. *Fluid Phase Equilib.* **2008**, *264*, 220–227.

(6) Duc, N. H.; Chauvy, F.; Herri, J. M. CO_2 capture by hydrate crystallization - A potential solution for gas emission of steelmaking industry. *Energy Convers. Manage.* **2007**, *48*, 1313–1322.

(7) Mohammadi, A. H.; Richon, D. Phase Equilibria of Clathrate Hydrates of Cyclopentane + Hydrogen Sulfide and Cyclopentane + Methane. *Ind. Eng. Chem. Res.* **2009**, submitted.

(8) Mohammadi, A. H.; Richon, D. Clathrate Hydrates of Cyclohexane + Hydrogen Sulfide and Cyclohexane + Methane: Experimental Measurements of Dissociation Conditions. *J. Chem. Eng. Data* **2009**, submitted.

(9) Mohammadi, A. H.; Richon, D. Equilibrium Data of Methyl Cyclohexane + Hydrogen Sulfide and Methyl Cyclohexane + Methane Clathrate Hydrates. *J. Chem. Eng. Data* **2009**, accepted.

(10) 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.

(11) 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.

(12) Mohammadi, A. H.; Anderson, R.; Tohidi, B. Carbon Monoxide Clathrate Hydrates: Equilibrium Data and Thermodynamic Modeling. *AIChE J.* **2005**, *51*, 2825–2833, quoted in ref 19.

(13) Adisasmito, S.; Frank, R. J.; Sloan, E. D. Hydrates of carbon dioxide and methane mixtures. *J. Chem. Eng. Data* **1991**, *36*, 68–71, quoted in ref 19.

(14) Jhaveri, J.; Robinson, D. B. Hydrates in the methane-nitrogen system. *Can. J. Chem. Eng.* **1965**, *43*, 75–78, quoted in ref 19.

(15) Mohammadi, A. H.; Richon, D. Equilibrium Data of Carbonyl Sulfide and Hydrogen Sulfide Clathrate Hydrates. *J. Chem. Eng. Data* **2009**, in press.

(16) Carroll, J. J.; Mather, A. E. Phase Equilibrium in the System Water-Hydrogen Sulphide: Hydrate-Forming Conditions. *Can. J. Chem. Eng.* **1991**, *69*, 1206–1212, quoted in ref 19.

(17) Selleck, F. T.; Carmichael, L. T.; Sage, B. H. Phase Behavior in the Hydrogen Sulfide-Water System. *Ind. Eng. Chem.* **1952**, *44*, 2219–2226, quoted in ref 19.

(18) Bond, D. C.; Russell, N. B. Effect of Antifreeze Agents on the Formation of Hydrogen Sulfide Hydrate. *Pet. Trans. AIME* **1949**, *179*, 192, quoted in ref 19.

(19) Sloan, E. D.; Koh, C. A. *Clathrate Hydrates of Natural Gases*, 3rd ed.; CRC Press, Taylor & Francis Group: Boca Raton, FL, 2008.

Received for review May 14, 2009. Accepted July 21, 2009. The financial support of Agence Nationale de la Recherche (ANR) is gratefully acknowledged.

JE9004257