Experimental Measurements of the Thermodynamic Equilibrium Conditions of Tetra-*n*-butylammonium Bromide Semiclathrates Formed from Synthetic Landfill Gases

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An isochoric equilibrium cell was used for measuring the solid−vapor−liquid equilibrium conditions of semiclathrates formed in an aqueous solution of tetra-*n*-butylammonium bromide (TBAB). The semiclathrates were formed from two different synthetic landfill gas (LFG) mixtures of CO_2 (1) + CH_4 (2), which had mole fractions of $x_1 = 0.4$ and $x_1 = 0.6$. The experimental temperature, pressure, and mass fraction of TBAB ranged from (286 to 293) K, from (3 to 6.5) MPa, and from (0.05 to 0.20), respectively. For both of the gases used in the present study, it was found that, at a given temperature, the pressure required to form semiclathrates is significantly lower than that required for forming gas hydrates from the same gases.

Introduction

The gas generated from the anaerobic decomposition of organic wastes in a landfill site is known as landfill gas (LFG). The major components of a LFG stream are methane (CH_4) and carbon dioxide (CO_2), both of which are potent greenhouse gases (GHG). Trace amounts of other components such as mercaptans may also be present in the LFG stream, which can create odors, degrade the air quality, and cause adverse health effects.[1] The LFG composition varies depending on the type of material deposited in the landfill site, landfill site age, and atmospheric conditions. This variation of LFG composition can be seen in Table 1, which presents the LFG compositions from Montreal and New York.

Once in the atmosphere, methane absorbs terrestrial infrared radiation that would otherwise escape to space; this property can contribute to the warming of the atmosphere. Furthermore, methane remains in the atmosphere for approximately (9 to 15) years, and it is over 20 times more effective in trapping heat in the atmosphere than carbon dioxide over a 100 year period.[4] Rather than being released directly into the atmosphere, if the methane in the LFG is separated from the carbon dioxide and the other constituents, it can instead be burned for onsite heat and power generation or, alternatively, sold.

Several separation technologies have been proposed to separate the CO_2 and CH_4 emissions from landfills, including gas adsorption, gas absorption, and membrane separation. As an alternative to the aforementioned methods for gas purification, several groups have proposed using gas hydrates to selectively remove components from a gas mixture.[5−7] While this technique can be highly selective, the primary challenge with this proposed technology is the high energy consumption, since elevated pressure and low temperature operations are required.

Similar to gas hydrates, semiclathrates formed in aqueous tetra-*n*-butylammonium bromide (TBAB) can be used selectively trap gas molecules. However, semiclathrates typically form at pressures much lower than those required for gas hydrate formation. Semiclathrates of tetrabutylammonium (TBA) and tetraisopentylammonium (TIPA) quaternary ammonium salts were discovered in the 1940s.[8] Since that time, other semiclathrates have been discovered and structurally analyzed by crystal X-ray crystallography such as those of trialkylsulfonium salts, tetraalkylphosphonium, and trialkylphosphine oxides.[9] In these crystal structures, unlike gas hydrates, some of the water lattice sites are replaced by the anion, whereas the alkyl chain (cation) occupies a large cage, which may be either a $5^{12}6^2$, $5^{12}6^3$, or $5^{12}6^4$ cages.[10−13] Small unoccupied 5^{12} cages are interspaced between some of the large cages. In a TBAB semiclathrate the Br^- is incorporated into the crystal lattice, whereas the $C_{16}H_{36}N^+$ occupies large cages (in this structure two $5^{12}6^2$ and two $5^{12}6^3$ cages). The smaller 5^{12} cages are filled with spheres to indicate that they could be filled with small molecules such as CH_4 and CO_2.

While semiclathrates have been known in the scientific community since the 1940s, it is only in the past decade that they have begun to garner attention for their potential applications in gas storage and separation. Thus, there is only a limited amount of thermodynamic data currently available in the open literature. It has been observed[14] that, at atmospheric pressure, TBAB semiclathrates could form at temperatures as high as 12 °C and that under these conditions, there were two distinct crystal types that would form. Two independent groups[15,16] measured the equilibrium conditions for TBAB semiclathrates formed from CO_2, N_2,and their mixtures for possible applications in removing CO_2 from flue gas. A recent study[17] presented equilibrium data for the formation of semiclathrates from CH_4, H_2, N_2, CO_2, and a natural gas mixture, in the presence of (0.05, 0.10, and 0.43) w_{TBAB} aqueous solutions, and concluded that

Table 1. Landfill Gas Composition in New York and Montreal

component	Montreal[2] x	New York City[3] x
CH_4	0.5563	0.5328
CO_2	0.3714	0.4559
O_2	0.0099	0.0007
H_2		0.00056
other	0.0624	0.01004

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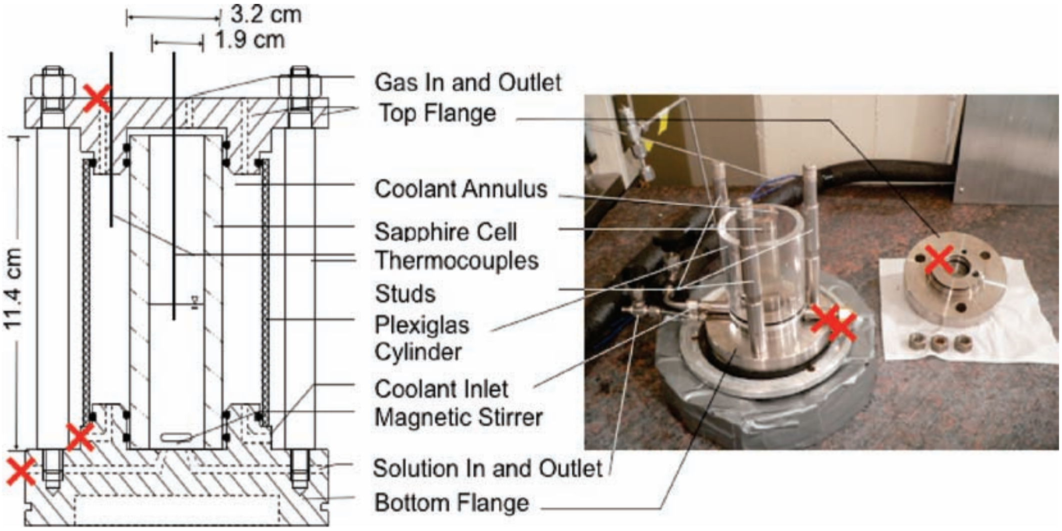

Figure 1. Schematic drawing and picture of equilibrium cell.

the hydration number of the resulting structures decreases as the TBAB mass fraction was increased. On the basis of the experimental evidence, they affirmed that methane molecules are trapped in the TBAB semiclathrate and that the formation pressure reduces when using more concentrated TBAB solutions. Japanese researchers[18] also investigated the potential use of semiclathrates for separation of the mixtures of $CH_4 + C_2H_6$, $CH_4 + C_3H_8$, $CH_4 + H_2S$, and $CO_2 + H_2S$. Deschamps and Dalmazzone[19] used differential scanning calorimetry to measure the incipient equilibrium conditions for the formation of semiclathrates from N_2, CO_2, CH_4, and their mixtures in the presence of $w_{TBAB} = 0.40$ aqueous solution. It should be noted that Deschamps and Dalmazzone[19] only performed experiments with an equimolar mixture of $CH_4 + CO_2$ in a $w_{TBAB} = 0.40$ aqueous solution and that they did not include any measurements of the gas phase composition.

In the current study, three-phase equilibrium data are obtained for two synthetic LFG mixtures of CO_2 (1) + CH_4 (2) with $x_1 = 0.4$ and 0.6, in the presence of (0.05, 0.10, and 0.20) w_{TBAB} aqueous solutions using an isochoric equilibrium cell. While it is recognized that a real LFG will also contain trace amounts of H_2S, which itself forms semiclathrates, the aim of this paper is to expand the amount of data that is available for the binary system of CO_2 and CH_4. Thus, ternary systems containing H_2S were not included in this study. The gas phase composition at the equilibrium point is also measured. Finally, while LFG treatment has been suggested as a possible application for the data obtained from the present study, it should also be noted that the data obtained in the present study may also potentially have applications in removing CO_2 from natural gas.

Experimental Apparatus, Materials, and Procedure

Apparatus. The apparatus that was used for the current study has been used by several groups at the University of Calgary.[20,21] However, for the current study, modifications were made to the apparatus to allow for the direct sampling of the gas phase. Briefly, the equilibrium cell itself is a sapphire tube with an inner diameter of 19.05 mm, an outer diameter of 31.75 mm, and a length of 114.3 mm, and it is placed concentrically inside Plexiglas cylinder. The sapphire tube was made of optical clarity using a random crystal orientation and was designed for working pressures up to 20 MPa at a temperature range of (250 to 400) K. All surfaces of the sapphire tube are polished to an 80/50 finish, considered a standard optical polish. A magnetic stir bar is placed inside the sapphire tube to ensure an intensive agitation. Both cylinders are held on the top and bottom by stainless steel flanges. To sample the gas phase, a withdrawal line was added to the flange. A stainless steel sampling chamber, whose internal volume is approximately 1 cm^3, was used to capture the gas phase sample. Figure 1 shows a mechanical drawing of the isochoric equilibrium cell and a picture with the main parts of the equilibrium cell assembly.

The space between the sapphire tube and the outer plexiglas tube is filled with an aqueous solution of ethylene glycol, which is circulated from a programmable temperature controller (Refrigerated Circulator unit, model 1167P distributed by VWR), to the reactor and back. The ethylene glycol solution flows at a constant volumetric flow rate and works as the coolant and heating media flowing in a continuous loop between the equilibrium cell assembly and the external programmable temperature controller. The entire assembly is insulated with fiber glass to minimize heat transfer from the surroundings. The equipment to measure pressure and temperature as well as the data acquisition hardware is the same as was used in a previous study.[21] The uncertainty in the temperature measurement is ± 0.5 K, and that of the pressure measurement is ± 27 kPa. Finally, an SRI 8610 gas chromatograph, having a thermal conductivity detector (TCD), was used to analyze the gas phase at the equilibrium point. The uncertainty in the measurement of the gas phase composition was ± 1.0 %.

Materials and Procedure. As noted earlier, the LFG composition varies depending on the material deposited in the landfill site, landfill age, and atmospheric conditions. The two synthetic LFG mixtures were supplied by Praxair Technology, Inc., and their composition was chosen to cover the range of CO_2 (1) and CH_4 (2) compositions in North American LFGs; one mixture was $x_1 = 0.6$, with a supplier's reported uncertainty in composition of ± 0.8 %, and the other was $x_1 = 0.40$, with a supplier's reported uncertainty in composition of ± 1.0 %. A $w_{TBAB} = 0.50$ aqueous solution, analytical grade, was purchased from Aldrich. This solution was used with deionized water (Millipore Simplicity water purification system, which produces ultrapure water with a resistivity of 18.2 MΩ at 298 K) to prepare aqueous solutions of (0.05, 0.10, and 0.20) w_{TBAB}.

The procedure that was used for the current study was almost identical to that used in previous studies,[20,22] except for an additional step that was required for sampling the gas phase. To briefly recap, this procedure involves cooling the reactor, at

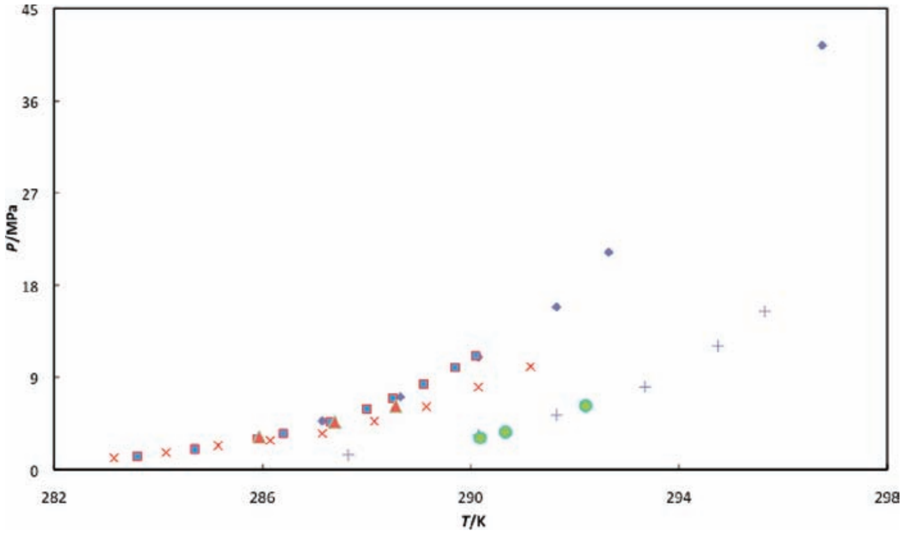

Figure 2. Comparison of incipient equilibrium formation conditions for semiclathrates of CH_4 formed in the presence of TBAB aqueous solutions. ◆, $w = 0.05$, Arjmandi et al.;[17] ■, $w = 0.05$, Mohammadi and Richon;[25] ⊥, $w = 0.05$, Li et al.;[24] ▲, $w = 0.05$, current study; +, $w = 0.20$, Arjmandi et al.;[17] ●, $w = 0.20$, current study.

a controlled rate, until hydrates form. After hydrates have formed, the system is slowly heated ($+0.1\ \text{K}\cdot\text{h}^{-1}$) until the temperature and pressure return to a value near the initial conditions. In an isochoric experiment, the equilibrium point is found as the pinch point in the heating curve.[23] Since the data acquisition program was written to directly display temperature versus pressure, the pinch point in the heating curve can be directly observed on the data acquisition computer's display. Once a change in the slope of the pressure versus temperature curve, as displayed by the data acquisition program, is observed, the sampling line is flushed with helium, and a gas phase sample is subsequently collected and then analyzed with the gas chromatograph.

Results and Discussion

Validation of Apparatus. Previous research studies[21] demonstrated that the equipment used in this research is able to accurately measure the incipient equilibrium conditions for the formation of gas hydrates. However, this was the first occasion that the apparatus was used to measure the equilibrium conditions for the formation of semiclathrates. Therefore, an initial study was carried out to establish the experimental methodology for semiclathrate. In particular, the appropriate heating rate needed to be established. Experiments were conducted to form TBAB semiclathrates with methane, and through a process of trial and error, it was found that a heating rate of $0.2\ \text{K}\cdot\text{h}^{-1}$ was the highest heating rate for which one could observe a clearly defined equilibrium point. Experiments were performed in duplicate, and it was found that they were reproducible to within a 95 % confidence interval. Figure 2 shows the results of this section, in which the data from the current study is compared to that which is already in the literature. From Figure 2, it is clear that the apparatus and procedure produce reliable results.

Experimental Results and Discussion. The incipient equilibrium conditions for the formation of semiclathrates from two mixtures of CO_2 (1) + CH_4 (2) in the presence of (0.05, 0.10, and 0.20) w_{TBAB} are reported herein as well as the gas phase composition at the equilibrium points. Tables 2 and 3 list the incipient equilibrium conditions of the formation of semiclathrates from gas mixtures made of $x_1 = 0.40$ and $x_1 = 0.60$, respectively. Figures 3 and 4 are the corresponding plots of the data. It should be noted that experiments at $w_{\text{TBAB}} = 0.40$ were attempted but were not considered successful because it was not possible, in those cases, to observe a well-defined equilibrium point in the $P-T$ trajectory. Also, at $w_{\text{TBAB}} = 0.40$, the magnetic stirrer was insufficient to agitate the more viscous solution.

From Figures 3 and 4 it can be seen that, for both gas mixtures, increasing the TBAB concentration decreases the required pressure for semiclathrate formation, at a given temperature. Also, a comparison of the two figures shows that,

Table 2. Three-Phase Solid−Liquid−Vapor Equilibrium Conditions for TBAB Semiclathrates Formed in the Presence of CO_2(1) + CH_4 (2) $x_1 = 0.40$ Gas Mixture (Cylinder Composition)

w_{TBAB}	T/K (± 0.5 K)	P/MPa	x_1
0.05	288.83	6.325	0.3438
	288.47	5.661	0.3334
	287.93	4.893	0.3455
	287.03	3.752	0.3395
	286.26	3.104	0.3423
0.10	291.02	6.370	0.3392
	290.64	5.741	0.3497
	289.74	4.672	0.3382
	288.96	3.925	0.3359
	288.14	3.011	0.3518
0.20	292.59	6.229	0.3502
	291.69	4.846	0.3624
	290.85	3.857	0.3565
	289.84	2.972	0.3435

Table 3. Three-Phase Solid−Liquid−Vapor Equilibrium Conditions for TBAB Semiclathrates Formed in the Presence of CO_2(1) + CH_4 (2) $x_1 = 0.60$ Gas Mixture (Cylinder Composition)

w_{TBAB}	T/K (± 0.5 K)	P/MPa	x_1
0.05	289.46	6.493	0.5441
	288.96	5.026	0.5211
	288.44	4.498	0.5245
	287.47	3.669	0.5289
	286.73	2.866	0.5336
0.10	291.41	6.54	0.5471
	290.47	4.974	0.5466
	289.36	3.775	0.5468
	288.51	2.828	0.5474
0.20	293.00	6.407	0.5452
	292.51	5.471	0.5453
	292.02	4.477	0.5461
	291.32	3.626	0.5464
	290.39	2.972	0.5473

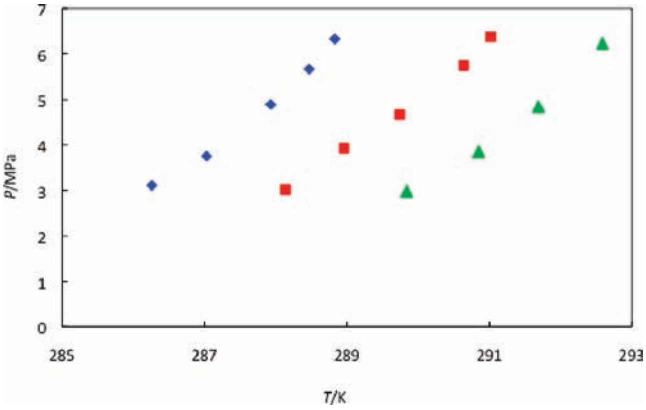

Figure 3. Incipient equilibrium formation conditions for semiclathrates formed from a gas mixture of CO_2 (1) + CH_4 (2) $x_1 = 0.40$ (cylinder composition) in the presence of TBAB aqueous solutions. ◆, $w_{TBAB} = 0.05$; ■, $w_{TBAB} = 0.10$; ▲, $w_{TBAB} = 0.20$.

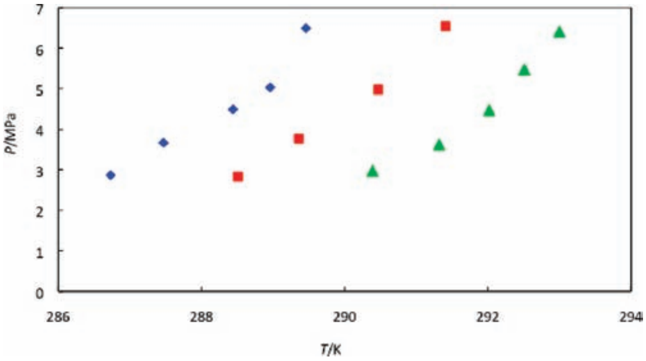

Figure 4. Incipient equilibrium formation conditions for semiclathrates formed from a gas mixture of CO_2 (1) + CH_4 (2) $x_1 = 0.60$ (cylinder composition) in the presence of TBAB aqueous solutions. ◆, $w_{TBAB} = 0.05$; ■, $w_{TBAB} = 0.10$; ▲, $w_{TBAB} = 0.20$.

for a constant mass fraction of TBAB and at a given temperature, increasing the mole fraction of methane in the feed gas will increase the pressure that is required for semiclathrate formation. Also, when the data from Figures 3 and 4 for the case of $w_{TBAB} = 0.20$ are compared to the data in Figure 2, it can be seen that the presence of CO_2 has reduced the pressure required to form semiclathrates at a given temperature. In Tables 2 and 3, it can be seen that the mole fraction of methane in the vapor phase is higher at equilibrium than compared to the cylinder composition. This is most likely a result of the high solubility of CO_2 in water.

At the time of writing, Deschamps and Dalmazzone[19] were the only others who had formed semiclathrates in an aqueous solution of TBAB from a mixture of CO_2 (1) + CH_4 (2). They reported the three-phase equilibrium conditions for the formation of semiclathrates from a $x_1 = 0.499$ gas mixture in the presence of $w_{TBAB} = 0.40$. However, their study did not include measurements of the vapor phase composition at equilibrium. Thus, a direct comparison of the present study's results with theirs is not possible.

Conclusions

Experiments were conducted in a isochoric equilibrium cell to measure the effect of TBAB concentration on the equilibrium conditions for semiclathrates formed from two synthetic LFG mixtures. Once an experimental procedure for forming and decomposing semiclathrates was established, experiments were conducted to form TBAB semiclathrates from two different mixtures of CO_2 (1) + CH_4 (2) with $x_1 =$ 0.4 and 0.6, in the presence of (0.05, 0.10, and 0.20) w_{TBAB} aqueous solutions, and at temperatures ranging from (286 to 293) K and pressures ranging from (3 to 6.5) MPa. It was found that, with both gas mixtures, the pressure required to form semiclathrates at a given temperature decreased as the TBAB concentration increased.

Literature Cited

(1) Farquhar, G. J.; Rovers, F. A. Gas Production During Refuse Decomposition. *Water, Air, Soil Pollut.* **1973**, *2*, 483–495.

(2) Eklund, B.; Anderson, E. P.; Walker, B. L.; Burrows, D. B. Characterization of Landfill Gas Composition at the Fresh Kills Municipal Solid-Waste Landfill. *Environ. Sci. Technol.* **1998**, *32*, 2233–2237.

(3) Brosseau, J.; Heitz, M. Trace Gas Compound Emissions From Municipal Landfill Sanitary Sites. *Atmos. Environ.* **1994**, *28*, 285–293.

(4) Methane. http://www.epa.gov/methane/scientific.html (accessed March 2010).

(5) Park, J.; Yu-Taek, S.; Jong-Won, L.; Huen, L. Spectroscopic analysis of carbon dioxide and nitrogen mixed gas hydrates in silica gel for CO_2 separation. *Catal. Today* **2006**, *115*, 279–282.

(6) Smirnov, L. F. New Technologies Using Gas Hydrates. *Theor. Found. Chem. Eng.* **1990**, *23*, 514–526.

(7) Dabrowski, N.; Windmeir, C.; Oellrich, L. Purification of Natural Gases With High CO_2 Content Using Gas Hydrates. *Energy Fuels* **2009**, *23*, 5603–5610.

(8) Fowler, D. L.; Loebenstein, W. V.; Pall, D. B.; Krauss, C. A. Some Unusual Hydrates of Quaternary Ammonium Salts. *J. Am. Chem. Soc.* **1940**, *62*, 1140–1142.

(9) Beurskens, G.; Jeffrey, G. A.; McMullan, R. K. Polyhedral Clathrate Hydrates VI: Lattice Type and Ion Distribution in Some New Peralkyl Ammoniun, Phosphonium and Sulfonium Salt Hydrates. *J. Chem. Phys.* **1963**, *39*, 3311–3315.

(10) McMullan, R. K.; Bonamico, M.; Jeffrey, G. A. Polyhedral Clathrate Hydrates XI: Structure of Tetramethylammonium Hydroxide Pentahydrate. *J. Chem. Phys.* **1963**, *39*, 3295–3310.

(11) McMullan, R. K.; Jeffrey, G. A. Polyhedral Clathrate Hydrates IX: Structure of Ethylene Oxide Hydrate. *J. Chem. Phys.* **1965**, *42*, 2725–2732.

(12) McMullan, R. K.; Mak, T. C. W.; Jeffrey, G. A. Polyhedral Clathrate Hydrates V: Structure of Tetra-*n*-butyl Ammonium Fluoride Hydrate. *J. Chem. Phys.* **1966**, *44*, 2338–2345.

(13) Shimada, W.; Shiro, M.; Kondo, H.; Takeya, S.; Oyama, H.; Ebinuma, T.; Narita, H. Tetra-*n*-butylammonium Bromide-Water (1/38). *Cryst. Struct. Commun.* **2005**, *61*, 65–66.

(14) Oyama, H.; Shimada, W.; Ebinuma, T.; Kamata, Y.; Takeya, S.; Nagao, J.; Narita, H. Phase Diagram, Latent Heat and Specific Heat of TBAB Semiclathrate Hydrate Crystals. *Fluid Phase Equilib.* **2005**, *234*, 131–135.

(15) 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.

(16) Fan, S.; Li, S.; Wang, J.; Lang, X.; Wang, Y. Efficient Capture of CO_2 from Simulated Flue Gas by Formation of TBAB or TBAF Semiclathrate Hydrates. *Energy Fuels* **2009**, *23*, 4202–4208.

(17) Arjmandi, M.; Chapoy, A.; Tohidi, B. Equilibrium Data of Hydrogen, Methane, Nitrogen, Carbon Dioxide and Natural Gas in Semi Clathrate Hydrates in Tetrabutyl Ammonium Bromide. *J. Chem. Eng. Data* **2007**, *52*, 2153–2158.

(18) Kamata, Y.; Yamakoshi, Y.; Ebinuma, T.; Oyama, H.; Shimada, W.; Narita, H. Hydrogen Sulfide Separation Using Tetra-*n*-butyl Ammonium Bromide Semi-clathrate (TBAB) Hydrate. *Energy Fuels* **2005**, *19*, 1717–1722.

(19) Deschamps, J.; Dalmazzone, D. Dissociation Enthalpies and Phase Equilibrium for TBAB Semi-clathrate Hydrates of N_2, CO_2, $N_2 + CO_2$ and $CH_4 + CO_2$. *J. Therm. Anal. Calorim.* **2009**, *98*, 113–118.

(20) Parent, J. S.; Bishnoi, P. R. Investigations into the nucleation behaviour of methane gas hydrates. *Chem. Eng. Commun.* **1996**, *144*, 51–64.

(21) Porz, L. O.; Clarke, M. A.; Oellrich, L. R. Experimental Investigation of Methane Hydrates Formation Condition in the Presence of KNO_3, $MgSO_4$ and $CuSO_4$. *J. Chem. Eng. Data* **2010**, *55*, 262–266.

(22) Schroeter, J. P.; Kobayashi, R.; Hildebrand, M. A. Hydrate Decomposition Conditions in the System H_2S-Methane-Propane. *Ind. Eng. Chem. Fundam.* **1983**, *22*, 361–364.

(23) Nixdorf, J.; Oellrich, L. R. Experimental determination of hydrate equilibrium conditions for pure gases, binary and ternary mixtures and natural gases. *Fluid Phase Equilib.* **1997**, *139*, 325–333.

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

(25) Mohammadi, A. H.; Richon, D. Phase Equilibria of Semi-Clathrate Hydrates of Tetra-*n*-butylammonium Bromide + Hydrogen Sulfide and Tetra-*n*-butylammonium Bromide + Methane. *J. Chem. Eng. Data* **2010**, *55*, 982–984.

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