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Experimental and Modeling Study on Phase Equilibria of Semiclathrate Hydrates of Tetra-*n*-butyl Ammonium Bromide + CH₄, CO₂, N₂, or Gas Mixtures

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ABSTRACT: Tetra-*n*-butyl ammonium bromide (TBAB) is most-widely used as a hydrate promoter in the separation of flue gases and CO₂ sequestration. Because of the complicity of semiclathrate hydrate formed by TBAB aqueous solution and gases, few researchers have investigated the thermodynamic modeling of phase equilibria of semiclathrate hydrates. In this work, the CH₄–N₂ hydrate dissociation conditions were determined in TBAB solution first, and then a thermodynamic model for gas hydrate proposed by Chen and Guo was extended for semiclathrate hydrates of gas mixtures in TBAB aqueous solution. The Patel–Teja equation of state (PT EoS) was used for calculation of the fugacity of the gas phase. To evaluate the activity of water and activity coefficients of TBAB in TBAB aqueous solution, a correlation on the basis of existing osmotic coefficient and activity coefficient values is employed. For modeling the hydrate phase, parameters for sII hydrates proposed in the Chen–Guo hydrate model were used to calculate the fugacity of gases in hydrate phase, and parameters of TBAB were obtained from the correlation with the literature dissociation data for the pure gas + TBAB + water system. Then the presented model was used to predict dissociation data for the gas mixtures + TBAB + water system, and the results show acceptable agreement with other literature data and the experimental data for CH₄–N₂ in this work.

1. INTRODUCTION

Large amounts of greenhouse gases including methane, carbon dioxide, carbon monoxide, hydrogen sulfide, etc. are released into the atmosphere every year, which result in air pollution and global warming. Therefore, separation of the aforementioned gases from the corresponding gas flows is of industrial and environmental significance from the past century up to now. Cryogenic distillation, pressure swing adsorption (PSA), membranes, and absorption with liquids are the widely used techniques currently applied for this purpose. These approaches have their own limitations such as high energy requirement, high cost, corrosivity, solvent loss, or low capacity. A novel technology called the hydrate formation/dissociation method, which has been recently proposed,^{1–6} has attracted much attention^{7–14} and does have wide application prospects.¹⁵

Under favorable conditions of temperature and pressure, light gases will form hydrates with water, and different gases have different hydrates formation conditions. The difference in gas hydrate properties of various gases including the chemical affinity of the hydrate cages to enclathrate specific gases and the difference in the corresponding phase behaviors can determine the possibility of such separation processes. For instance, the hydrate phase can be enriched in component(s) of interest, while the concentration of other gas(s) can be increased in the gas phase at equilibrium.¹⁶

Tetra-*n*-butyl ammonium bromide (TBAB) forms semiclathrate hydrate with water such that it can reduce the gas hydrate formation pressures greatly.¹⁷ In TBAB hydrate cavities, the TBA⁺ is engaged in tetrakaidecahedra and pentakaidecahedra (large) (50% of each), and the gaseous component, such as CH₄, CO₂, N₂, and H₂S, is trapped in dodecahedral small cages.¹⁸ As a kind of semiclathrate hydrates,

TBAB hydrates show great potential application in gas storage and transportation, separation of flue gases, and CO₂ sequestration.^{19–22} To design the efficient separation processes using hydrate formation technology, accurate and reliable phase equilibrium data should be obtained. Johnny Deschamps et al.²³ investigated phase equilibrium for TBAB semiclathrate hydrates of N₂, CO₂, N₂ + CO₂, and CH₄ + CO₂. Bahman Tohidi et al.²⁴ presented equilibrium data of H₂, CH₄, N₂, CO₂, and natural gas in semiclathrate hydrates of TBAB. Mohammadi et al.^{16,25} reported experimental dissociation data for semiclathrate hydrates of TBAB + H₂S, CH₄, CO₂, N₂, or H₂.

Unfortunately, modeling phase equilibria of semiclathrate hydrate systems has been rarely investigated in the literature. Joshi et al.²⁶ extended the hydrate model of Chen and Guo²⁷ for semiclathrate hydrate of CH₄, CO₂, and N₂ in aqueous solution of TBAB. It is observed that the Chen and Guo's model is simple, concise, and more flexible to apply not only for the clathrate system of pure gases and gas mixtures but also for hydrate systems in the presence of inhibitors.²⁸ Mohammadi and co-workers²⁹ used traditional van der Waals–Platteeuw (vdW-P) solid solution theory for modeling the hydrate phase and proposed a thermodynamic model for prediction of phase equilibria of semiclathrate hydrates of the CO₂, CH₄, or N₂ + TBAB aqueous solution. However, the thermodynamic modeling proposed in the above two examples of literature are the prediction of phase equilibria of TBAB and different pure gases, and models for phase equilibria of TBAB and gas

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mixtures systems have not yet been developed in open literature.

In this study, the CH₄ (37.52 mol %)-N₂ hydrate dissociation data in TBAB (10 wt %) solution are observed first. Then the calculation of sII hydrate of Chen and Guo's model²⁷ is modified for predicting phase equilibria of semicathrate hydrate of gas mixtures in TBAB aqueous solution. In addition, parameters of TBAB in Chen and Guo' hydrate model²⁷ are obtained from the correlation with the literature¹⁶ dissociation data. It is shown that the proposed modified model predicts the TBAB semicathrate hydrate dissociation condition well.

2. EXPERIMENTAL WORK

The composition of feed gas is prepared by Beijing AP Beifen Gas Industry Company. TBAB is prepared by Shanghai Sinopharm Chemical Reagent Company, and the purity of it is analytical pure. The experimental apparatus used in this study and the experimental procedures are the same as we proposed in our previous work.¹⁵ The method called "isochoric pressure search"^{4,5,15,30–33} is used to obtain the dissociation data of CH₄-N₂ gas mixtures in TBAB aqueous solution.

3. MODELING

3.1. Development of the Thermodynamic Model. For the traditional van der Waals-Platteeuw (vdW-P) model, the liquid water-hydrate-gas/vapor equilibrium conditions are calculated by equating the fugacity of water in the aqueous (f_w^L) and in the hydrate (f_w^H) phases

$$f_w^L = f_w^H \quad (1)$$

where f is fugacity, subscript w denotes water, and superscripts L and H represent the liquid and hydrate phases, respectively.

According to Chen and Guo,²⁷ the equilibrium conditions are calculated by equating the fugacity of gas in the gas phase and in the hydrate phase:

$$f_i^G = f_i^H = x_i f_i^{H,0} (1 - \sum_j \theta_j)^\alpha \quad (2)$$

However, for TBAB semicathrate hydrates, both some small gases (N₂, CO₂, CH₄, etc.) and TBAB are involved in the formation of hydrate. Consequently eq 2 can be comprehended as the following equations:

$$f_j^G = f_j^H = x_j f_j^{H,0} (1 - \sum_j \theta_j)^\alpha \quad \text{for gases} \quad (3)$$

$$f_M^L = f_M^H = x_M f_M^{H,0} (1 - \sum_j \theta_j)^\alpha \quad \text{for TBAB} \quad (4)$$

$$\sum_i x_i = x_M + \sum_j x_j = 1 \quad (5)$$

In this study, the model of Chen and Guo²⁷ is modified for predicting phase equilibria of semicathrate hydrate of gas mixtures in TBAB aqueous solution, and the hydrate parameters of TBAB in the model are obtained by the correlation with dissociation data for pure gas + TBAB + water systems in the literature.¹⁶

The application of the two-step hydrate formation mechanism proposed by Chen and Guo²⁷ is described as follows:

First step: The formation of a stoichiometric basic hydrate through a quasi-chemical reaction between water and basic semicathrate hydrate former. It should be pointed out that the gas species is assumed to be capable of forming a basic semicathrate hydrate in this study, although the amount of them is small. The formation of a basic semicathrate hydrate can be illustrated by the following quasi-chemical reaction equation



where S represents TBAB and gas species; λ_2 stands for the molecular number of S per water molecule in the basic semicathrate hydrate. On the basis of the so far knowledge about the structures of the semicathrate hydrates of TBAB, the hydration number is found to be 26 for type A and 38 for type B.³⁴ Experimental study on crystal growth of semicathrate hydrate of TBAB¹⁸ shows that each hydrate cell unit of the investigated semicathrate is composed of 2 TBA⁺ and 2 Br[−] along with 52 water molecules for type A and 76 for type B. The TBA⁺ cation is trapped in two large tetrakaidecahedra and pentakaidecahedra, respectively. It should be pointed out that a total of four similar large cavities are involved, and, hence, λ_2 equals to 8/52 for type A and 8/76 for type B. During this step, the so-called linked cavities,²⁷ the small cavities (S^{12}), are formed automatically.

Second step: The adsorption of small size gas molecules (e.g., N₂, CO₂, CH₄, etc.) into the empty linked cavities in basic semicathrate hydrate and formation of the stable hydrate. The partial occupation of the linked cavities by help gas molecules will lower the chemical potential of the basic hydrate and results in the nonstoichiometric property of the final semicathrate hydrates formed.

Based on the above stated two-step formation mechanism, the final modeling of the semicathrate hydrate formed can be expressed as

$$f_i = f_i^H = x_i f_i^{H,0} (1 - \sum_j \theta_j)^\alpha \quad (7)$$

$$\sum_j \theta_j = \frac{\sum_j f_j^G C_j}{1 + \sum_j f_j^G C_j} \quad (8)$$

$$\sum_i x_i = 1 \quad (9)$$

where $\alpha = \lambda_1/\lambda_2$; λ_1 is the number of linked cavities per water molecule in the basic semicathrate hydrate. Each hydrate cell unit has 6 small cavities, and consequently λ_1 equals to 6/52 for type A and 6/76 for type B.

It should be pointed out that f_i in eq 7 equals to f_j^G for gases and f_M^L (eq 15) for TBAB. In eq 7

$$f_i^{H,0} = f_i^{H,0}(T) f_i^{H,0}(P) f_i^{H,0}(a_w) \quad (10)$$

where

$$f_i^{H,0}(T) = \exp\left(\frac{-\sum_j A_{jM} \theta_j}{T}\right) A' \exp\left(\frac{B'}{T - C'}\right) \quad (11)$$

$$f_i^{H,0}(P) = \exp\left(\frac{\beta P}{T}\right) \quad (12)$$

$$f_i^{H,0}(a_w) = a_w^{-1/\lambda_2} \quad (13)$$

θ in eq 8 is the fraction of linked cavities (5^{12}) occupied by small gas molecules (CO_2 , CH_4 , N_2 , etc., no TBAB). f_j^G is the fugacity of gas. The fugacity of gas is calculated with Patel-Teja EOS.³⁵ C_j is the so-called Langmuir constant of the guest gas molecules in the linked cavities and correlated as an Antoine-type equation:

$$C = X \exp\left(\frac{Y}{T - Z}\right) \quad (14)$$

The constants X , Y , and Z were determined against the rigorous Langmuir constants C calculated from the Lennard-Jones potential function. The fitted X , Y , and Z values for typical gas species are listed in Table 1.

Table 1. Antoine Constants for Calculating the Langmuir Constants in Eq 14

gas	$X \times 10^6/\text{bar}^{-1}$	Y/K	Z/K
CH_4	2.3048	2752.29	23.01
CO_2	1.6464	2799.66	15.9
N_2	4.3151	2472.37	0.64

In eq 11, A_{jM} are the binary interaction parameters specifying the guest–guest interaction between components j (small gas molecules) and M (TBAB). $A_{jM} = A_{Mj}$ and $A_{jj} = A_{MM} = 0$. The A_{jM} values fitted from the common corresponding hydrate dissociation data for the pure gas + TBAB + water system¹⁶ are given in Table 2. It should be pointed out that the semicathrate

Table 2. Recommended Values for the Cross-Parameter A_{jM} (TBAB Semicathrate Hydrate)

component	CO_2	CH_4	N_2
5 wt % TBAB	410	220	80
10 wt % TBAB	380	110	70
25 wt % TBAB	50	−50	−100
50 wt % TBAB	−260	−150	−160

structure can be changed from type A to type B³⁶ or vice versa.^{1,16,36} It leads to the change of the hydration number and semicathrate structure parameters β with the varying TBAB concentrations. In this work, the semicathrate structure parameter β is set to a const, and the change of the semicathrate structure is corrected by the binary interaction parameters A_{jM} , which causes large changes in A_{jM} .

β in eq 12 is the hydrate structural parameter, $\beta = 3.5 \text{ K/bar}$ for type B TBAB sc hydrate, and $\beta = 2.8 \text{ K/bar}$ for type A.

It is worth pointing out that several researchers^{18,37,38} observed two types of TBAB semicathrate hydrate structures, A and B, for varying TBAB concentrations. From the phase diagram of TBAB hydrate crystals (types A and B), it is observed that 18 wt % is a critical weight percentage. Type B has a higher melting point below 18 wt %, while above 18 wt %, type A has a higher melting point. Consequently, we indicate that the type of the semicathrate hydrate is type B when the TBAB concentration is below 18 wt %, while above 18 wt %, the semicathrate hydrate is type A.

Parameters A' , B' , and C' for TBAB are determined by fitting the hydrate equilibrium data for the pure gas + TBAB + water system.¹⁶ The regressed values of A' , B' , and C' for the gases and TBAB used in this work are listed in Table 3. Values of A' , B' , and C' for the gases are the same as sII hydrate in the model of Chen and Guo.²⁷

Table 3. Antoine Constants for Calculating $f_i^0(T)$ in Eq 11

component	$A'/10^{23}\text{bar}$	B'/K	C'/K
CO_2	3.4474	−13470	6.79
CH_4	5.2602	−13088	4.08
N_2	6.8165	−12783	−1.10
TBAB type A ^a	6.3491	−26596	−111
TBAB type B ^a	3.2498	−18620	5.43

^aValues fitted in this work from dissociation data for the pure gas + TBAB + water system.

The same as in ref 29, fugacity of the hydrate promoter (TBAB) in the aqueous phase needs to be determined as well, and eq 12 can be applied for this purpose

$$f_M^L = x_M^L \gamma_M P_M^{\text{sat}} \exp\left(\frac{\nu_M^L(P - P_M^{\text{sat}})}{RT}\right) \quad (15)$$

where γ_M represents the activity coefficient of the hydrate promoter (TBAB) in the aqueous solution, and the subscript M stands for TBAB.

In TBAB aqueous solution, the activity coefficient of the TBAB salt is calculated through the corresponding values proposed by Lindenbaum and Boyd³⁹ and Amado and Blanco,⁴⁰ and the correlation was proposed by Ali Eslamimaneh²⁹ to calculate the activity coefficient of TBAB as follows:

$$\gamma_M = -0.5057w_M^3 + 1.1603w_M^2 - 1.3689w_M + 0.7655 \quad (16)$$

The activity of water in the TBAB aqueous solution is also calculated through the corresponding values proposed by Lindenbaum and Boyd³⁹ and Amado and Blanco,⁴⁰ and the correlation was proposed in this work to calculate the activity of water as follows:

$$\ln a_w = -0.03321w_M^2 - 0.09463w_M - 2.5874 \times 10^{-4} \quad (17)$$

Here, w_M is the weight fraction of TBAB in solution.

The density (ρ) of the TBAB aqueous solution (and consequently the molar volume (ν_M^L)) has been determined using the correlation of Söhnel and Novotny⁴¹ with the recommended values by Blandria and co-workers^{42,43}

$$\rho_M = \rho_w + B_1(100w_M) + B_2(100w_M)^2 + B_3(100w_M)^3 \quad (18)$$

where

$$B_i = q_i + r_i(T/K) + s_i(T/K)^2 \quad (19)$$

where q_i , r_i , and s_i are empirical constants, which are given in Table 4. In eq 18 and eq 19, ρ_M is calculated in g/cm^3 .

3.2. Calculation Procedure. The calculation procedure for determining the semicathrate hydrate formation conditions of a gas mixture with given composition is summarized in the schematic flow diagram shown in Figure 1. For simple gas hydrates (formed by pure gas), a similar procedure can be applied.

4. RESULTS AND DISCUSSION

The measured dissociation conditions of semicathrate hydrates of CH_4 (37.52 mol %)- N_2 in the presence of 0.1 mass fraction of TBAB aqueous solution are reported in Table 5.

4.1. Pure Gas + TBAB Systems. The performance of the model for the prediction of the semicathrate hydrate

Table 4. Constants in Eq 19

q_1	q_2	q_3	r_1	r_2	r_3	s_1	s_2
4.549×10^{-4}	5.304×10^{-4}	-7.091×10^{-4}	5.693×10^{-6}	-3.099×10^{-6}	4.088×10^{-8}	-1.707×10^{-8}	4.570×10^{-6}

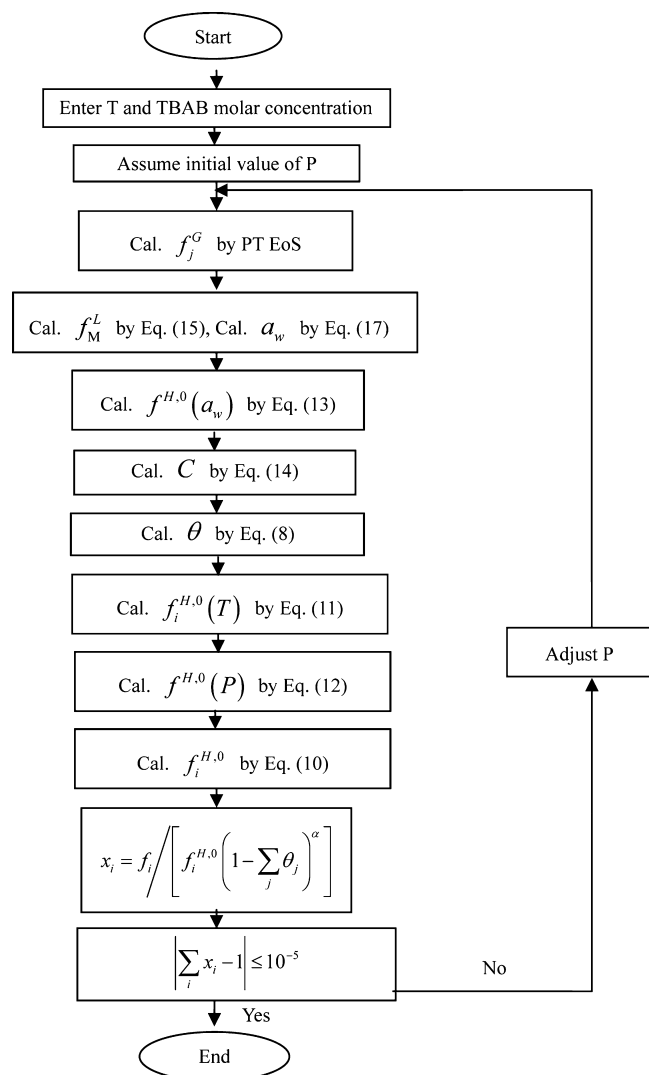


Figure 1. Flow diagram for calculating the formation pressure of semicathrate hydrate at a given temperature.

Table 5. Dissociation Data of sc Hydrate of CH₄-N₂ in TBAB Aqueous Solution

parameter	value					
T/K	282.15	283.15	284.15	285.15	286.15	287.15
P/MPa	0.76	1.22	2.04	3.03	4.40	5.84

dissociation conditions for the CO₂/CH₄/N₂ + TBAB systems in the liquid solution-hydrate-vapor/gas equilibrium region has been first examined. The obtained results are shown in Figures 2–4. The experimental data on phase equilibria of the pure gas hydrate system for CO₂, CH₄, and N₂ are also shown in Figures 2–4, respectively, for comparison. It is observed from Figures 2–4 that the model prediction results are in good agreement with the experimental data in all three cases. It is necessary to point out that the bold solid lines in Figures 2–4 are actually the predictions of Chen and Guo's model.²⁷

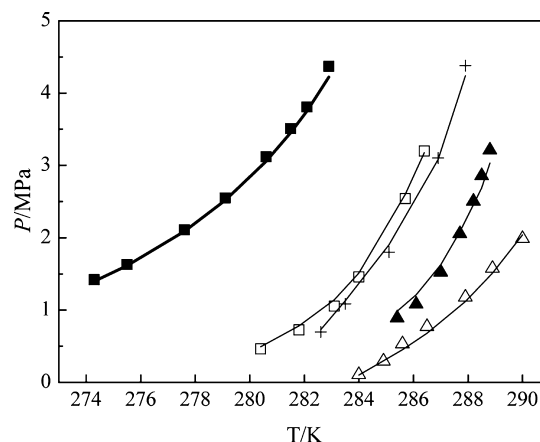


Figure 2. Dissociation conditions of clathrate/semicathrate hydrates for carbon dioxide + water/TBAB aqueous solution systems. Symbols stand for the experimental data, and curves refer to the predicted values using Chen and Guo's model or the modified model for TBAB sc hydrates in this work. ■, the CO₂ + water system (Adisasmito, S.; Sloan, E. D. et al.⁴⁴); □, CO₂ in the presence of 0.05 weight fraction TBAB aqueous solution (Mohammadi, A. H.; Richon, D. et al.¹⁶); ▲, CO₂ in the presence of 0.10 weight fraction TBAB aqueous solution (Mohammadi, A. H.; Richon, D. et al.¹⁶); △, CO₂ in the presence of 0.25 weight fraction TBAB aqueous solution (Mohammadi, A. H.; Richon, D. et al.¹⁶); +, CO₂ in the presence of 0.50 weight fraction TBAB aqueous solution (Mohammadi, A. H.; Richon, D. et al.¹⁶); Bold solid curve, Chen and Guo's model predicted results for the CO₂ + water system (AARD = 1.5); Solid curves, modified model predicted results in this work (AARD = 5.4).

Equation 20 is used to calculate the error between the model results and experimental results

$$\text{AARD} = (100/N) \sum_i^N |P_{i,\text{pred}}^{\text{diss}} - P_{i,\text{exp}}^{\text{diss}}| / P_{i,\text{exp}}^{\text{diss}} \quad (20)$$

where N is the number of the experimental data points, and the subscript *pred* stands for the predicted values.

It should be pointed out again that parameters of TBAB were fitted from dissociation data for pure gas + TBAB + water systems and then used to predict results in Figure 5 for the mixture gas + TBAB + water system.

Several researchers^{18,37,38} observed two types of TBAB semicathrate hydrate structures, A and B, for varying TBAB concentrations. From the phase diagram of TBAB hydrate crystals (type A and B), it is observed that 18 wt % is a critical weight percentage. Type B has a higher melting point below 18 wt %, while above 18 wt %, type A has a higher melting point. As a result, in Figures 2, 3, 4, and 5, it is indicated that the type of the semicathrate hydrate is type B when TBAB concentration is below 18 wt %, while above 18 wt %, the semicathrate hydrate is type A.

4.2. Gas Mixtures + TBAB Systems. The predicted phase equilibria of the gas mixtures + TBAB aqueous solution systems are sketched in Figure 5. It is observed from Figure 5 that predicted results show good agreement with the experimental and literature data.

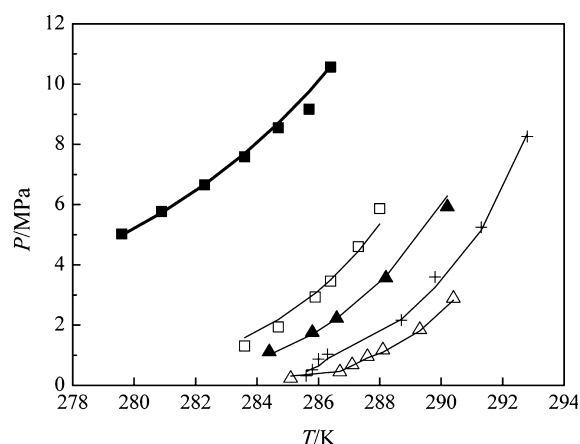


Figure 3. Dissociation conditions of clathrate/semiclathrate hydrates for methane + water/TBAB aqueous solution systems. Symbols stand for the experimental data, and curves refer to the predicted values using Chen and Guo's model or the modified model for TBAB sc hydrates in this work. ■, the CH_4 + water system (Adisasmito, S.; Sloan E. D. et al.⁴⁴); □, CH_4 in the presence of 0.05 weight fraction TBAB aqueous solution (Mohammadi, A. H.; Richon, D. et al.²⁵); ▲, CH_4 in the presence of 0.10 weight fraction TBAB aqueous solution (Mohammadi, A. H.; Richon, D. et al.¹⁶); △, CH_4 in the presence of 0.25 weight fraction TBAB aqueous solution (Mohammadi, A. H.; Richon, D. et al.¹⁶); +, CH_4 in the presence of 0.50 weight fraction TBAB aqueous solution (Mohammadi, A. H.; Richon, D. et al.¹⁶); Bold solid curve, Chen and Guo's model predicted results for the CH_4 + water system (AARD = 1.6); Solid curves, modified model predicted results in this work (AARD = 8.7).

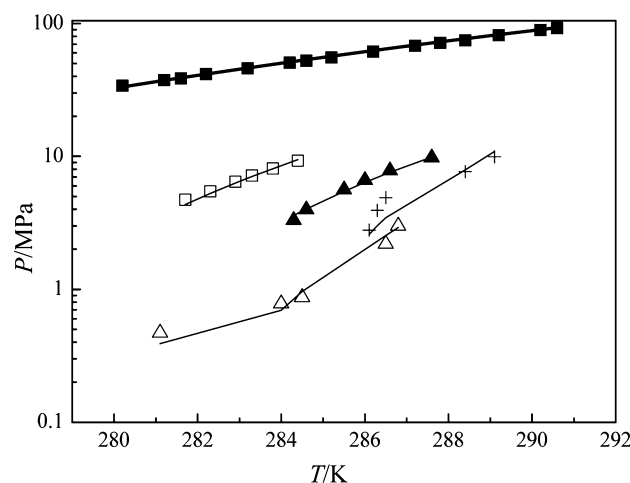


Figure 4. Dissociation conditions of clathrate/semiclathrate hydrates for nitrogen + water/TBAB aqueous solution systems. Symbols stand for the experimental data, and curves refer to the predicted values using Chen and Guo's model or the modified model for TBAB sc hydrates in this work. ■, the N_2 + water system (van Cleeff, A.; Diepen, G. A. M.⁴⁵); □, CH_4 in the presence of 0.05 weight fraction TBAB aqueous solution (Mohammadi, A. H.; Richon, D. et al.¹⁶); ▲, N_2 in the presence of 0.10 weight fraction TBAB aqueous solution (Mohammadi, A. H.; Richon, D. et al.¹⁶); △, N_2 in the presence of 0.25 weight fraction TBAB aqueous solution (Mohammadi, A. H.; Richon, D. et al.¹⁶); +, N_2 in the presence of 0.50 weight fraction TBAB aqueous solution (Mohammadi, A. H.; Richon, D. et al.¹⁶); Bold solid curve, Chen and Guo's model predicted results for the N_2 + water system (AARD = 1.5); Solid curves, modified model predicted results in this work (AARD = 7.7).

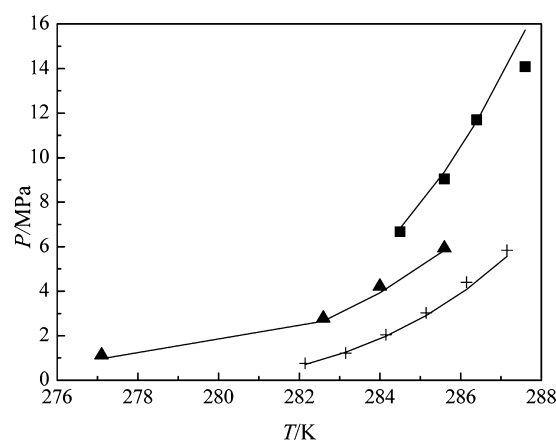


Figure 5. Dissociation conditions of clathrate/semiclathrate hydrates for gas mixtures + TBAB aqueous solution systems. Symbols stand for the experimental data, and curves refer to the predicted values using the modified model for TBAB sc hydrates in this work. ■, CO_2 (15.1 mol %) + N_2 in the presence of 0.05 weight fraction TBAB aqueous solution (Mohammadi, A. H.; Richon, D. et al.⁴⁶); ▲, CO_2 (39.9 mol %) + N_2 in the presence of 0.05 weight fraction TBAB aqueous solution (Mohammadi, A. H.; Richon, D. et al.⁴⁶); +, CH_4 (37.52 mol %) + N_2 in the presence of 0.05 weight fraction TBAB aqueous solution in this work; Solid curve, modified model predicted results in this work (AARD = 5.4).

Many comprehensive researchers share a common outlook that the phase behavior of semiclathrate hydrates may be complicated and difficult to analyze.^{1,36} 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.⁴⁷ In addition, some evidence has shown that there are some discrepancies even in the produce experimental data for the semiclathrate hydrate systems so far. For this reason, the selected dissociation data from the literature in this work were obtained by the same researchers. Because of the corresponding dissociation data selected from the literatures, it is worth pointing out the temperature range of the proposed model is 280–292 K. There will be big errors when the temperature is out of the range. The model is proposed by the experimental efforts for prediction of the phase equilibria of semiclathrate hydrates, especially for the gas mixtures + TBAB + water system. Unfortunately it could not predict the structure I and structure II hydrate.

5. CONCLUSIONS

In this study, the hydrate dissociation data of CH_4 – N_2 gas mixtures in the presence of TBAB aqueous solution were first measured. In addition, a modified model based on the model of Chen and Guo was proposed to calculate/estimate the dissociation conditions of the semiclathrate hydrates of CO_2 / CH_4 / N_2 or gas mixtures in the presence of TBAB aqueous solution. The model was developed on the basis of the calculation of structure II hydrate in Chen and Guo's model. The PT EoS was applied for calculation of fugacity of gas phase, and a correlation on the basis of existing osmotic coefficient and activity coefficient values is employed to estimate the activity of water and the activity coefficient of TBAB in TBAB aqueous solution. The optimal parameters of TBAB in the hydrate model were obtained minimizing the deviation of the calculated model results compared to the data of CO_2 / CH_4 / N_2 + TBAB aqueous solution systems. The fitted parameters were

later used to predict the semiclathrate hydrate dissociation conditions of gas mixtures containing CO₂, CH₄, and N₂ in the presence of TBAB aqueous solution. The test model results indicate that the proposed model is adequate for engineering applications.

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Notes

The authors declare no competing financial interest.

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NOMENCLATURE

- A' = Antoine constants for calculating $f_i^{H,0}(T)$ in eq 7
 A_{ij} = cross interaction parameter
 a = activity
 B' = Antoine constants for calculating $f_i^{H,0}(T)$ in eq 7
 C = Langmuir constant
 C' = Antoine constants for calculating $f_i^{H,0}(T)$ in eq 7
 f = fugacity of gas species and TBAB
 f^0 = fugacity of gas species and TBAB in equilibrium with the unfilled basic hydrate
 S = species
 P = pressure
 T = temperature
 w = weight fraction
 X = Antoine constant for calculating Langmuir constant in eq 10
 x = mole fraction of basic hydrate
 Y = Antoine constant for calculating Langmuir constant in eq 10
 Z = Antoine constant for calculating Langmuir constant in eq 10

Greek letters

- α = structural parameter, $\alpha = \lambda_1/\lambda_2$
 β = structural parameter, $\beta = 3.5$ K/bar for type B TBAB hydrate and $\beta = 2.8$ K/bar for type A
 γ = activity coefficient
 θ = fraction of the linked cavities occupied by guest molecules
 λ_1 = number of linked cavities per water molecule, $\lambda_1 = 6/78$ for type B and $\lambda_1 = 6/52$ for type A
 λ_2 = number of gas molecules per water molecule in basic hydrate, $\lambda_2 = 8/78$ for type B and $\lambda_2 = 8/52$ for type A

Subscripts

- L = liquid
 H = hydrate
 G = gas
 i = species i
 j = species j , small gas components such as CH₄, CO₂, N₂
 w = water
 M = hydrate promoter TBAB
 $diss$ = dissociation
 $pred$ = prediction

REFERENCES

- (1) Eslamimanesh, A.; Mohammadi, A. H.; Richon, D.; Naidoo, P.; Ramjugernath, D. Application of gas hydrate formation in separation processes: a review of experimental studies. *J. Chem. Thermodyn.* **2012**, *46*, 62–71.
- (2) Kang, S. P.; Lee, H. Recovery of CO₂ from flue gas using gas hydrate: thermodynamic verification through phase equilibrium measurements. *Environ. Sci. Technol.* **2000**, *34*, 4397–4400.
- (3) Linga, P.; Kumar, R.; Englezos, P. The clathrate hydrate process for post and pre-combustion capture of carbon dioxide. *J. Hazard. Mater.* **2007**, *149*, 625–629.
- (4) Belandria, V.; Eslamimanesh, A.; Mohammadi, A. H.; Theveneau, P.; Legendre, H.; Richon, D. Compositional analysis and hydrate dissociation conditions measurements for carbon dioxide + methane + water system. *Ind. Eng. Chem. Res.* **2011**, *50*, 5783–5794.
- (5) Belandria, V.; Eslamimanesh, A.; Mohammadi, A. H.; Richon, D. Gas hydrate formation in carbon dioxide + nitrogen + water system: compositional analysis of equilibrium phases. *Ind. Eng. Chem. Res.* **2011**, *50*, 4722–4730.
- (6) Lee, H. J.; Lee, J. D.; Linga, P.; Englezos, P.; Kim, Y. S.; Lee, M. S.; Kim, Y. D. Gas hydrate formation process for pre-combustion capture of carbon dioxide. *Energy* **2010**, *35*, 2729–2733.
- (7) Seo, Y.; Lee, H. A new hydrate-based recovery process for removing chlorinated hydrocarbons from aqueous solutions. *Environ. Sci. Technol.* **2001**, *35*, 3386–3390.
- (8) Sun, C. Y.; Ma, C. F.; Chen, G. J.; Zhang, S. X. Experimental and simulation of single equilibrium stage separation of (methane + hydrogen) mixtures via forming hydrate. *Fluid Phase Equilib.* **2007**, *261*, 85–91.
- (9) Zhang, L. W.; Chen, G. J.; Sun, C. Y.; Fan, S. S.; Ding, Y. M.; Wang, X. L.; Yang, L. Y. The partition coefficients of ethylene between hydrate and vapor for methane + ethylene + water and methane + ethylene + SDS + water systems. *Chem. Eng. Sci.* **2005**, *60*, 5356–5362.
- (10) Zhao, J. Z.; Zhao, Y. S.; Shi, D. X. Experiment on methane concentration from oxygen-containing coal bed gas by THF solution hydrate formation. *J. China Coal Soc.* **2008**, *33*, 1419–1424.
- (11) Li, X. S.; Xia, Z. M.; Chen, Z. Y.; Yan, K. F.; Li, G.; Wu, H. J. Gas hydrate formation process for capture of carbon dioxide from fuel gas mixture. *Ind. Eng. Chem. Res.* **2010**, *49*, 11614–11619.
- (12) Kamata, Y. et al. Hydrogen sulfide separation using TBAB hydrate. In *Proceedings of the 5th international conference on gas hydrates*. **2005**, Vol. 4, p 4033.
- (13) Zhang, B. Y.; Wu, Q.; Zhu, Y. M. Effect of THF on the thermodynamics of low-concentration gas hydrate formation. *J. China Univ. Min. Technol.* **2009**, *38*, 203–208.
- (14) Zheng, Z.; Wang, S. L. Separation technology for coalbed methane-air mixture based on hydrate. *J. Filtr. Sep.* **2008**, *18*, 5–9.
- (15) Sun, Q.; Guo, X. Q.; Liu, A. X.; Liu, B.; Huo, Y. S.; Chen, G. Y. Experimental study on the separation of CH₄ and N₂ via hydrate formation in TBAB solution. *Ind. Eng. Chem. Res.* **2011**, *50*, 2284–2288.
- (16) Mohammadi, A. H.; Eslamimanesh, A.; Belandria, V.; Richon, D. Phase equilibria of semi-clathrate hydrates of CO₂, N₂, CH₄, or H₂ + tetra-n-butyl ammonium bromide aqueous solution. *J. Chem. Eng. Data* **2011**, *56*, 3855–3865.
- (17) Kamata, Y.; Yamakoshi, Y.; Ebinuma, T. Hydrogen sulfide separation using tetra-n-butyl ammonium bromide semi-clathrate (TBAB) hydrate. *Energy Fuels* **2005**, *19*, 1717–1722.
- (18) Shimada, W.; Shiro, M.; Kondo, H.; Takeya, S.; Oyama, H.; Ebinuma, T.; Narita, H. Tetra-n-butyl-ammonium bromide – water (1/38). *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2005**, *61*, 065–066.
- (19) Kamata, Y.; Oyama, H.; Shimada, W.; Ebinuma, T.; Takeya, S.; Uchida, T.; Nagao, J.; Narita, H. Separation of gas molecule using tetra-n-butyl ammonium bromide semi-clathrate hydrate crystals. *Jpn. J. Appl. Phys.* **2004**, *43*, 362.
- (20) Duc, N. H.; Chauvy, F.; Herri, J. M. CO₂ capture by hydrate crystallization—a potential solution for gas emission of steelmaking industry. *Energy Convers. Manage.* **2007**, *48*, 1313.
- (21) Hao, W. F.; Wang, J. Q.; Fan, S. S.; Hao, W. B. Evaluation and analysis method for natural gas hydrate storage and transportation processes. *Energy Convers. Manage.* **2008**, *49*, 2546.

- (22) Gholinezhad, J.; Chapoy, A.; Tohidi, B. Experimental clathrate dissociations for the hydrogen + water and hydrogen + tetra butyl ammonium bromide + water systems. *Chem. Eng. Res. Des.* **2011**, *89*, 1747.
- (23) 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.
- (24) Arjmandi, M.; Chapoy, A.; Tohidi, B. Equilibrium data of hydrogen, methane, nitrogen, carbon dioxide, and natural gas in semi-clathrate hydrates of tetra butyl ammonium bromide. *J. Chem. Eng. Data* **2007**, *52*, 2153–2158.
- (25) Mohammadi, A. H.; Richon, D. Phase equilibria of semi-clathrate hydrates of tetra-n-butylammonium bromide + hydrogen sulfide and tetra-n-butyl ammonium bromide + methane. *J. Chem. Eng. Data* **2010**, *55*, 982–984.
- (26) Joshi, A.; Mekala, P.; Sangwai, J. S. Modeling phase equilibria of semiclathrate hydrates of CH_4 , CO_2 and N_2 in aqueous solution of tetra-n-butyl ammonium bromide. *J. Nat. Gas Chem.* **2012**, *21*, 459–465.
- (27) Chen, G. J.; Guo, T. M. A new approach to gas hydrate modelling. *Chem. Eng. J.* **1998**, *71*, 145–151.
- (28) Chen, G. J.; Ma, Q. L.; Guo, T. M. A new mechanism for hydrate formation and development of thermodynamic model. *J. Chem. Ind. Eng. (Huagong Xuebao)* **2000**, *51*, 626.
- (29) Eslamimanesh, A.; Mohammadi, A. H.; Richon, D. Thermodynamic modeling of phase equilibria of semi-clathrate hydrates of CO_2 , CH_4 , or N_2 + tetra-n-butyl ammonium bromide aqueous solution. *Chem. Eng. Sci.* **2012**, *81*, 319–328.
- (30) Tohidi, B.; Burgass, R. W.; Danesh, A.; Ostergaard, K. K.; Todd, A. C. Improving the accuracy of gas hydrate dissociation point measurements. *Ann. N. Y. Acad. Sci.* **2000**, *912*, 924–931.
- (31) 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.
- (32) Mohammadi, A. H.; Afzal, W.; Richon, D. Experimental data and predictions of dissociation conditions for ethane and propane simple hydrates in the presence of distilled water and methane, ethane, propane, and carbon dioxide simple hydrates in the presence of ethanol aqueous solutions. *J. Chem. Eng. Data* **2008**, *53*, 683–686.
- (33) Tumba, K.; Reddy, P.; Naidoo, P.; Ramjugernath, D.; Eslamimanesh, A.; Mohammadi, A. H.; Richon, D. Phase equilibria of methane and carbon dioxide clathrate hydrates in the presence of aqueous solutions of tributylmethylphosphonium methylsulfate ionic liquid. *J. Chem. Eng. Data* **2011**, *56*, 3620–3629.
- (34) 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 semi-clathrate hydrate crystals. *Fluid Phase Equilib.* **2005**, *234*, 131–135.
- (35) Patel, N. C.; Teja, A. S. A new cubic equation of state for fluids and fluid mixtures. *Chem. Eng. Sci.* **1982**, *37*, 463–473.
- (36) SECOHYA (Separation of CO_2 by Hydrate Adsorption) project of Agence Nationale de la Recherche (ANR), *internal reports*, France, 2007–2011.
- (37) Fukushima, S.; Takao, S.; Ogoshi, H.; Ida, H.; Matsumoto, S.; Akiyama, T.; Otsuka, T. Development of high-density cold latent heat with clathrate hydrate. *NKK Tech. Rep.* **1999**, *166*, 65.
- (38) 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.
- (39) Lindenbaum, S.; Boyd, G. E. Osmotic and activity coefficients for the symmetrical tetra alkyl ammonium halides in aqueous solution at 25 °C. *J. Phys. Chem.* **1964**, *68*, 911–917.
- (40) Amado, G. E.; Blanco, L. H. Isopiestic determination of the osmotic and activity coefficients of dilute aqueous solutions of symmetrical and unsymmetrical quaternary ammonium bromides with a new isopiestic cell at 298.15K. *Fluid Phase Equilib.* **2005**, *233*, 230–233.
- (41) Söhnel, O.; Novotny, P. *Densities of Aqueous Solutions of Inorganic Substances*; Elsevier Science Pub. Co.: Amsterdam, 1985.
- (42) Belandria, V.; Mohammadi, A. H.; Richon, D. Volumetric properties of the (tetrahydrofuran + water) and (tetra-n-butyl ammonium bromide + water) systems: experimental measurements and correlations. *J. Chem. Thermodyn.* **2009**, *41*, 1382–1386.
- (43) Chen, L. F.; Soriano, A. N.; Li, M. H. Vapor pressures and densities of the mixed-solvent desiccants (glycols + water + salts). *J. Chem. Thermodyn.* **2009**, *41*, 724–730.
- (44) Adisasmito, S.; Sloan, E. D. *Hydrates of carbon dioxide and methane mixtures* **1991**, *36*, 68.
- (45) van Cleeff, A.; Diepen, G. A. M. Gas hydrates of nitrogen and oxygen. *Recl. Trav. Chim.* **1960**, *44*, 2219.
- (46) Mohammadi, A. H.; Eslamimanesh, A.; Belandria, V.; Richon, D.; Naidoo, P.; Ramjugernath, D. Phase equilibrium measurements for semi-clathrate hydrates of the ($CO_2 + N_2$ + tetra-n-butylammonium bromide) aqueous solution system. *J. Chem. Thermodyn.* **2012**, *46*, 57–61.
- (47) Li, D. L.; Du, J. W.; Fan, S. S.; Liang, D. Q.; Li, X. S. Clathrate dissociation conditions for methane + tetra-n-butyl ammonium bromide (TBAB) + water. *J. Chem. Eng. Data* **2007**, *52*, 1916–1918.