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Thermodynamic model of phase equilibria of tetrabutyl ammonium halide (fluoride, chloride, or bromide) plus methane or carbon dioxide semiclathrate hydrates

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1. Introduction

Clathrate hydrates [1], or simply hydrates, are known as a type of ice-like inclusion compound formed when small guest molecules of gases (such as methane, carbon dioxide, nitrogen) or volatile liquids (such as tetrahydrofuran, acetone) are physically encaged in cavities formed by strongly hydrogen-bonded water (host) molecules under suitable conditions of low temperature and specified pressure. Conventionally, gas hydrates can form three typical crystalline structures: structure I (sI), structure II (sII) and structure H (sH). Gas hydrate was regarded as the reason for blockage of natural gas transportation pipelines [2] since 1934. In modern society, more attention was focused on gas hydrate, as it became a promising medium for many positive applications, such as gas storage [3,4], gas separation [5,6], energy storage [7], water desalination [8], separation of close-boiling point compounds [9-12] and so on. However, the condition of high pressure and low temperature required for the hydrate formation is one of the greatest obstacles to realize these hydrate-based technologies.

Recently, semiclathrate hydrate (SCH) has gained great attention due to its relatively low equilibrium pressure and high equilibrium temperature. SCH was first identified by Fowler et al. [13]. They reported that the addition of some quaternary

ABSTRACT

In this work, based on the van der Waals–Platteeuw (vdW–P) theory, a thermodynamic approach is proposed to determine the phase equilibria of semiclathrate hydrates formed with tetrabutyl ammonium halide (fluoride, chloride, or bromide) and guest gas (CH₄ or CO₂). The Peng–Robinson equation of state (PR-EoS) and electrolyte-Non-Random Two-Liquid (e-NRTL) activity model are employed to obtain the fugacity of gaseous hydrate formers and activity coefficients of species in the aqueous phase, respectively. In addition, two modifications for evaluations of vapor pressure of water in the empty hydrate lattice and Langmuir constants relating to the salt concentrations in aqueous solution and temperature are applied. It is shown that the model results are in acceptable agreement with the experimental data on phase equilibria for studied systems over wide temperature, pressure, and salt concentration ranging from 280.1 to 304.8 K, from 0.172 to 9.932 MPa, and from 0.02 to 0.35, respectively.

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ammonium salts, such as tetrabutyl ammonium bromide (TBAB), tetrabutyl ammonium chloride (TBAC) and tetrabutyl ammonium fluoride (TBAF), could form hydrates with water molecules at atmospheric pressure and room temperature. In 1969 [effrey [14]] studied its structure through detailed X-ray structural analysis and named it as semiclathrate hydrate. Unlike the typical hydrate structures whose cages are solely comprised of water molecules, the structure of SCH is constructed with a polyhedral water-anion framework formed by water molecules and anions through hydrogen bonding. The cations are located in four-compartment cavities, which are composed by tetrakaidecahedron $(5^{12}6^2, T)$ cavities and pentakaidecahedron (51263, P) cavities. And small gas molecules could be encaged in the empty dodecahedron $(5^{12}, D)$ cavities. It was reported that the most common structures of SCH were hexagonal structure-I (HS-I), tetragonal structure-I (TS-I), and cubic superstructure-I (CSS-I) with unit cell formula of $2P \cdot 2T \cdot 3D \cdot 40H_2O$, $4P \cdot 16T \cdot 10D \cdot 172H_2O$, and $48T \cdot 16D \cdot 368H_2O$, respectively. Compared with clathrate hydrate, SCH has the advantage of moderate pressure-temperature conditions. And among SCH forming compounds, TBAB [15-24], TBAC [25-30], and TBAF [30-33] are perhaps the most promising ones for industrial applications, especially gas separation.

To design efficient hydrate-based separation processes, accurate and reliable equilibrium data are essential and should be obtained. Comprehensive researchers have conducted experiments to get the equilibrium data of SCH. Meanwhile several researchers have investigated the structures of TBAB, TBAC and





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TBAF SCH. However, the theoretical attempts to proposing reliable and predictive models to represent or predict SCH phase equilibrium conditions are limited. In 2011 Paricaud [34] showed a thermodynamic model based on vdW-P model and statistical associating fluid theory with variable range for electrolytes (SAFT-VRE). They predicted equilibrium conditions of $(TBAB+CO_2)$ hydrate. In 2012 Joshi et al. [35] calculated phase equilibria of $(TBAB + CH_4, +CO_2, or +N_2)$ SCH based on the model of Chen–Guo. In 2012 Eslamimanesh et al. [36] also presented a model for $(TBAB + CH_4, +CO_2, or +N_2)$ SCH phase equilibria estimation based on vdW-P model. In 2014 Fukumoto et al. [37] predicted the equilibrium conditions of semiclathrate hydrates formed with $(TBAB/TBAC/TBAF/TBPB + CO_2 + H_2O)$ by employing the thermodynamic approach proposed by Paricaud [34]. Since the relevant studies are still at the demonstrating stage and only one SCH forming compound is involved, it is of much significance to develop a thermodynamic model for phase equilibria calculation and estimation of SCH formed with various SCH forming compounds, such as TBAF, TBAC, and TBAB.

In this study, a thermodynamic model, based on the vdW–P theory, is proposed for SCH formed with TBAF/TBAC/TBAB aqueous solutions and guest gas (CH₄ or CO₂). Two modifications for evaluations of vapor pressure of water in the empty hydrate lattice and Langmuir constants relating to the salt concentration in aqueous solution and temperature are applied. The Peng–Robinson (PR-EoS) equation is used to calculate the fugacity of gaseous hydrate former. Additionally, the electrolyte-Non-Random Two-Liquid (e-NRTL) activity model is employed to obtain the activity coefficients of species in the aqueous phase.

2. Model description

To get the three phase equilibrium conditions of TBAX (X = F, Cl, Br)+gas+H₂O system, the thermodynamic model is developed by equating the fugacity of water in the aqueous phase, f_w^L , and hydrate phase, f_w^H :

$$f_{\rm w}^{\rm L} = f_{\rm w}^{\rm H} \tag{1}$$

where *f* is fugacity, subscript w represents water, and superscripts L and H denote the liquid phase and hydrate phase, respectively. The fugacity of water in liquid phase is given by the following equation [36]:

$$f_{\rm w}^{\rm L} = x_{\rm w}^{\rm L} \gamma_{\rm w}^{\rm L} P_{\rm w}^{\rm sat} \exp\left(\frac{v_{\rm w}^{\rm L} (P - P_{\rm w}^{\rm sat})}{RT}\right)$$
(2)

where x_w^L , γ_w^L , γ_w^{sat} , and v_w^L are mole fraction, activity coefficient, vapor pressure and molar volume of water in liquid phase, respectively, and the superscript sat stands for the saturation condition.

$$x_{\rm w}^{\rm L} = \frac{1}{1 + 0.001 \times 2 \times m \times 18.0153} - x_{\rm g}^{\rm L}$$
(3)

where,

$$m = \frac{1000x_{\text{cation}}}{18.0153x_{\text{w}}} \tag{4}$$

$$x_{g}^{L} = \frac{f_{g}^{G}}{H_{g-w} \exp[\nu_{g}^{v}(P - P_{w}^{sat})/R/T]}$$
(5)

$$H_{g-w} = (10^{A+B/T+C \times \log T+D \times T}) \times 0.1$$
(6)

Table 1

Parameters of gases used in PR-EoS calculation.

Gas	$T_{\rm c}^{\rm a}/{\rm K}$	P _c ^b /MPa	w ^c
CH ₄	190.56	4.599	0.0114
CO ₂	304.13	7.377	0.2239

^a Critical temperature.

^b Critical pressure.

^c Acentric factor.

$$P_{\rm w}^{\rm sat} = 10^{-6} \exp(73.649 - \frac{7258.2}{T} - 7.3037 \times \ln T + 4.1653 \times 10^{-6} T^2)$$
(7)

$$\nu_{\rm w}^{\rm L} = \frac{1000 \times 0.30542^{\left[1 + \left(1 - \frac{T}{647.13}\right)^{0.081}\right]}}{5.459} \tag{8}$$

where *m* is the molality of aqueous solution in mol kg⁻¹, and x_g^L stands for the solubility of the gaseous hydrate former in liquid phase. The superscript G represents gas phase, and *R* and *T* are universal gas constant in J/(mol K) and temperature in K, respectively. The fugacity of guest gas in gas phase is calculated from the Peng–Robinson equation of state (PR-EoS) with the parameters reported in Table 1. v_g^{∞} stands for partial molar volume at infinite dilution, which is determined as 34.5 and 33.9 (cm³ mol⁻¹) for CH₄ and CO₂, respectively. H_{g-w} (MPa) is the Henry's constant of gas in water. The parameters in Eq. (6) are listed in Table 2 [36]. The activity coefficient of water in liquid phase, γ_{w}^L , is determined using the electrolyte-Non-Random Two-Liquid (e-NRTL) activity model with the parameters reported in Table 3 [38].

The fugacity of water in hydrate phase is given by the following equation:

$$f_{\rm w}^{\rm H} = f_{\rm w}^{\beta} \exp(\frac{-\Delta\mu^{\beta-{\rm H}}}{RT}) \tag{9}$$

where the superscript β stands for empty hydrate lattice and $\Delta \mu^{\beta-H}$ represent the fugacity of the hypothetical empty hydrate lattice and the chemical potential difference of water in the filled and empty hydrate lattice, which are given by the following equations [36]:

$$f_{\rm w}^{\beta} = P_{\rm w}^{\beta} \exp(\frac{\nu_{\rm w}^{\beta}(P - P_{\rm w}^{\beta})}{RT})$$
(10)

$$\nu_{\rm w}^{\beta}(11.835 + 2.217 + 10^{-5}T + 2.242 \times 10^{-6}T^2) \frac{10^{-30}N_{\rm A}}{N_{\rm w}^{\beta}} \\ - 8.006 \times 10^{-9}P + 5.448 \times 10^{-12}P^2$$
 (11)

$$P_{\rm w}^{\rm \beta} = 0.1 \, \exp(17.44 - \frac{6003.9}{T} + h \times w_{\rm p}) \tag{12}$$

where N_A is Avogadro's number, N_W^{w} is the number of water molecules in a unit hydrate cell, and w_p is the weight fraction of TBAX in aqueous solution. The unit of pressure, *P*, in Eq. (11) is MPa. The parameter *h* in Eq. (12) is an adjustable parameter for different systems. It is proposed to have a relation with the salt mass fraction of as follows:

Table 2	
Values of constants A–D in Eq. (6).	

Gas	CH ₄	CO ₂
Α	147.788	21.6215
B/K	-5768.3	-1499.8
С	-52.295	-5.6495
D^{-1}	0.018616	0.000206

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