RAPID COMMUNICATION

A theoretical prediction of cage occupancy and heat of dissociation of THF-CH₄ hydrate

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Abstract−This work presents a theoretical prediction of the cage occupancy of CH₄ in small cages and the heat of dissociation for THF-CH₄ hydrate using the predictive Soave-Redlich-Kwong group contribution method combined with the UNIFAC model. The predicted cage occupancy of CH₄ gradually increases with increasing pressure, indicating that the CH₄ molecules could readily be encaged in the small 5^{12} cages of the sII hydrate framework stabilized by THF molecules. The molar enthalpy of encagement of CH₄ in the small 5^{12} cages of the sII clathrate hydrate is estimated to be 26.7±1.7 kJ mol⁻¹.

Key words: Gas Hydrate, Guest, Cage Occupation, Heat of Dissociation, Methane, Tetrahydrofuran

INTRODUCTION

Gas hydrates are non-stoichiometric inclusion compounds formed by the interactions between water hosts and relatively small guest molecules. Depending on the difference in cavity shape and size of the gas hydrates, they have been classified into three distinct structures: structure I (sI), structure II (sII), and structure H (sH). The unit crystal of the sI hydrate consists of two small 5^{12} and six large $5^{12}6^2$ cages, whereas the sII hydrate has sixteen 5^{12} and eight $5^{12}6^4$ cages [1]. It is also known that the sH clathrate hydrate is composed of three types of cages, 5^{12}, $4^35^66^3$, and $5^{12}6^8$. Interestingly, they require large guest molecules such as adamantane and methylcyclohexane with smaller help gas for cage stability [2,3].

Over the past 60 years, considerable attention has been given to research on natural gas hydrates, since the plugging of gas pipelines in natural gas transportation is primarily caused by gas hydrate formation between water and guest components such as methane, ethane, propane, and other light hydrocarbons. Therefore, many studies on the phase equilibrium, kinetics, and spectroscopic investigation of gas hydrates have been reported in the literature [1]. On the other hand, gas hydrates are considered as a potential energy source for the future economy because a huge amount of methane in the form of the gas hydrate exists in the permafrost zone and the subsea sediment [4]. Some studies suggested that natural gas hydrates also have potential for gas storage and transportation applications [5,6]. For practical applications of gas hydrate to these technologies and processes, a detailed knowledge of the host-guest interaction, thermodynamic stability, and cage occupancy behavior of guests of gas hydrates would be of particular importance.

When the CH₄ molecules form the sI hydrates, they can occupy both the 5^{12} and $5^{12}6^2$ cages of the sI hydrate framework. The occupancy of CH₄ molecules in the small 5^{12} cage slightly varies with the formation conditions because of their non-stoichiometric nature. In general, the small cages 5^{12} are less occupied by CH₄ molecules than the large $5^{12}6^2$ cages. This can be attributed to the effect of the

molecular size of guests and the interaction between hosts and guests on the cage occupancy. Tetrahydrofuran (THF) by itself forms sII clathrate hydrate with water molecules in aqueous solutions. It is also well-known that THF can form the sII hydrate with CH₄ as a small-cage guest. In this case, the THF molecules occupy only the large $5^{12}6^4$ cages. Even though there have been several studies on the phase equilibria of the THF-CH₄ binary hydrates [7-9], the information for the occupancy behavior of CH₄ molecules in the cages and the heat of dissociation is rarely reported in the literature [10]. In addition, an important clue to how guest-host interactions occur in gas hydrate may come from study on the occupancy behavior of guest in a single cage. To our best knowledge, there is no detailed information on the interaction between host water and guest molecules in a single cage. In this study, we provide a theoretical prediction of the occupancy behavior of CH₄ molecules in the small 5^{12} cage and corresponding enthalpy change by CH₄ encagement.

THERMODYNAMIC MODEL

1. Phase Equilibria of Gas Hydrate

The chemical potential difference between the empty hydrate and filled hydrate phases, $\Delta\mu_w^{MT-H}(=\mu_w^{MT}-\mu_w^{H})$, is obtained from the following equation

$$\Delta\mu_w^{MT-H} = RT\sum_m \nu_m \ln\left(1+\sum_j C_{mj}\hat{f}_j^V\right) \tag{1}$$

The fugacity of water in the hydrate phase, $\hat{f}_w^H$, is derived as follows:

$$\hat{f}_w^H = f_w^{MT}\exp\left(\frac{-\Delta\mu_w^{MT-H}}{RT}\right) = f_w^{MT}\exp\left[-\sum_m \nu_m \ln\left(1+\sum_j C_{mj}\hat{f}_j^V\right)\right] \tag{2}$$

Previously, we presented a unique expression for the fugacity of water in the filled hydrate phase as follows [11,12]:

$$\hat{f}_w^H = f_w^L\exp\left[\frac{\Delta\mu_w^0}{RT} - \int_{T_0}^T \frac{\Delta h_w^{MT-I}+\Delta h_w^{fus}}{RT^2}dT + \int_0^P \frac{\Delta\upsilon_w^{MT-I}+\Delta\upsilon_w^{fus}}{RT}dP\right.$$
$$\left. -\sum_m \nu_m \ln\left(1+\sum_j C_{mj}\hat{f}_j^V\right)\right] \tag{3}$$

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The fugacities of supercooled water and all components in the vapor phase were calculated using the predictive Soave-Redlich-Kwong (PSRK) group contribution method combined with the UNIFAC model [13-16].

2. PSRK Group Contribution Method

The PSRK group contribution method is based on the SRK equation of state [17],

$$P = \frac{RT}{\upsilon - b} - \frac{a(T)}{\upsilon(\upsilon + b)} \tag{4}$$

where the mixture parameter b is derived from the conventional mixing rule,

$$b = \sum_{i=1}^{n} x_i b_i \tag{5}$$

Huron and Vidal originally presented a new method to derive a mixing rule in connection with the excess Gibbs energy [18]. The equation relating excess Gibbs energy at infinite pressure to the a/b parameter of the SRK equation of state is given as follows:

$$g_\infty^E = RT \left[\ln \varphi - \sum_{i=1}^{n} x_i \ln \varphi_i \right] \tag{6}$$

The simplest first-order approximation is used in the PSRK model:

$$\alpha = \frac{1}{A_1} \left[\frac{g_0^E}{RT} + \sum_{i=1}^{n} x_i \ln \left(\frac{b}{b_i} \right) \right] + \sum_{i=1}^{n} x_i \alpha_i \tag{7}$$

The recommended value of $A_1 = -0.64663$ in the PSRK model yields better results at higher pressures. We note that the use of the group contribution concept minimizes the parameter fitting or estimating efforts and has the advantage of accurately predicting the phase behavior of a multicomponent system without introducing new interaction parameters.

3. Heat of Dissociation of Gas Hydrate

The heat of dissociation of gas hydrate has been usually determined from three-phase equilibria using the Clausius-Clapeyron equation as follows:

$$\frac{d \ln P}{d(1/T)} = -\frac{\Delta H_d}{zR} \tag{8}$$

Considering the effect of compressibility and solubility of gas components on heat of dissociation of gas hydrates, we provided an expression for the heat of dissociation using the Clausius-Clapeyron equation as follows [19]:

$$\frac{d \ln P}{d(1/T)} = -\frac{\Delta H_d + n x_g \Delta H_s}{z^* R} \tag{9}$$

$$z^* = \frac{1}{y_g} \left(1 - \frac{n x_g}{1 - x_g} \right) z^{vap} - n \frac{P \Delta \upsilon}{RT} \tag{10}$$

where n is the hydrate number (water/guest ratio), ΔH_s is the heat of dissolution of guest component in water, x_g is the mole fraction of guest component in water, y_g is the mole fraction of guest in vapor phase, z^{vap} is the compressibility factor of vapor phase, and $\Delta \upsilon$ is the difference in volume per mole of water between hydrate and water. In this work, we do not take into account the solubility cor-

Table 1. Kihara potential parameters for guest-host interaction

Guest	a, Å	σ, Å	ε/k, K	Temp. range, K
CH$_4$	0.30	3.2161	157.6	148-320
THF	0.988	2.8600	327.6	272-278

rection, because there is no information on the heat of dissolution of CH$_4$ in the solution of water and THF.

RESULTS AND DISCUSSION

Table 1 presents Kihara potential parameters for guest-water interactions of guest components and the temperature ranges of equilibrium data used for data reduction. The core parameter a of THF was calculated using the correlation equation suggested by Tee et al. [20] The Kihara potential parameters of THF were determined using the values for thermodynamic properties of empty hydrate lattice suggested by Handa and Tse [21] and temperature-composition (T−x) data of pure THF hydrate in the concentration range up to ~10 mol% THF [22-26]. The PSRK model with the optimized Kihara parameters predicts well the T−x behavior of pure THF hydrate with an average absolute deviation (AAD) of 0.24% and a maximum deviation in temperature of 2.8 K. The Kihara potential
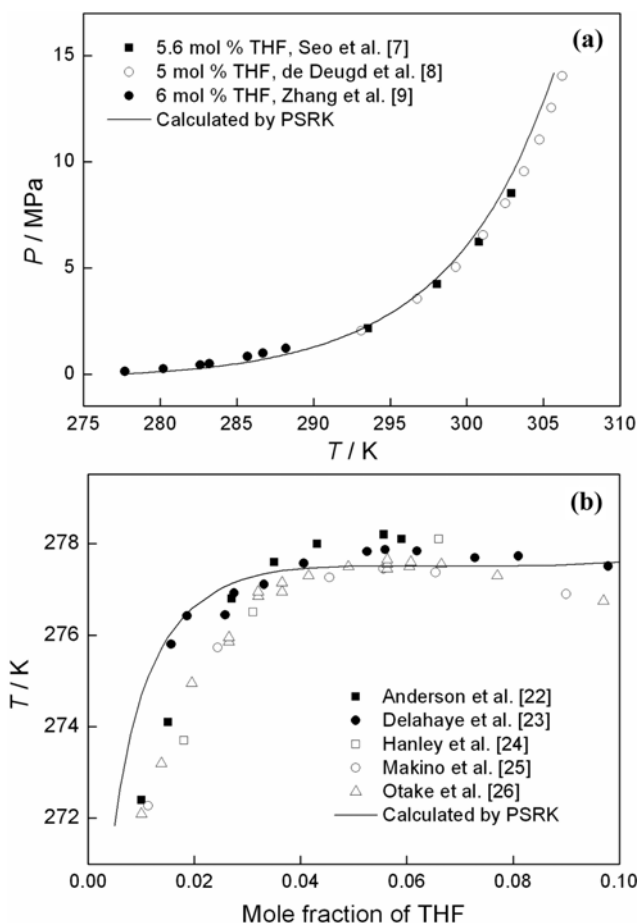

Fig. 1. Experimental data and theoretical prediction for dissociation pressures of THF-CH$_4$ hydrate (a) and temperature-composition behavior of pure THF hydrate (b).

parameters of CH$_4$ were determined by fitting the experimental data obtained in this work for 5.56 mol% THF-CH$_4$ hydrates (sII) as well as simple CH$_4$ hydrate data (sI). Fig. 1 shows the experimental data [7-9,22-26] and theoretical predictions using the PSRK model for the THF-CH$_4$ hydrate and pure THF hydrate. The PSRK model predicts well the phase behavior of both hydrate systems, as shown in Fig. 1. We also note that the new set of Kihara parameters of CH$_4$ provides reasonable predictions with an AAD of 5.9% in pressure for 92 data points of simple CH$_4$ sI hydrates [1].

The occupancy behavior of CH$_4$ molecules in the small 5^{12} cages of sII hydrate can also be predicted at incipient dissociation conditions by the PSRK model. Fig. 2 shows that the cage occupancy of CH$_4$ gradually increases with increasing pressure, which is very different from pure CH$_4$ hydrates appearing almost the same hydration number at all incipient dissociation conditions. This indicates that, with a small increase of pressure, the CH$_4$ molecules could readily be trapped in the small 5^{12} cages of the sII hydrate framework stabilized by THF molecules. Fig. 3 shows the Clausius-Clapeyron plot to calculate the heat of dissociation of THF-CH$_4$ hydrates. The heat of dissociation of THF-CH$_4$ hydrates (per 1 gram of the
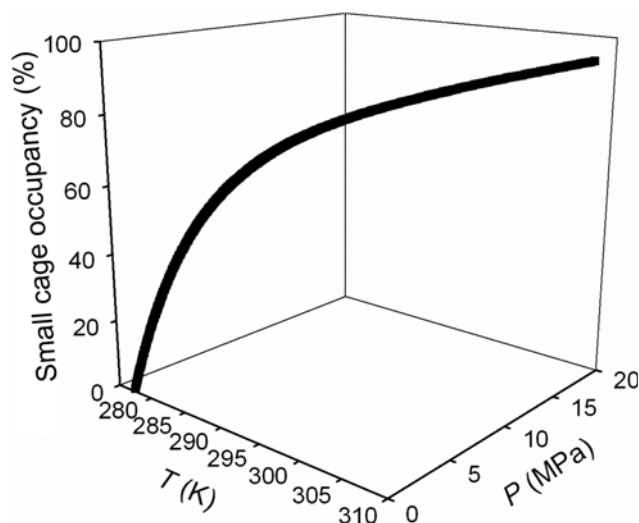
hydrate) increases with increasing the cage occupancy of CH$_4$. At the cage occupancy of CH$_4$ lower than 10%, the Clausius-Clapeyron approximation cannot be applied to estimate the heat of dissociation, because the gas volume released by the hydrate dissociation might not be identical to the total volume change by the phase transition. However, as shown in Fig. 3, the heat of dissociation extrapolated to a limiting condition of zero-occupancy of CH$_4$ was found to be 278 J g^{-1}, which may be estimated to the heat of fusion of pure THF hydrate. This is comparable to the literature value of 263 J g^{-1} at 277.3 K [27]. Furthermore, the molar enthalpy of encagement of CH$_4$ in the small 5^{12} cages of the sII clathrate hydrate is estimated to be 26.7±1.7 kJ mol^{-1}.

Fig. 2. Theoretical prediction of cage occupancy of CH$_4$ molecules in small cages of THF-CH$_4$ hydrates.

Fig. 3. Relationship between cage occupancy and heat of dissociation of THF-CH$_4$ hydrates.

NOMENCLATURE

a   : parameter in the SRK equation of state
b   : parameter in the SRK equation of state
C_{mj} : Langmuir constant of component j on the cavity of type m
f_w^L : fugacity of pure water in liquid phase
f_w^{MT} : fugacity of water in empty hydrate lattice
$\hat{f}_w^H$: fugacity of water in hydrate phase
$\hat{f}_i^V$: fugacity of component i in vapor phase
g_0^E : excess Gibbs energy at zero pressure
g_∞^E : excess Gibbs energy at infinite pressure
Δh_w^{fus} : molar enthalpy difference between water and ice
Δh_w^{MT-I} : enthalpy difference between empty hydrate lattice and ice
ΔH_d : heat of dissociation
ΔH_s : heat of dissolution
υ : molar volume
$\Delta \upsilon_w^{fus}$: molar volume difference between water and ice
$\Delta \upsilon_w^{MT-I}$: volume difference between empty hydrate lattice and ice
x_i : mole fraction of component i in mixture
x_g : mole fraction of gas component in liquid phase
y_g : mole fraction of gas component in gas phase
z   : coordination number of the cavity
α : parameter in the SRK equation of state, α=a/bRT
ε : Kihara energy parameter
φ : fugacity coefficient
μ_w^H : chemical potential of water in filled hydrate lattice
μ_w^{MT} : chemical potential of water in empty hydrate lattice
$\Delta \mu_w^{MT-H}$: difference in chemical potential of water between empty and filled hydrate lattice
$\Delta \mu_w^0$: difference in chemical potential of water between empty hydrate lattice and water at T$_0$ and zero absolute pressure
ν_m : the number of cavities of type m per water molecule in the hydrate lattice

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REFERENCES

1. E. D. Sloan, *Clathrate hydrates of natural gases*, Marcel Dekker,

New York (1998).

2. K. A. Udachin, C. I. Ratcliffe and J. A. Ripmeester, *J. Supramol. Chem.*, **2**, 405 (2002).

3. J. A. Ripmeester, J. S. Tse, C. I. Ratcliffe and B. M. Powell, *Nature*, **325**, 135 (1987).

4. Y. F. Makogon, S. A. Holditch and T. Y. Makogon, *J. Petrol. Sci. Eng.*, **56**, 14 (2007).

5. J. S. Gudmundsson, M. Parlaktuna and A. A. Khokhar, *SPE Prod. Facil.*, **9**, 69 (1994).

6. Y. Seo, S. Lee, I. Cha, J. D. Lee and H. Lee, *J. Phys. Chem. B*, **113**, 5487 (2009).

7. Y. T. Seo, S. P. Kang and H. Lee, *Fluid Phase Equilib.*, **189**, 99 (2001).

8. R. M. de Deugd, M. D. Jager and J. D. Arons, *AIChE J.*, **47**, 693 (2001).

9. Q. Zhang, G. J. Chen, Q. Huang, C. Y. Sun, Z. Q. Guo and Q. L. Ma, *J. Chem. Eng. Data*, **50**, 234 (2005).

10. T. A. Strobel, C. A. Koh and E. D. Sloan, *Fluid Phase Equilib.*, **280**, 61 (2009).

11. J.-H. Yoon, M.-K. Chun and H. Lee, *AIChE J.*, **48**, 1317 (2002).

12. J.-H. Yoon, Y. Yamamoto, T. Komai and T. Kawamura, *AIChE J.*, **50**, 203 (2004).

13. H. Holderbaum and J. Gmehling, *Fluid Phase Equilib.*, **70**, 251 (1991).

14. K. Fischer and J. Gmehling, *Fluid Phase Equilib.*, **121**, 185 (1996).

15. J. Gmehling, J. Li and K. Fischer, *Fluid Phase Equilib.*, **141**, 113 (1997).

16. S. Horstmann, K. Fischer and J. Gmehling, *Fluid Phase Equilib.*, **167**, 173 (2000).

17. G. Soave, *Chem. Eng. Sci.*, **27**, 1197 (1972).

18. M. J. Huron and J. Vidal, *Fluid Phase Equilib.*, **3**, 255 (1979).

19. J.-H. Yoon, Y. Yamamoto, T. Komai, H. Haneda and T. Kawamura, *Ind. Eng. Chem. Res.*, **42**, 1111 (2003).

20. L. S. Tee, S. Gotoh and W. E. Stewart, *Ind. Eng. Chem. Fund.*, **5**, 356 (1966).

21. Y. P. Handa and J. S. Tse, *J. Phys. Chem.*, **90**, 5917 (1986).

22. R. Anderson, A. Chapoy and B. Tohidi, *Langmuir*, **23**, 3440 (2007).

23. A. Delahaye, L. Fournaison, S. Marinhas, I. Chatti, J.-P. Petitet, D. Dalmazzone and W. Furst, *Ind. Eng. Chem. Res.*, **45**, 391 (2006).

24. H. J. M. Hanley, G. J. Meyers, J. W. White and E. D. Sloan, *Int. J. Thermophys.*, **10**, 903 (1989).

25. T. Makino, T. Sugahara and K. Ohgaki, *J. Chem. Eng. Data*, **50**, 2058 (2005).

26. K. Otake, T. Tsuji, I. Sato, T. Akiya, T. Sako and M. Hongo, *Fluid Phase Equilib.*, **171**, 175 (2002).

27. Y. P. Handa, *Can. J. Chem.*, **62**, 1659 (1984).