

Molecular Cage Occupancy of Clathrate Hydrates at Infinite Dilution: Experimental Determination and Thermodynamic Significance

Jiwoong Seol,[†] Jong-Won Lee,[‡] Do-Youn Kim,^{†,§} Satoshi Takeya,^{||} John A. Ripmeester,[⊥] and Huen Lee^{*,†}

Department of Chemical and Biomolecular Engineering (BK21 Program) and Graduate School of EEWS, Korea Advanced Institute of Science and Technology (KAIST), 373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, Republic of Korea, Department of Environmental Engineering, Kongju National University, 275 Budae-dong, Cheonan, Chungnam 331-717, Republic of Korea, Research Institute of Instrumentation Frontier, National Institute of Advanced Industrial Science and Technology, Central 5, 1-1-1, Higashi, Tsukuba, Japan, and Steacie Institute for Molecular Sciences, National Research Council Canada, Ottawa, Ontario K1A 0R6, Canada

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This study focuses on the cage occupancy of guest molecules in the infinitely dilute state. At the extreme conditions of highly diluted guest concentrations the direct measurements of the cage occupancy ratio representing the competitive inclusion of multiguest species appear to be so difficult because of spectroscopic intensity limitation, but its thermodynamic significance might be considerable due to the fact that the infinite-dilution value of the cage occupancy ratio can provide the valuable thermodynamic information as a very unique and guest-specific parameter. To experimentally identify gaseous guest populations in structure I (sI) and structure II (sII) cages, we used the solid-state nuclear magnetic resonance (NMR), gas chromatography, and direct gas measurements. Furthermore, we derived the simple and generalized thermodynamic equation related to cage occupancies at infinite dilution from the van der Waals–Platteeuw model. Both experimental and predicted values agree well within the experimental error range.

Introduction

The unique molecular characteristics and guest dynamics of clathrate hydrates have been quite intensively explored for both scientific and technological interests using a variety of microscopic and macroscopic approaches. In particular, the reliable spectroscopic analysis of inclusion/exclusion phenomena of guest molecules occurring in the host–guest networks becomes indispensable for a clear understanding of the guest occupancy pattern greatly affected by an enclosing cage framework.^{1–3} The storage capacity of gaseous guest molecules in clathrate hydrate materials might be significantly enhanced by tuning the highly flexible cage lattice, which might be successfully achieved by an adequate variation of sensitive parameters.^{4,5} However, preceding to close the examination of this complicated guest behavior at the molecular level, the equilibrium guest population of clathrate hydrates having more than binary guests must be more precisely determined over the entire concentration range in the *a priori* and, more significantly, in the infinitely diluted state, where one guest species is nearly all depleted over another guest one. Accordingly, we propose a new characteristic guest-dependent variable, designated as the cage occupancy ratio at infinite dilution, like various types of thermodynamic parameters at infinite dilution. The most common example might be the activity coefficient at infinite dilution, which plays an essential role in the fluid-phase equilibria. To establish the basic concept

of this specific parameter, we attempted to carry out (1) the experimental measurements of cage occupancy over the entire concentration range, more focusing particularly on the highly diluted state of a specific guest, and (2) thermodynamic analysis for generalizing the extreme occupancy behavior with the adaptation of the simple van der Waals–Platteeuw model. For this purpose, we specially chose the binary gaseous mixture of CO₂ and CH₄ over any mixture concentrations due to its structure consistency.⁶ Moreover, we note that both CO₂ and CH₄ guests can be well-clathrated in a structure II small cage (sII-S) together with a water-soluble (or insoluble) liquid promoter. The cage occupancy ratio of the binary guests is expected to largely deviate from that of single guest depending on the distinctive host–guest interactions, which of course are strongly affected by the specific molecular details of the guest component. For structural and quantitative analysis as well as data cross-checking, we used the solid-state nuclear magnetic resonance (NMR), gas chromatography (GC), powder X-ray diffraction (PXRD), and direct gas release methods.

Experimental Methods

Pure ice was grated with a 100 μm sieve at 77 K and pressurized with the mixed gas of CO₂ and CH₄ at 4.0 MPa and 268 K. To attain the equilibrium state, the samples were matured at least for 7 days. We used ground ice powder to form the hydrate samples in this study, which is the same procedure as in our previous work.⁷ In our previous work, ice powder could be converted into gas hydrate sufficiently fast without any mechanical stirring. During the sample preparation, we kept pressurized ice powder for about 2 days until no pressure drops due to hydrate formation are observed. Then, thermal cycling across 273 K was used more than three times in order to convert unreacted water contents into gas hydrates. After 5 days, the

* To whom correspondence should be addressed. Tel.: +82-42-350-3917. Fax: +82-42-350-3910. E-mail: h_lee@kaist.ac.kr.

[†] KAIST.

[‡] Kongju National University.

[§] Current address: Research and Development Center, SK Engineering and Construction, 192-18 Kwanhun-dong, Jongno-gu, Seoul 110-300, Republic of Korea.

^{||} National Institute of Advanced Industrial Science and Technology.

[⊥] National Research Council Canada.

samples reached a steady state without any further pressure drop. For powder X-ray diffraction analysis to identify crystal structures of hydrate samples, we used the Rigaku D/max-RB with low temperature equipment. The apparatus has a maximum capacity of 12 kW and can be operated up to 83 K. Cu K α , with a wavelength of 1.5406 Å, was used as a light source, and the experiments were performed from 5.0 to 70.0° within a 2 θ angle with 0.05° step and 6 s of step time. During the diffraction measurements, the experimental temperature was maintained at about 153 K to prevent the dissociation of gas hydrate by using liquid nitrogen. The PXRD data confirmed that the mixed CO₂ + CH₄ hydrates form sI for all compositions.

To observe molecular behaviors in the hydrate samples, the ¹³C NMR spectra were recorded at 200 K by placing the hydrate samples in a 4 mm o.d. Zr rotor that was loaded into the variable-temperature (VT) probe on a Bruker 400 MHz solid-state NMR spectrometer. All spectra were recorded at a Larmor frequency of 100.6 MHz with magic angle spinning (MAS) at about 5 kHz under high-power proton decoupling (HPDEC). A pulse length of 2 μ s and pulse repetition delay of 20 s with radio frequency field strengths of 50 kHz corresponding to 5 μ s 90° pulses were used. The downfield carbon resonance peak of adamantane, assigned a chemical shift of 38.3 ppm at 300 K, was used as an external chemical shift reference. For the mixed sI hydrate samples of CO₂ compositions over 80 mol %, ¹³CH₄ gas was used to obtain intensified CH₄ peaks. The fractional cage occupancy of methane can be reliably determined directly from NMR peak intensity, but two peaks representing the encaged CO₂ in a structure I small cage (sI-S) and structure I large cage (sI-L) are known to be inseparable (Figure 1). This spectroscopic difficulty led us to adopt the GC for direct determination of CO₂ occupancy. We used the following equation:

$$-\Delta\mu_w^o = \frac{RT}{23} [3 \ln(1 - \theta_{L1} - \theta_{L2}) + \ln(1 - \theta_{S1} - \theta_{S2})] \quad (1)$$

where $\Delta\mu_w^o$ is the chemical potential of the empty lattice relative to ice, as commonly reported in the literature, θ denotes cage occupancy, the subscripts 1 and 2 indicate CO₂ and CH₄, respectively, and L and S are large and small cages, respectively. The cage occupancies of CH₄ are simply determined from the area integration of the NMR peak and the mole ratios of CO₂ and CH₄ captured in hydrate that are known from GC analysis,

$$\frac{A_L}{A_S} = \frac{3\theta_{L2}}{\theta_{S2}} \quad (2)$$

$$\frac{M_1}{M_2} = \frac{\theta_{S1} + 3\theta_{L1}}{\theta_{S2} + 3\theta_{L2}} \quad (3)$$

The A_L/A_S is the area ratio of the ¹³C NMR peaks of CH₄, while M_1/M_2 is the mole ratio of CO₂ and CH₄ measured with GC. Assuming the nearly full occupation of guests 1 and 2 in sI-L,

$$\theta_{L1} + \theta_{L2} = 0.98 \quad (4)$$

In general, experimental values of cage occupancy reported by many researchers are located between 0.98 and 0.99.⁸ In addition, considering moderate pressure conditions and other modeling work,⁹ we used a cage occupancy of 0.98 in large cages for the binary CH₄ + CO₂ system. Combining the above eqs 1–4, we can determine the CO₂ as well as CH₄ distributions in sI-S and sI-L.

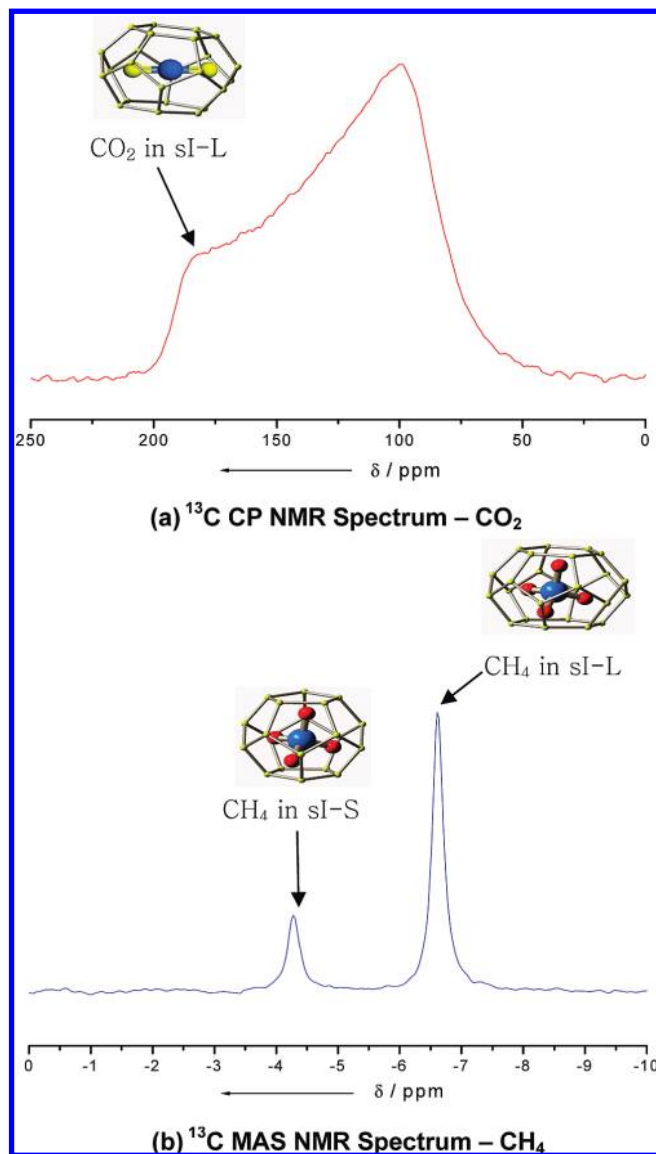


Figure 1. ¹³C NMR spectra for pure CO₂ and CH₄ hydrates.

For the sII hydrate sample, a stoichiometric 5.56 mol % tetrahydrofuran (THF) solution was prepared, frozen, grated using a 100 μ m sieve at 77 K, and then allowed to react with the CH₄ and CO₂ mixture. The GC was used to analyze the hydrate-phase compositions.

Results and Discussion

I. sI (CO₂ + CH₄). The crystal structure of the hydrates were obtained to be sI by the PXRD, and the measured lattice parameters (11.81 ± 0.02 Å at 123 K) over the whole CO₂ concentration range showed good agreement with reported ones.¹⁰ The solid-state ¹³C NMR spectra representing CH₄ distributions in hydrate cages at various mixed gas concentrations are shown in Figure 2. Figure 3 shows a plot of the cage occupancy ratio ($\theta_{L,CH_4}/\theta_{S,CH_4}$) against gas-phase compositions, which is calculated using guest distributions in Figure 2. As it can be seen in this figure, the $\theta_{L,CH_4}/\theta_{S,CH_4}$ values continue to decrease below unity with increased CO₂, eventually dropping below 0.5 at dilute CH₄ concentrations in the gas mixture. This guest occupancy pattern implies that when two guest species of CO₂ and CH₄ compete for filling the empty cages, sI small cages can be easily occupied by CH₄ than CO₂ molecules, while CO₂, having larger molecular diameter than CH₄, becomes more

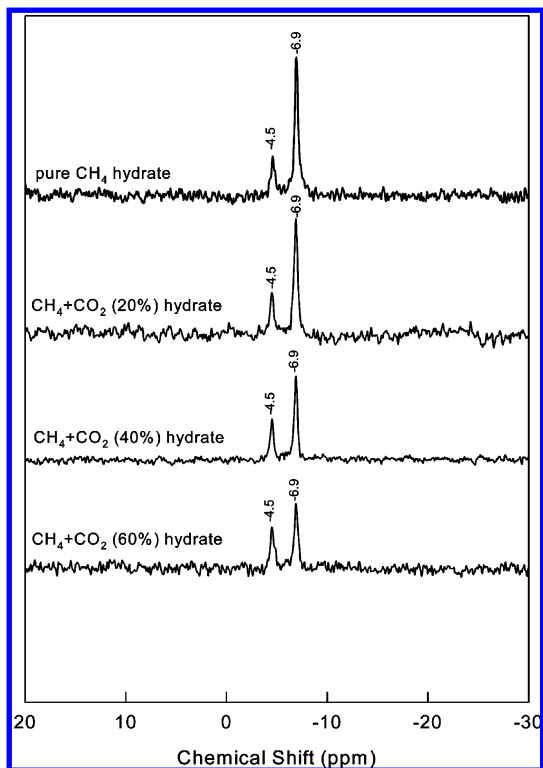


Figure 2. ^{13}C NMR spectra for mixed $\text{CH}_4 + \text{CO}_2$ hydrates made from various gas concentrations.

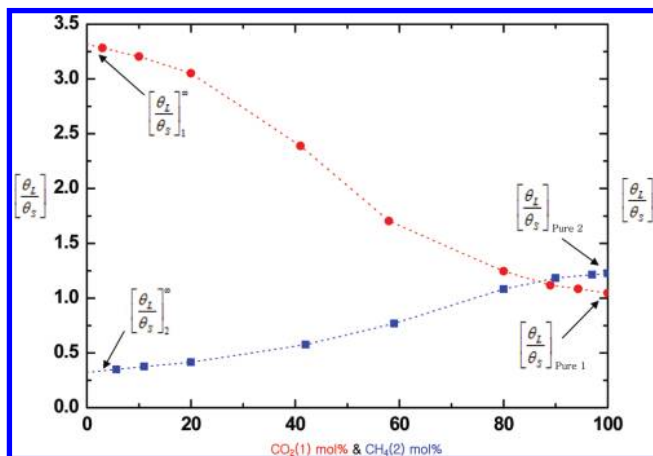


Figure 3. Cage occupancy ratios for CO_2 (filled circles, 1) and CH_4 (filled squares, 2) molecules as a function of composition of the source gas. The cage occupancy ratio for both CH_4 and CO_2 decreases as the concentration of CO_2 in the source gas increases.

active in occupying sI-L $5^{12}6^2$ cages.¹¹ Here, we define the cage occupancy ratio at the infinite dilution of CH_4 , $[\theta_L/\theta_S]_1^\infty$. This limiting value refers to the CH_4 population in the large excess of CO_2 and is found to be around 0.33 according to the present experimental results.

However, GC in addition to solid-state NMR was also used to identify CO_2 distribution in hydrate cages because CO_2 molecules in small and large cages cannot be distinguished in a quantitative way from NMR itself. The cage occupancy ratios for both guest molecules decrease as the CO_2 concentration increases over the whole range. At both extremes of pure and infinitely dilute states, the cage occupancy ratio for CH_4 and CO_2 changed from 1.27 to 0.33 and from 3.30 to 1.05, respectively. Considering the large cage occupancy of 0.98, the ratio around 1.05 indicates that small cage occupancy of CO_2 molecules is about 0.93, while smaller cage occupancy in the

small cages was reported by Udachin et al.¹² with single crystal samples. Such a difference can be mainly explained by different sample preparation methods as well as some unknown factors because the cage occupancy is strongly dependent on formation conditions. However, the cage occupancy of 0.93 is close to the value reported by Ikeda et al.,¹³ whose samples were also prepared from ground ice powder and through thermal cycling. As expected, the CO_2 guests are more preferably encaged in sI-L than sI-S at low CO_2 concentration, while the CO_2 occupancy in sI-S gradually increases as the CO_2 concentration increases, eventually reaching unity or approximately thereabouts. Thermodynamic properties at infinite dilution have been extensively used for modeling complex fluid-phase equilibria because of their unique role in understanding molecular interactions. Accordingly, the cage occupancy behavior of binary or multiguests at infinite dilution might comprise a certain physicochemical significance that can be useful as the fundamental information for analyzing a variety of inclusion phenomena. As the first approach we attempted to use the simple van der Waals–Platteeuw model,¹⁴ which is expressed as

$$\theta_{ml} = \frac{C_{ml}f_l}{1 + \sum_i C_{mi}f_i} \quad (5)$$

$$f_l = \phi_l y_l P \quad (6)$$

where θ_{ml} indicates the cage occupancy of component l in cage m , C_{ml} the Langmuir constant of component l in cage m , f_l the fugacity of component l , y_l the mole fraction of component l in the vapor phase, and P the pressure. In this step, we should note that the van der Waals–Platteeuw model fundamentally assumes that free energy difference does not depend on the nature of the guest. Then,

$$\theta_{s1} = \frac{C_{s1}f_1}{1 + C_{s1}f_1 + C_{s2}f_2} \quad \text{and} \quad \theta_{L1} = \frac{C_{L1}f_1}{1 + C_{L1}f_1 + C_{L2}f_2} \quad (7)$$

$$\theta_{s2} = \frac{C_{s2}f_2}{1 + C_{s1}f_1 + C_{s2}f_2} \quad \text{and} \quad \theta_{L2} = \frac{C_{L2}f_2}{1 + C_{L1}f_1 + C_{L2}f_2} \quad (8)$$

In addition, the cage occupancy ratio for each hydrate cage is as follows:

$$\frac{\theta_{L1}}{\theta_{s2}} = \frac{C_{L1}(1 + C_{s1}f_1 + C_{s2}f_2)}{C_{s1}(1 + C_{L1}f_1 + C_{L2}f_2)} \quad \text{and} \quad \frac{\theta_{L2}}{\theta_{s2}} = \frac{C_{L1}(1 + C_{s1}f_1 + C_{s2}f_2)}{C_{s1}(1 + C_{L1}f_1 + C_{L2}f_2)} \quad (9)$$

At the infinite dilution of CH_4 or CO_2 , both (y_2 and f_2) and (y_1 and f_1) approach zero and the cage occupancy ratio of both at infinite dilution can be expressed by the following equation:

$$\left[\frac{\theta_L}{\theta_S}\right]_1^\infty = \frac{C_{L1}(1 + C_{s2}f_2)}{C_{s1}(1 + C_{L2}f_2)} \quad \text{and} \quad \left[\frac{\theta_L}{\theta_S}\right]_2^\infty = \frac{C_{L2}(1 + C_{s1}f_1)}{C_{s2}(1 + C_{L1}f_1)} \quad (10)$$

As the $C_{mi}f_i$ value is much higher than unity, particularly at a relatively high pressure of 4.0 MPa,

$$1 + C_{m1}f_1 \cong C_{m1}f_1 \quad (11)$$

Then, the multiplication of both ratios at infinitely dilute conditions becomes

$$\left[\frac{\theta_L}{\theta_S} \right]_1^\infty \left[\frac{\theta_L}{\theta_S} \right]_2^\infty = \frac{C_{L1}C_{S2}f_2C_{L2}C_{S1}f_1}{C_{L1}C_{S2}f_2C_{L2}C_{S1}f_1} = 1 \quad (12)$$

Our experimental data come out to be

$$\lim_{y_1 \rightarrow 0} \left(\frac{\theta_{L1}}{\theta_{S1}} \right) = \left[\frac{\theta_L}{\theta_S} \right]_1^\infty = 3.30 \quad \text{and} \quad \lim_{y_2 \rightarrow 0} \left(\frac{\theta_{L2}}{\theta_{S2}} \right) = \left[\frac{\theta_L}{\theta_S} \right]_2^\infty = 0.331$$

Those values are selected at a concentration of 5/95 CO₂/CH₄ and 95/5 CO₂/CH₄, respectively. Therefore,

$$\left[\frac{\theta_L}{\theta_S} \right]_1^\infty \left[\frac{\theta_L}{\theta_S} \right]_2^\infty = 1.09 \quad (13)$$

It is noteworthy that the experimentally determined value also approaches unity. We note that eq 12 shows a definite relationship between the cage occupancies of binary guests without having any other thermodynamic variables such as chemical potential, Langmuir constants, and so on. This result further implies that the cage occupancy ratios of specific guest species at infinite dilution possess their own molecular characteristics in an ice-like hydrate matrix. More significantly, during the derivation of eq 12, no drastic assumptions were made and thus this equation can be extended to other hydrate systems as a generalized thermodynamic consequence.

II. sII Hydrate (THF + CO₂ + CH₄). We apply the basic sI concepts to sII having a water-soluble liquid guest and binary gaseous guests.

$$\theta_{S1} = \frac{C_{S1}f_1}{1 + C_{S1}f_1 + C_{S2}f_2} \quad \text{and} \quad \theta_{S2} = \frac{C_{S2}f_2}{1 + C_{S1}f_1 + C_{S2}f_2} \quad (14)$$

Then

$$\theta_{S1}^{\infty} = \lim_{y_1 \rightarrow 0} \theta_{S1} \approx \frac{C_{S1}f_1^\infty}{1 + C_{S2}f_2} \quad \text{and} \quad \theta_{S2}^{\infty} = \lim_{y_2 \rightarrow 0} \theta_{S2} \approx \frac{C_{S2}f_2^\infty}{1 + C_{S1}f_1} \quad (15)$$

The cage occupancy ratio of infinite dilution to pure sII becomes

$$\frac{\theta_{S1}^{\infty}}{\theta_{S1}^{\text{pure1}}} = \frac{C_{S1}f_1^\infty}{1 + C_{S2}f_2} \frac{1 + C_{S1}f_1}{C_{S1}f_1} \quad \text{and} \quad \frac{\theta_{S2}^{\infty}}{\theta_{S2}^{\text{pure2}}} = \frac{C_{S2}f_2^\infty}{1 + C_{S1}f_1} \frac{1 + C_{S2}f_2}{C_{S2}f_2} \quad (16)$$

where $\theta_{S1}^{\text{pure1}}$ and $\theta_{S2}^{\text{pure2}}$ represent the small cage occupancy fractions of gaseous guests 1 and 2 in their pure sII hydrate systems, respectively. The experimentally determined values for THF + CO₂ (1) and THF + CH₄ (2) are $\theta_{S1}^{\text{pure1}} = 0.42 \pm 0.03$ and $\theta_{S2}^{\text{pure2}} = 0.81 \pm 0.04$, respectively.

Thus, the product of those two terms becomes

$$\left(\frac{\theta_{S1}^{\infty}}{\theta_{S1}^{\text{pure1}}} \right) \left(\frac{\theta_{S2}^{\infty}}{\theta_{S2}^{\text{pure2}}} \right) \approx \frac{f_1^\infty f_2^\infty}{f_1^{\text{pure1}} f_2^{\text{pure2}}} = y_1^\infty y_2^\infty \quad (17)$$

For diluted solution, the $f_i = y_i f_i^{\text{pure}}$ can be applied well with a reasonable accuracy.

The equilibrium hydrate data of the THF + CO₂ + CH₄ system are presented in Figure 4. At 8.2/91.8 CO₂/CH₄ and 94.2/5.8 CO₂/CH₄

$$\left(\frac{\theta_{S1}^{\infty}}{\theta_{S1}^{\text{pure1}}} \right) \left(\frac{\theta_{S2}^{\infty}}{\theta_{S2}^{\text{pure2}}} \right) = 4.668 \times 10^{-3} \quad \text{and} \quad y_1^\infty y_2^\infty = 4.756 \times 10^{-3}$$

As it can be seen from the above calculations, both results showed good agreement. Even at the guest compositions of 40.8/59.2 CO₂/CH₄ and 83.3/16.7 CO₂/CH₄, at which binary guests both occupy substantial fractions in the clathrate hydrate, the eq 14 is found to be still valid, as follows.

$$\left(\frac{\theta_{S1}}{\theta_{S1}^{\text{pure1}}} \right) \left(\frac{\theta_{S2}}{\theta_{S2}^{\text{pure2}}} \right) = 6.447 \times 10^{-2} \quad \text{and} \quad y_1 y_2 = 6.814 \times 10^{-2}$$

Finally, we tested this equality at one hydrate composition of 47.0/53.0 CO₂/CH₄.

$$\left(\frac{\theta_{S1}}{\theta_{S1}^{\text{pure1}}} \right) \left(\frac{\theta_{S2}}{\theta_{S2}^{\text{pure2}}} \right) = 2.586 \times 10^{-1} \quad \text{and} \quad y_1 y_2 = 2.491 \times 10^{-1}$$

Here, we can presumably conclude that eq 17, even though it was derived at the highly dilute condition of guest compositions, is suited for the entire composition range with the adaptation of the following generalized expression.

$$\left(\frac{\theta_{S1}}{\theta_{S1}^{\text{pure1}}} \right) \left(\frac{\theta_{S2}}{\theta_{S2}^{\text{pure2}}} \right) = y_1 y_2 \quad (18)$$

However, we need to realize that the real values of $\theta_{S1}/\theta_{S1}^{\text{pure1}}$ and $\theta_{S2}/\theta_{S2}^{\text{pure2}}$ are not equal to y_1 and y_2 , respectively, but the products are the same.

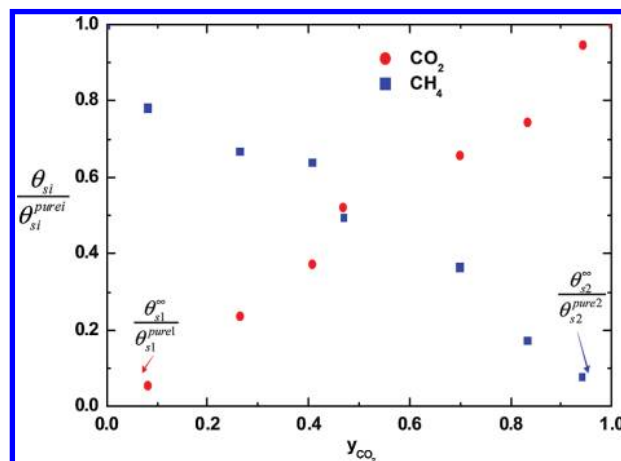


Figure 4. Cage occupancy ratios for CO₂ (filled circles, 1) and CH₄ (filled squares, 2) molecules as a function of composition of the source gas in THF + CO₂ + CH₄. The cage occupancy ratios for both CH₄ and CO₂ decrease as the concentration of CO₂ in source gas increases.

As pointed out by researchers,¹⁵ the gas distribution equilibria given by activity coefficients of a solute in a solution at infinite dilution are very useful for evaluating Gibbs free energy, that is, the chemical potential for hydrate formation. Even though we used ice as a starting material to react with the binary gas mixture, gas solubility in ice is thought to play a critical role in forming binary hydrates. Such evaluation can be very useful when we deal with a hydrate-base including a diluted guest such as gas separation. In addition, understanding phase behaviors at infinite dilution can be critical when explaining the tuning mechanism in the binary hydrate system. We showed that the statistical thermodynamic equation agrees reasonably well with our experimental data. However, we used some assumptions (e.g., sufficiently large driving force during hydrate formation) to apply the equation to our experimental results. Therefore, the prediction equation is not necessarily more reliable than experimentally obtained results. Rather, those two methods should be combined properly for evaluating formation behaviors at infinite dilution.

Conclusions

In this study, we first attempted to thermodynamically derive the hydrate–cage occupancy relationship of binary guests at the infinitely dilute state. The resulting equation was found to explain experimentally obtained spectroscopic results well. The limitation of the present approach is that the binary guests compete with each other in order to occupy the empty cages and should be both truly and stably engaged with substantial fractions. We expect that the binary guest relationship can be extended and generalized to the multiguest systems irrespective of guest molecular details. Further research on (1) how to handle structure H (sH) hydrates, (2) the extension of narrowly limited infinite dilution to the full concentration range, and (3) how to treat other organic host materials besides water is required to achieve a better understanding of the unique guest occupancy pattern. However, the most significant feature of this work is to provide the characteristic variable defined at infinite guest dilution state, which might play a significant role in understanding guest occupancy details and, furthermore, to seek a clue

for designing and synthesizing the most efficient hydrate structures to store gaseous molecules for a specific purpose.

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