^{13}C NMR Analysis and Gas Uptake Measurements of Pure and Mixed Gas Hydrates: Development of Natural Gas Transport and Storage Method using Gas Hydrate

Yu-Taek Seo and Huen Lee[†]

Department of Chemical Engineering, Korea Advanced Institute of Science and Technology,
373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, Korea
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Abstract−^{13}C NMR spectra were obtained for pure CH_4, mixed CH_4+THF, and mixed CH_4+Neohexane hydrates in order to identify hydrate structure and cage occupancy of guest molecules. In contrast to the pure CH_4 hydrates, the NMR spectra of the mixed CH_4+THF hydrate verified that methane molecules could occupy only the small portion of 5^{12} cages because the addition of THF, water-soluble guest component, to aqueous solution prevents the complete filling of methane molecules into small cages. Furthermore, from these NMR results one important conclusion can be made that methane molecules can't be enclathrated at all in the large $5^{12}6^4$ cages of structure II. In addition, gas uptake measurements were carried out to determine methane amount consumed during pure and mixed hydrate formation process. The moles of methane captured into pure CH_4 hydrate per mole of water were found to be similar to the full occupancy value, while the moles of methane captured into the mixed CH_4+THF hydrate per moles of water were much lower than the ideal value. The overall results drawn from this study can be usefully applied to storage and transportation of natural gas.

Key words: Hydrate, ^{13}C NMR Analysis, Methane, THF, Neohexane

INTRODUCTION

Gas hydrates are crystalline compounds that are formed by physically stable interaction between water and relatively small guest molecules. At high pressure and low temperature conditions water molecules are connected by hydrogen bonds and form various structures of cavities. The low molecular-weight gas molecules such as methane, nitrogen, and carbon dioxide are captured into these cavities and finally transformed to solid hydrates. These non-stoichiometric crystalline compounds are divided into three distinct structures I, II, and H, which differ in cavity size and shape [Sloan, 1998]. A new mixed structure consisting of alternating stacks of structures H and II was also reported in the recent literature [Udachin and Ripmeester, 1999]. Recently, many researchers have suggested the potential application of crystal hydrate nature to large-scale storage and transportation of natural gas. Gudmundsson et al. in 1994 proposed an efficient transportation means of natural gas as frozen hydrate that could remain stable at atmospheric pressure and below a freezing point of water. A hydrate slurry process using the mixture of frozen hydrate and refrigerated crude oil was also described and surveyed as an alternative method for natural gas transportation [Gudmundsson et al., 2002]. Zhong et al. in 2000 investigated experimentally the effect of surfactant on gas hydrate formation. They reported that the micellar solutions were found to increase gas hydrate formation rate and also observed that the formed hydrate particles were packed as a symmetrical and porous mass. The storage capability of each hydrate structure was investigated by Khokhar et al. They also examined the PVP effect on the formation kinetics of structure H hydrate. In our previous studies, the stabilization effect

of cyclic ethers such as THF and 1,4-dioxane on hydrate formation was also examined in another previous study [Seo and Lee, 2001; Seo et al., 2001] to determine the degree of equilibrium shift due to the presence of these stabilizers. As related research concerning the mixed hydrate, three-phase equilibria consisting of vapor, water-rich liquid and solid hydrate were measured in the previous study [Seo and Lee, 2001; Lee et al., 2002] to examine the phase boundary of hydrate stability region for the aqueous solutions containing two guest molecules of carbon dioxide and methane.

All significant investigations concerning the storage of natural gas were mainly focused on the absolutely captured amount of methane gas largely depending on hydrate-forming conditions. However, any attempts to draw the NMR information related to actual cage occupancy have not yet been done in spite of its importance to industrial applications. The NMR technique can provide both qualitative and quantitative hydrate characteristics such as structure types, cage occupancies, and guest-component compositions [Ripmeester and Ratcliff, 1988]. All these characteristics could be used to develop the hydrate-based process. In this connection, we focused on understanding inclusion phenomena as well as structural characteristics of various hydrate-forming systems with both quantitative and qualitative results of the NMR analysis. A predictive model based on statistical thermodynamics was also developed to predict hydrate equilibrium conditions and cage occupancies of guest molecules. The calculated cage occupancies were compared with the measured data from NMR spectroscopy. As an indirect approach, methane gas uptake into gas hydrate was also measured and compared with cage occupancy results obtained from NMR spectroscopy.

EXPERIMENTAL SECTION

Three phase equilibria of hydrate, water-rich liquid, and vapor

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[†]To whom correspondence should be addressed.
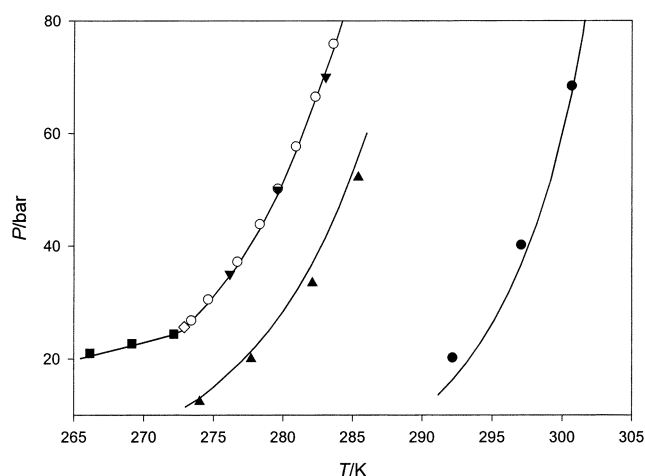E-mail: h_lee@kaist.ac.kr

(H-L$_w$-V) and hydrate, ice, and vapor (H-I-V) were first measured as a preliminary basis to validate hydrate formation condition. The detailed experimental apparatus and procedure were described in the previous work [Seo et al., 2000]. Basically, the apparatus was constructed to measure hydrate dissociation pressures through visual observation of phase transitions.

To identify hydrate structure and cage occupancy of guest molecules, a Bruker DSX400 NMR spectrometer was used in this study. Spectra were recorded at 243 K by placing samples within a 4 mm o.d. Zirconia rotor loaded into a variable temperature probe. All ^{13}C NMR spectra were recorded at a Larmor frequency of 100.6 MHz with magic angle spinning (MAS) at about 3 kHz. A pulse length of 2 μs and pulse repetition delay of 10-20 s under proton decoupling were employed when the radio frequency field strengths of 50 kHz corresponding to 5 μs 90° pulses were used. Cross-Polarization (CP) MAS spectra were also acquired for checking the signals from gas components. The down-field carbon resonance peak of adamantane, assigned a chemical shift of 38.3 ppm at 300 K, was used as an external chemical shift reference. The hydrate samples were prepared in a mechanically stirred reactor as shown in Fig. 1. Pure methane hydrate (structure I) was formed from finely powdered ice particles that were crushed in a mortar and pestle. Large ice particles were remove.
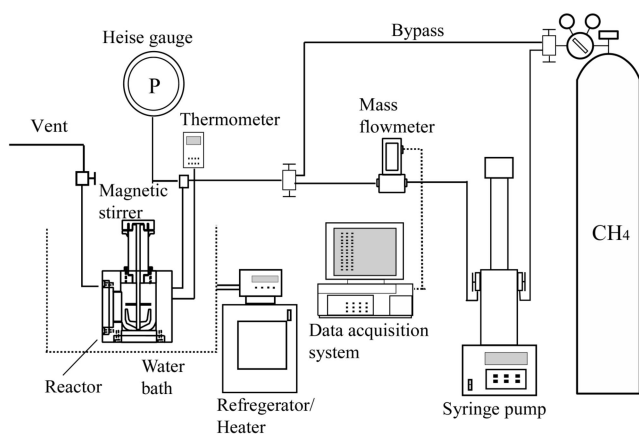
Many literature sources exist for three-phase equilibria (H-L$_w$-V) of the binary methane and water system, and with the aid of these experimental data several proper thermodynamic models were also developed to predict the equilibrium conditions. The presence of third components clearly makes a drastic difference in phase behavior. Therefore, three phase equilibria, H-L$_w$-V, of the CH$_4$+THF+ water and four phase equilibria, H-L$_w$-L$_{hc}$-V, of the CH$_4$+Neohxane+ water systems were preliminarily measured at various temperature conditions, and the overall results were presented in Table 1 and Fig. 2. The CH$_4$+water equilibrium data were taken for checking the used experimental apparatus and compared with the literature data [Adisasmito et al., 1991]. As shown in Fig. 2, the presence of THF and neohexane induced a hydrate-forming condition to be more favorable by lowering pressure and raising temperature for forming the mixed hydrates compared with the corresponding condition of pure methane hydrate. It must be noted that THF itself can play a role in forming structure II hydrate as a guest molecule and

Table 1. Three-phase equilibria of the binary CH$_4$+water, ternary CH$_4$+THF+water and CH$_4$+neohexane+water systems

System		Pressure (bar)	Temperature (K)
CH$_4$+water	H-I-V	21.0	266.2
		22.7	269.1
		24.4	272.2
	H-L$_w$-V	35.0	276.2
		50.0	279.6
		70.0	283.2
CH$_4$+THF+water	H-L$_w$-V	20.2	292.1
		40.2	297.0
		68.4	300.6
CH$_4$+neohexane+water	H-L$_{hc}$-L$_w$-V	12.4	274.0
		20.0	277.7
		33.4	282.1
		52.2	285.4

Fig. 2. Experimental and predicted hydrate dissociation pressures of pure CH$_4$ hydrate ("○" represents the results of Adisasmito et al., "▼" and "■" are this work for H-L$_w$-V and H-I-V respectively), mixed CH$_4$+THF hydrate ("●" is this work) and mixed CH$_4$+neohexane hydrate ("▲" is this work). Solid lines are predicted from the statistical thermodynamic model.

only occupy the large cages because of its size. The formation of mixed hydrate from methane and THF was also verified as structure II; the main function of THF is to stabilize the formed hydrate structure judging from the H-L$_w$-V phase boundary shown in Fig. 2. It was known that neohexane itself couldn't participate in forming the hydrate structure, but could be forming structure H hydrate in the presence of help gas like methane and also stabilize the hydrate structure, reducing the hydrate formation pressure at corresponding temperature of pure CH$_4$ hydrate. The stabilization effect of THF on hydrate formation was found to be higher than that of neohexane from above phase behavior. However, this stabilizing phenomenon can be also created by shifting the hydrate forming H-L$_w$-V phase boundary to the H-I-V phase boundary, which greatly reduces the required equilibrium pressure. In the present study, this

Fig. 1. Experimental apparatus for gas uptake measurements.

pressure reduction was made by using ice particles at a lower temperature than the lower quadruple point (272.2 K and 25 bar for methane) at which the four phases of hydrate-ice, water-rich liquid, and vapor (H-I-L_w-V)-coexisted. The H-I-V phase boundary emanated from this lower quadruple point and moved to a lower temperature and pressure region. Accordingly, the hydrate formation pressure could be reduced below 25 bar.

For the prediction of hydrate phase equilibria, several predictive models have been reported adopting the statistical thermodynamic approach proposed by van der Waals and Platteeuw [van der Waals and Platteeuw, 1959]. The chemical potential of water in the hydrate phase was related to that in the hypothetical empty hydrate lattice. The fractional occupancy of guest molecules in the hydrate cavity is given by classical interaction between host water molecules and an encaged guest molecule in each cage with the assumption that the lattice cavity is spherically symmetric. The Kihara potential with the spherical core assumption is used for the cavity potential function [Parrish and Prausnitz, 1972]. The Kihara hard-core parameter, a, is given in the literature [Lundgaard and Mollerup, 1991], while the energy and size parameters, ε and σ which are included in θ_{ki}, are determined by regressing the experimental data of hydrate phase equilibria with Eq. (1) and Eq. (2) for chemical potential difference of water:

$$\Delta\mu_w^{MT-H} = RT\sum_i \nu_i \ln\left(1 + \sum_k \theta_{ki}\right) \quad (1)$$

$$\frac{\Delta\mu_w^H}{RT} = \frac{\Delta\mu_w^0}{RT_0} - \int_{T_0}^{T}\frac{\Delta h_w}{RT^2}dT + \int_{P_0}^{P}\frac{\Delta\nu_w}{RT}dP - \ln\gamma_w\chi_w \quad (2)$$

where ν_i is the number of type i cages per water molecule, and θ_{ki} the fractional occupancy of type i cages with type k guest molecules, γ_w and χ_w are activity coefficient and mole fraction of water, respectively. All the structure parameters of structure I, II and H hydrate were cited from the literature. In addition, Δh_w and $\Delta\nu_w$ are the molar difference in enthalpy and volume between the hypothetical empty hydrate cage and pure ice or liquid water phase [Holder et al., 1988; Englezos, 1992]. To calculate the solubility of structure II guest molecules, THF, the last term expressed in Eq. (2) was replaced with water activity by using the proper EOS because of the significant solubility of THF molecules. The SRK-EOS incorporated with an MHV2 mixing rule was used to determine the corresponding fugacity. The modified UNIFAC was chosen and applicable to the structure II and H hydrate systems because no binary interaction parameters are available for the pairs consisting of liquid and gaseous guests. All the UNIFAC parameters used in this study were cited from the literature [Reid et al., 1987]. A new approach for calculating the fugacity of ice and predicting the H-I-V equilibria for structure I methane hydrate was attempted in this work. At the lower quadruple point the following expressions must hold for the fugacity of ice and pure liquid water [De Swaan Arons and Diepen, 1963]:

$$\ln f_w^I = \ln P_{vp}^{sat,I} + \int_0^P \frac{\nu_w^I}{RT}dP \quad (3)$$

and

$$\ln f_w^L = \ln P_{vp}^{sat,L} + \int_0^P \frac{\nu_w^L}{RT}dP \quad (4)$$

Table 2. Optimized kihara parameters of methane, THF, and neohexane determined from the measured three-phase equilibrium data

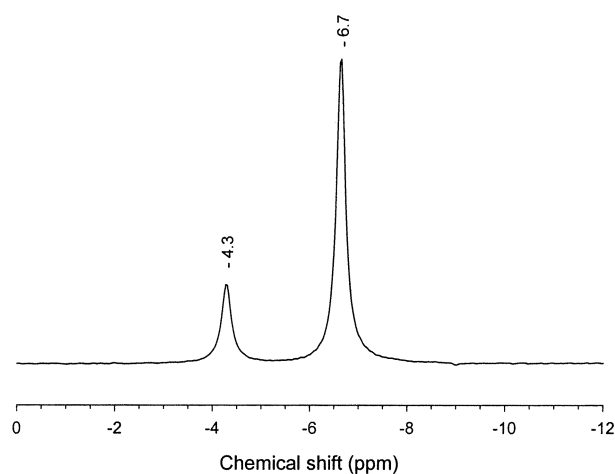|	a (Å)	σ (Å)	ε/κ (K)
CH_4	0.3000	3.3000	154.54
THF	0.9643	3.2038	243.27
Neohexane	1.0481	3.1126	348.26

Using the Clausius-Clapeyron equation, the fugacity of ice is related to that of pure liquid water by the following:

$$f_w^I = f_w^L \exp\left(-\int_{T^0}^{T}\frac{\Delta h_w^{fus}}{RT^2}dT + \int_0^P \frac{\Delta\nu_w^{fus}}{RT}dP\right) \quad (5)$$

This equation does not need the expression of the vapor pressure of ice and only uses the physical property difference between the ice and supercooled liquid water. Therefore, regardless of temperature range of the hydrate system considered, we can obtain a unique expression for the fugacity of water in the filled hydrate phase. The equilibrium P-T data was used to determine the Kihara parameters of THF and neohexane. The resulting values are presented in Table 2, and these calculated Kihara parameters were used to predict hydrate equilibrium pressures. Both experimental and predicted results agreed well for all the systems examined in this study.

1. NMR Spectroscopic Analysis

One of objectives of this work was to compare the formed structures and compositions of mixed hydrates encaging two different types of guest molecules with those of simple hydrates encaging only a kind of guest molecules. Although the small 5^{12} cages commonly exist in all hydrate structures, the symmetry and size of these small cages were different and their behavior toward guest molecules should be quite different [Ripmeester and Ratcliffe, 1998]. Accordingly, the guest molecules captured into these cages showed different chemical shifts in NMR spectra. Due to this chemical shift difference, the obtained NMR peaks could be used as a unique indicator of structure type. Figs. 3-5 represent three ^{13}C NMR spectra, which were used to identify the chemical shifts of CH_4 in the

Fig. 3. ¹³C MAS NMR spectra of pure CH₄ hydrate (structure I) at 243 K. Methane molecules were represented by two peaks, small cages at −4.3 ppm and large cages at −6.7 ppm.
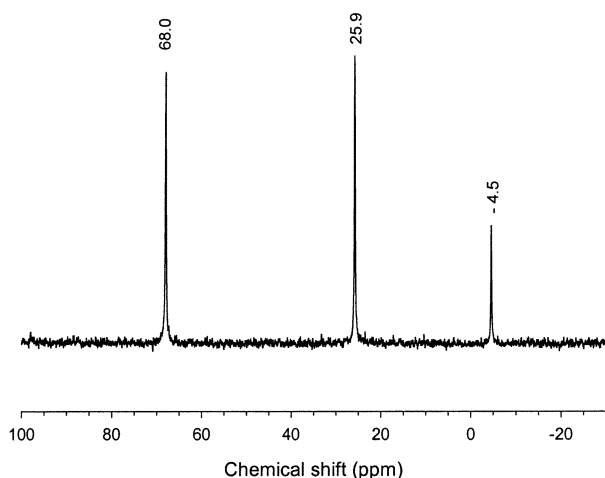
Fig. 4. [13]**C MAS NMR spectra of mixed CH₄+THF hydrate (structure II) at 243 K. Methane molecules occupied only in small cages and appeared at about −4.5 ppm and THF molecules occupied in large cages were represented by two resonances (-C-C- at 25.9 ppm, -C-O-C- at 68.0 ppm).**

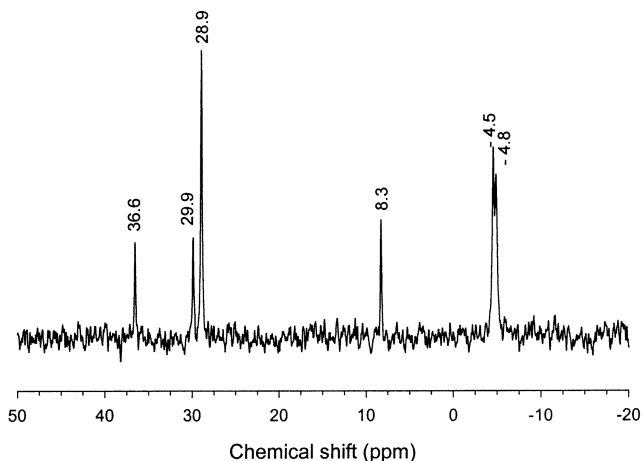**Fig. 5.** [13]**C MAS NMR spectra of mixed CH₄+Neohexane (structure H) hydrate at 243 K. Methane molecules are represented by two peaks, small cages at −4.5 ppm and medium cages at −4.9 ppm. Neohexane molecules occupyingthe large cages are represented by four distinct peaks from 8.3 to 36.6 ppm.**

cages of structure I, II, and H hydrate. The signals from gas phase components were checked not only by the chemical shifts of peaks but also by comparing CP-MAS and MAS spectra of the same sample. Fortuitously, all peaks in our MAS spectra were confirmed to be from hydrates but not from gas phase components. Fig. 3, representing pure CH₄ hydrate, indicates that methane molecules were captured into both small and large cages of structure I and showed peaks of small cages at −4.3 and large cages at −6.7 ppm. The large cage peak was intenser than the small cage one, confirming the methane molecules in large cages were abundant in structure I [Subramanian et al., 2000]. Fig. 4 is the ^{13}C NMR spectrum of mixed CH₄+THF hydrate having two guest molecules of methane and THF. Methane molecules were found to be occupied only in the small cages of structure II hydrate, represented by one peak (at about −4.5 ppm).

However, THF molecules were captured in a large fraction of large cages and identified by two resonances (-C-C- at 25.9 ppm, -C-O-C- at 68.0 ppm). Although the stoichiometric ratio of small to large cages appeared to be 2 : 1 in the unit cell of structure II hydrate, the corresponding NMR spectra indicated that the intensity of methane peak was quite low, which naturally confirmed that only a small fraction of small cages was filled with methane molecules. Subramanian et al. in 1999 also obtained similar results for mixed CH₄+ THF hydrate from Raman spectroscopic analysis and suggested that the larger guest molecule THF almost exclusively occupies the large cages, thus restricting CH₄ to only small cages in the hydrate. However, they didn't report the absolute cage occupancy values. Fig. 5 shows the ^{13}C NMR spectra of mixed CH₄+Neohexane hydrate having guest molecules of methane and neohexane. The large $5^{12}6^8$ cages are filled with neohexane only, represented by four distinct peaks from 8.3 to 36.6 ppm. On the other hand, methane molecules were found to enter both the small 5^{12} and medium $4^35^66^3$ cages of structure H hydrate, represented by two peaks (small cages at −4.5 ppm, medium cages at −4.8 ppm). The size of small cages of structure H was assumed to be the same as that of structure II hydrate [Sloan, 1998]; therefore, the chemical shift of methane in small cages of mixed CH₄+Neohexane hydrate was the same as that of mixed CH₄+THF hydrate. The stoichiometric ratio of small to medium cages appears to be 3 : 2 in the unit cell of structure H hydrate. In this connection, the relative integrated intensities of NMR spectra showed the value of area ratio, $A_{M,CH_4}/A_{S,CH_4}$=0.8168, confirming the methane molecules in small cages were more abundant in medium cages of structure H.

The relative integrated intensities of ^{13}C MAS spectra must be combined with the following statistical thermodynamic expression representing the chemical potential of water in structure I hydrate in order to determine the occupancies of methane in the small and large cages.

$$\mu_w(h) - \mu_w(h^o) = \frac{RT}{23}[3\ln(1-\theta_{L,CH_4}) + \ln(1-\theta_{S,CH_4})] \qquad (6)$$

where $\mu_w(h^o)$ is the chemical potential of water molecules of a hypothetical empty lattice and, θ_S and θ_L the fractional occupancy of small and large cages, respectively. When the hydrate is in equilibrium with ice, the left side of Eq. (6) becomes $\mu_w(ice) - \mu_w(h^o) = -\Delta\mu_w^o$, where $\Delta\mu_w^o$ is the chemical potential of the empty lattice relative to ice and has been reported in the literature. The value of $\Delta\mu_w^o(h^o)$ used in Eq. (6) was 1,297 J/mol, because this value corresponds to structure I hydrate. The relative cage occupancy ratio, $\theta_{S,CH_4}/\theta_{L,CH_4}$, could be determined from Fig. 3 and was found to be 0.8160. This value was substituted into Eq. (6) to obtain individual cage occupancies of θ_{S,CH_4}=0.8054 and θ_{L,CH_4}=0.9870.

However, for the mixed CH₄+THF hydrate verified as structure II, Eq. (6) must be changed as follows:

$$\mu_w(h) - \mu_w(h^o) = \frac{RT}{17}[\ln(1-\theta_{L,THF}-\theta_{L,CH_4}) + 2\ln(1-\theta_{S,CH_4})] \qquad (7)$$

The $\Delta\mu_w^o(h^o)$ value was 883.8 J/mol for structure II hydrate. For the mixed CH₄+THF hydrate, $\theta_{S,CH_4}/\theta_{L,THF}$=0.3703 and θ_{L,CH_4}=0 because no resonance line exists in the NMR spectra representing methane molecules occupied in the large cages. Two relative occupancy ratios listed above were also substituted into Eq. (7) and the resulting cage

Table 3. Cage occupancies of CH₄, THF and neohexane in corresponding cages of structures I, II, and H

System	Thermodynamic model			NMR analysis		
	θ_{S, CH_4}	θ_{L, CH_4}, θ_{M, CH_4}	$\theta_{L, THF}$, $\theta_{L, NH}$	θ_{S, CH_4}	θ_{L, CH_4}, θ_{M, CH_4}	$\theta_{L, THF}$, $\theta_{L, NH}$
Pure CH₄ hydrate	0.8108	0.9727	-	0.8054	0.9870	-
Mixed CH₄+THF hydrate	0.3897	0.0003	0.9997	0.3701	-	0.9989
Mixed CH₄+Neohexane hydrate	0.7792	0.8190	0.9999	0.7248	0.8880	0.9996

occupancies were found to be θ_{S, CH_4}=0.3699, θ_{L, CH_4}=0, and $\theta_{L, THF}$= 0.9989. It must be noted that the occupancy of methane molecules in small cages appeared to be quite different for mixed CH₄+THF hydrate from the pure CH₄ hydrate. The meaningful and interesting feature is that for the mixed CH₄+THF hydrate the small cage occupancy by methane was found to be quite low as θ_{S, CH_4}=0.3699 compared with that of the pure CH₄ hydrate, θ_{S, CH_4}=0.8054.

For the mixed CH₄+Neohexane hydrate verified as structure H, following equation was used.

$$\mu_w(h) - \mu_w(h^o) = \frac{RT}{34}[3\ln(1-\theta_{S, CH_4}) + 2\ln(1-\theta_{M, CH_4}) + \ln(1-\theta_{L, NH})] \tag{8}$$

The value of $\Delta\mu_w^o(h^o)$ used in Eq. (8) was 1187.5 J/mol corresponding to the value of structure H hydrate [Kang et al., 1999]. The relative cage occupancy ratio, $\theta_{S, CH_4}/\theta_{M, CH_4}$, could be determined from Fig. 5 and was found to be 0.8162. This value was substituted into Eq. (8) to obtain individual cage occupancies of θ_{S, CH_4}=0.7248, θ_{M, CH_4} =0.8880, and $\theta_{E, NH}$=0.9996. The overall NMR analysis results are summarized in Table 3 along with the values calculated from the hydrate equilibrium model by using Eqs. (1) and (2). Both the NMR spectroscopic results and calculated values from the suggested model were found to be in good agreement. The preference for THF over methane in the large cavities of structure II was successfully expected on the suggested thermodynamic model. These results imply that the van der Waals model appears to be still accurate and reliable for pure and mixed hydrates.

In this work NMR spectroscopic results provided the relative integrated intensity data for both guest molecules, which could be used to calculate the exact cage occupancies of each guest molecules.

2. Gas Uptake Measurement

We have also carried out gas uptake measurements in order to estimate methane amount consumed during pure and mixed hydrate formation process. Pure CH₄ hydrate was formed from powdered ice at a temperature of 272.2 K. The corresponding H-I-V equilibrium pressure was found to be about 25 bar, and the formation was conducted at 50 bar. During the formation process, the ice particles were continuously ground to provide fresh ice surface for further reaction and maximize the contacting surface area between ice and methane micro-domains. The moles of methane participating in converting ice to hydrate per mole of water, $n_{g/w}$, were 0.1577. Pure CH₄ hydrate is known to be structure I and have the ideal stoichiometry of 8CH₄·46H₂O. Accordingly, the ideal value of $n_{g/w}$ becomes 0.1739. As can be expected, the actual experimental values of $n_{g/w}$ appeared to be lower than the ideal one, and the resulting occupancy ratio was estimated as 90% for formed hydrate cages. From the previous NMR spectrum of Fig. 3, the cage occupancies of small and large cages were θ_{S, CH_4}=0.7880 and θ_{L, CH_4}=0.9879 and the occupancy

ratio was found to be about 89% for hydrate cages. The results from gas uptake measurement coincide with the NMR spectroscopic result. Besides the guest molecule uptake phenomenon concerned with pure CH₄ hydrate, the mixed CH₄+THF hydrate was also investigated to examine the occupancy of methane molecules in the presence of THF. For this ternary mixture consisting of water, CH₄, and THF, the H-L$_w$-V equilibrium pressure was determined to be about 20 bar at a temperature of 292.2 K. Accordingly, the uptake measurement of methane in aqueous 5.6 mol% THF solution was conducted at 40 bar and the resulting value of $n_{g/w}$ was 0.0423. As shown in Fig. 4, the NMR spectrum of the mixed CH₄+THF hydrate verified that methane molecules could be captured only into the small cages, but not in the large cages of structure II hydrate. Therefore, the ideal stoichiometry of the mixed CH₄+THF hydrate can be written as 16CH₄·8THF·136H₂O, which means that the ideal value of $n_{g/w}$ becomes 0.1176. The occupancy ratio was estimated as 36% for hydrate cages and this result agreed well with the NMR analysis result that showed the occupancy ratio of 37% for hydrate cages. The mixed CH₄+Neohexane hydrate was identified as structure H and the methane molecules occupied both small and medium cages. From the ideal stoichiometry of the mixed CH₄+Neohexane hydrate, 5CH₄·1Neohexane·34H₂O, the ideal value of $n_{g/w}$ becomes 0.1471. However, the actual experimental values of $n_{g/w}$ appeared to be 0.1087 and the resulting occupancy ratio was about 74% for hydrate cages. The NMR analysis result also showed the occupancy ratio of 72% for hydrate cages, which was a little lower than the result of gas uptake measurement. Table 4 gives the comparison of the occupancy ratios occurring in hydrate cages of pure and mixed hydrates determined from the gas uptake measurements with those obtained from the NMR analysis. However, at the present stage it needs to be again emphasized that both the direct NMR spectrum and corresponding gas uptake capacity provide two important macro- and microscopic cage characteristics. One is the total amount of methane captured into hydrate cages and the other the absolute cage occupancies of small and large cages. This two-cage information must be highly valuable for understanding the storage capacity of gas hydrate.

Table 4. Occupancy ratios of methane in hydrate cages of pure and mixed hydrates

System	Occupancy ratio	
	NMR analysis	Gas uptake measurement
Pure CH₄ hydrate	89%	90%
Mixed CH₄+THF hydrate	37%	36%
Mixed CH₄+Neohexane hydrate	72%	74%

Table 5. Gas uptake measurements for the pure CH$_4$ and mixed CH$_4$+THF, CH$_4$+neohexane hydrates

System	Exp. condition (K, bar)	n$_{g/w}$ (mol)*	Storage capacity (vol./vol.)#
Pure CH$_4$ hydrate	272.2, 50	0.1577	156.2
Mixed CH$_4$+THF hydrate	292.2, 40	0.0423	51.7
Mixed CH$_4$+Neohexane hydrate	277.5, 40	0.1087	116.8

*: The moles of methane captured into hydrate per mole of water.

#: The ratio of methane volume captured into hydrate cages to total hydrate volume.

The storage capacity of gas hydrate can be conceptually defined as the ratio of methane volume captured into hydrate cages to total hydrate volume. As discussed earlier, the volume of methane captured into hydrate cages was directly determined from the moles of methane obtained from the gas uptake measurements. The total hydrate volume was calculated from the mass of water used to form hydrate and the density of hydrate defined as the following equation [Sloan, 1998].

$$\rho = \frac{N_w \cdot NW_w + \sum_{j=1}^{c} \sum_{i}^{N} \theta_{ij} \nu_i MW_j}{N_{avo} \cdot V_{cell}} \qquad (9)$$

Where ρ represents the density of hydrate, the indices i, j, and w the cage, guest and water molecules, respectively, N_w the number of water molecules per unit cell, N_{avo} Avogadro's number, V_{cell} the volume of unit cell, MW is molecular weight, and θ_{ij} the fractional occupancies of guest molecules in the small and large cages. Actual θ_{ij} values were determined from the ^{13}C NMR spectra as shown in Figs. 3-5. The storage capacities of pure CH$_4$, mixed CH$_4$+THF, and mixed CH$_4$+Neohexane hydrates are listed in the fourth column of Table 5. Pure CH$_4$ hydrate formed from powdered ice has the storage capacity of 156.2 vol./vol. But in the presence of a third component, THF and Neohexane, the storage capacities were found to be 51.72 vol./vol. for the mixed CH$_4$+THF hydrate and 116.8 vol./vol. for the mixed CH$_4$+Neohexane hydrate. The addition of a third component makes hydrate formation pressure considerably reduced and thus favorable hydrate formation conditions could be induced. But the above low storage capacities of mixed hydrate suggest that its negative function is to diminish the storage capacities, especially in case of mixed CH$_4$+THF hydrate due to the exclusive occupation of THF. Accordingly, it is worthwhile to consider that the powdered ice can be used as better natural gas storage medium because of its low hydrate formation pressure and high storage capacity.

CONCLUSIONS

^{13}C NMR spectra were obtained for the pure CH$_4$, mixed CH$_4$+THF, and mixed CH$_4$+Neohexane hydrates in order to identify hydrate structure and cage occupancy. Although the small 5^{12} cages were common to structures I and II, the resonance lines of methane molecule captured into these two cages were found to be not identical and therefore used as a unique indicator of structure type. In particular, the NMR spectra of the mixed CH$_4$+THF hydrate verified that methane molecules could be occupied only in a small portion of 5^{12} cages because the addition of THF, water-soluble guest component, to aqueous solution prevents the complete filling of methane molecules into small cages. Furthermore, from these NMR

results one important conclusion can be made that methane molecules can't be enclathrated at all in the large $5^{12}6^4$ cages of structure II. Gas uptake measurements were also carried out to determine methane amount consumed during pure and mixed hydrate formation process. The moles of methane captured into pure CH$_4$ hydrate per mole of water were found to be a little lower than the full occupancy ratio, while the moles of methane captured into the mixed CH$_4$+THF hydrate per moles of water were much lower than the ideal value. Both gas uptake determination and structure identification carried out in the present investigation might be very valuable for developing a potential application to storage and transportation of natural gas.

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