순수 및 혼합 가스 하이드레이트의 구조 규명을 위한 ^{13}C NMR 연구 및 가스 흡착 측정

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^{13}C NMR Analysis and Gas Uptake Measurements of Pure and Mixed Gas Hydrates

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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.[1] The new mixed structure consisted of alternating stacks of structures H and II was also reported in the recent literature.[2] Recently, many researchers have suggested the potential application of crystal hydrate nature to large-scale storage and transportation of natural gas. Gudmundsson et al. 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.[3-4] Zhong et al. 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.[5] 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.[6]

All the significant investigations mentioned above were mainly focused on the absolutely captured amount of methane gas largely depending on hydrate-forming conditions and reflected the positive factors concerning the feasibility of gas storage in hydrates. 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.[7] 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. As hydrate forming systems, we select the ice powder for structure I, and THF solution for structure II, and methylcylohexane (MCH) for structure H hydrate formation.

Experimental Section

To identify hydrate structure and cage occupancy of guest molecules, a Bruker 400 MHz solid-state 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 variable temperature probe. All ^{13}C NMR spectra were recorded at a frequency of 100.6 MHz with magic angle spinning (MAS) at about 2 kHz. The radio frequency field strengths of 70 kHz corresponding to 4 μs 90^{o} pulses were used. The adamantane that 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. The reactor maintained at a constant temperature of 273.16 K was filled with the liquid mixtures of water and neohexane, and then subsequently pressurized with pure CH_4 gas to higher pressure than the corresponding three-phase equilibrium pressure at the same temperature. By stirring aqueous mixture solid hydrate formation was proceeded through induction, nucleation, and growth periods, successively. When hydrate formation process was completed, the formed hydrates were sampled by keeping both the cell and Zr-rotor immersed in liquid nitrogen to prevent any hydrate dissociation or distortion. This Zr-rotor having hydrate samples was then inserted to the solid-state NMR.

Results and Discussion

Thermodynamic Phase Behavior Many researchers have been studied the three-phase equilibria (H-L_w-V) of the binary methane and water system and developed thermodynamic model to predict the equilibrium conditions.

The various methods for storing natural gas to hydrates were developed based on this thermodynamic information. However, The addition of third component like ether compounds or surfactants has been also studied to improve the hydrate formation 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+MCH+water systems were preliminarily measured at various temperature conditions and the overall results were presented in Figure 1. The CH_4+water equilibrium data were taken for checking the used experimental apparatus and compared with the literature data.[11] As shown in Figure 1, the presence of THF and MCH induced a hydrate-forming condition to be more favorable by lowering pressure and raising temperature for forming the mixed hydrates when 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 only occupy the large cages because of its size. The formation of mixed hydrate from methane and THF was also verified as structure II and the main function of THF is to stabilize the formed hydrate structure when judging from the H-L_w-V phase boundary shown in Figure 1. It was known that MCH itself couldn't participate the forming of hydrate structure, but could be formed 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 MCH 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 pressure reduction was made by using ice particles at the 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 lower temperature and pressure region. Accordingly the hydrate formation pressure could be reduced below 25 bar. The phase behavior at lower region of the lower quadruple point suggested that the hydrate structure could be stabilized by decreasing the temperature without adding third components and changing the hydrate structure as shown in Figure 1.

NMR Spectroscopic Analysis Although the small 5^{12} cages commonly exist to all hydrate structures, the symmetry and size of these small cages were different and their behavior toward guest molecules should be quite different. Accordingly the guest molecules captured into these cages showed the different chemical shifts in NMR spectra. Due to this chemical shifts difference, the obtained NMR peaks could be used as a unique indicator of structure type. Figure 2-4 represents a stacked plot of three ^{13}C NMR spectra, which were used to identify the chemical shifts of CH_4 in the 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. Figure 2 representing pure CH_4 hydrate indicated 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 cages peak was more intense than the small cage one, confirming the methane molecules in large cages was abundant in structure I. Figure 3 was the ^{13}C NMR spectrum of mixed CH^4+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 peaks (at about - 4.5 ppm). However, THF molecules were captured in the 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 were appear 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 were filled with methane molecules. Subramanian et al. also obtained similar results for mixed CH_4+THF hydrate from Raman spectroscopic analysis and suggested that the larger guest molecule THF almost exclusively occupies the large cages thus restricting CH_4 to only small cages in the hydrate. However, they didn't show the absolute cage occupancy values. Figure 4 was the ^{13}C NMR spectra of mixed CH_4+MCH hydrate having guest molecules of methane and MCH. The large $5^{12}6^8$ cages are filled with MCH only, represented by five distinct peaks from 23.2 to 35.7 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 and therefore the chemical shift of methane in small cage of mixed CH_4+MCH hydrate was same as that of mixed CH_4+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, $A_{M,CH4}/A_{S,CH4} = 0.7719$, confirming the methane molecules in small cages was more abundant in medium cages of structure H.

Gas uptake measurements Pure CH_4 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. The moles of methane participating in converting ice to hydrate per mole of water, $n_{g/w}$, were 0.1577. Pure CH_4 hydrate is known to be structure I and have the ideal stoichiometry of $8CH\cdot46H_2O$. 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 Figure 2, the cage occupancies of small and large cages were $\theta_{S,CH4}$= 0.7880 and $\theta_{L,CH4}$=0.9879 and the occupancy ratio was found to be about 88% for hydrate cages. The results from gas uptake measurement coincide with the NMR spectroscopic result. Besides the guest molecule uptake phenomenon concerned with pure CH_4 hydrate, the mixed CH_4+THF hydrate was also investigated to examine the occupancy of methane molecules in the presence of THF. For this ternary mixture consisting of water, CH_4, 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 Figure 3, the NMR spectrum of the mixed CH_4+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 CH_4+THF hydrate can be written as $16CH_4\cdot8THF\cdot136H_2O$, 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 CH_4+MCH hydrate was identified as structure H and the methane molecules occupied both small and medium cages. From the ideal stoichiometry of the mixed CH_4+MCH hydrate, $5CH_4\cdot1MCH\cdot34H_2O$, 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 80% for hydrate cages, which was a little higher than the result of gas uptake measurement.

Table 1. Gas Uptake Measurements for the Pure CH_4 and Mixed CH_4 + THF, CH_4 + MCH Hydrates.

System	Exp. condition (K, bar)	$^*n_{g/w}$ (mol)	Occupancy ratio	#Storage capacity (vol./vol.)
Pure CH_4 hydrate	272.2, 50	0.1577	90 %	156.2
Mixed CH_4 + THF hydrate	292.2, 40	0.0423	36 %	51.7
Mixed CH_4 + MCH hydrate	277.5, 40	0.1087	74 %	116.8

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

Acknowledgement

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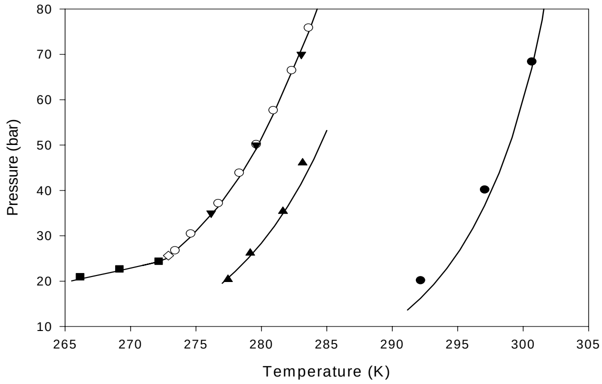

Figure 1. Experimental and predicted hydrate dissociation pressures of pure CH_4 hydrate ("○" represents the results of Adisasmito et al. "▼" and "■" are this work for H-L_w-V and H-I-V respectively), mixed CH_4+THF hydrate ("●" is this work) and mixed CH_4+MCH hydrate ("▲" is this work). Solid lines are predicted from the statistical thermodynamic model.

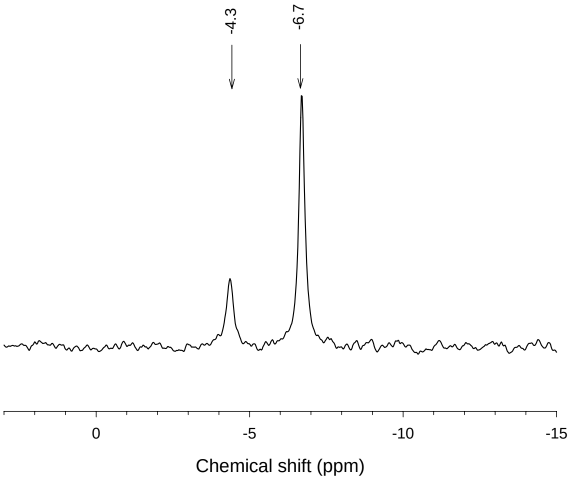

Figure 2. ^{13}C MAS NMR spectra of pure CH_4 hydrate at 243 K.

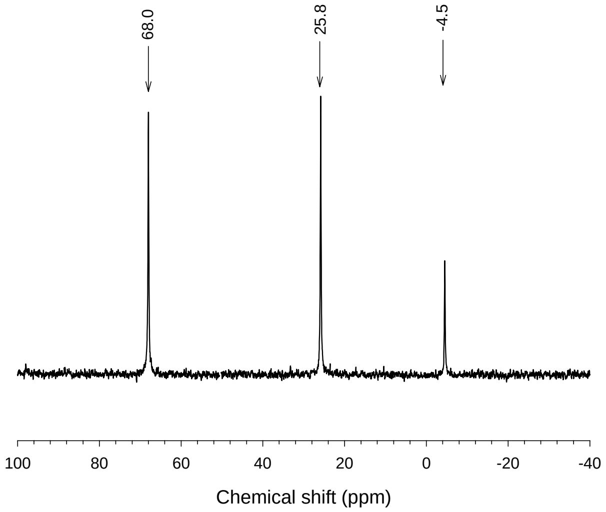

Figure 3. ^{13}C MAS NMR spectra of mixed CH_4 +THF hydrate at 243 K.

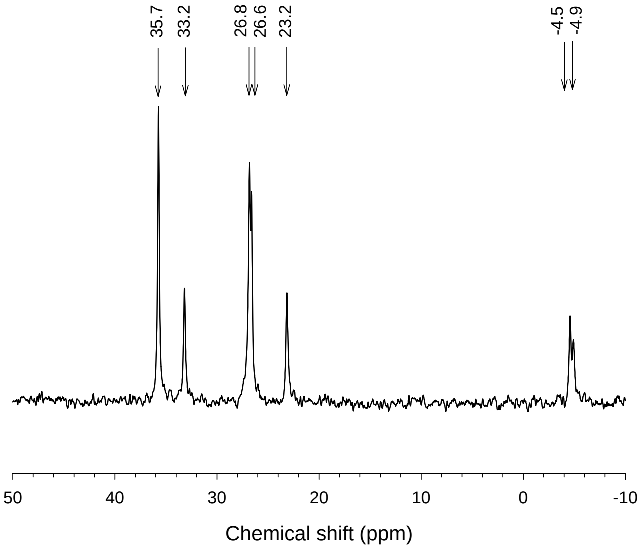

Figure 4. ^{13}C MAS NMR spectra of mixed CH_4 +MCH hydrate at 243 K.