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Spectroscopic Studies of Gas Hydrates

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Key words : Hydrate(하이드레이트), NMR analysis(NMR 분석), Raman analysis(Raman 분석)

Abstract : ^{13}C NMR spectra were obtained for pure CH_4 hydrate in order to identify hydrate structure and cage occupancy of guest molecule. The NMR technique can provide both qualitative and quantitative hydrate characteristics. The moles of methane captured into pure CH_4 hydrate per mole of water were found to be similar to the full occupancy value. The overall results drawn from this study can be usefully applied to storage and transportation of natural gas.

Nomenclature

θ_L : large cage occupancy of CH_4
θ_S : small cage occupancy of CH_4
R : universal gas constant
T : Temperature

subscrip

w : water

1. Introduction

Gas hydrates are crystalline compounds that are formed by physically stable interaction between water and relatively small guest moles occupied in the cavities built by water molecules. Natural gas components like methane, ethane, propane, isobutene and carbon dioxide are known to form hydrates at low temperature and high pressure(1). Gas hydrates crystalline in two cubic structures (sI and sII) and one hexagonal structure (sH). The number and size of the cavities differ in both the structures. The methaneforms structure I hydrate in pure water and can form structure H hydrates with liquid hydrocarbon like 2,2-dimethylbutane(2). In case of aqueous miscible compounds like acetone and THF, they form structure II hydrate with methane.

Typically, in hydrate formation studies, macroscopic quantities like pressure, temperature and fluid-phase compositions are measured whereas hydrate-phase properties such as structure type, cage occupancies, and guest composition, are predicted using models that are based on the theory of van der Waals and Platteeuw. NMR is very useful spectroscopic methods that can be used to obtain structural and compositional information about the solid hydrate phase. The presence of a cage-dependent chemical shift for enclathrated guest molecule suggests that ^{13}C NMR should provide a direct, nondestructive technique for the determination of gas hydrate structure and other microscopic properties. In this contribution, we present results obtained with CP/MAS ^{13}C NMR techniques on structure I hydrate and confirm that the cage-dependent ^{13}C chemical shift of enclathrated methane can be used to determine the hydrate structure. Quantitative determination of the gas distribution over the different cages was then used to determine the hydration number of methane hydrate.

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2. Experimental

2.1 Apparatus

The experimental apparatus was designed to measure the volumetric consumption rate of hydrate-forming gas during hydrate formation. A schematic diagram of the experimental apparatus was shown in Figure 1. It consists of largely three parts: a semi-batch stirred tank reactor with a temperature and pressure control system, measurement system, and a data acquisition system. Cylindrical type reactor of which internal volume was about 150 cm3 was made of 316 stainless steel with two sight glasses equipped at the bottom and the side of the reactor. Sight glasses provided visual observation of the state of contents during hydrate formation inside the reactor. Rubber o-rings were used to seal the reactor and glasses and tested up to approximately 95 bar. A mechanically driven magnetic stirrer (Total Engineering Co., Korea) vigorously agitated water loaded in the reactor. Magnetic stirrer had a built-in frequency generator that provided stable speed control to the range of 200 to 1600 rpm, and gave strong agitation power which enable to stir solid particles.

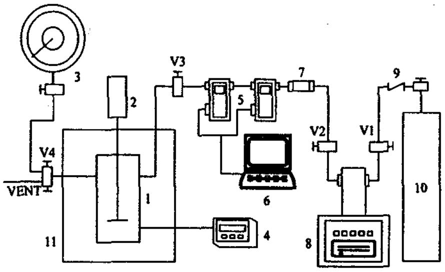

Figure 1. Schematic diagram of experimental apparatus of formation kinetics of clathrate hydrate: 1, reactor; 2, mechanical magnetic stirrer; 3, pressure gauge; 4, thermometer; 5, high-pressure digital flowmeter; 6, data acquisition system; 7, check valve; 8, micro flow syringe pump; 9, line filter; 10, gas cylinder; 11, constant temperature water bath.

Fig. 1 Experimental apparatus

2.2 Sample Preparation

Powdered ice was obtained by freezing deuterated water (Aldrich, 99.9%) in refrigerator and then crushing the ice in a mortar and pestle. Large ice particles were removed with a 300μm sieve, and the powdered ice was placed in the reactor that was already cooled in liquid nitrogen. The reactor was closed and put into the bath containing water-ethanol mixture as circulating fluid. The bath temperature was controlled by external refrigerator/heater. Before the hydrate forming gas was introduced into the system, the ice was allowed to stabilize at 1.0 ℃. The gas was introduced rapidly with the desired pressure, then the agitation and data acquisitionwas started. As the pressure decreased due to gas consumption induced by hydrate formation, the syringe pump supplemented the shortage with no pulsation into the reactor to maintain the system pressure. After the reaction reached steady state, the reactor were cooled slowly to 20.0 ℃ and opened. The powdered hydrate sample was transferredto 4 mm Zr-rotors. The sample was kept in liquid nitrogen throughout this process to prevent the sample from dissociation. The rotor were then placed into the stator assembly of CP/MAS probehead previously cooled to 30.0 ℃. ^{13}C NMR spectra were recorded on a Bruker DSX-400 MHz solid state FT-NMR spectrometer. Single-shot cross-ploarization (CP) sequences were used with contact times of 0 ~ 12 ms and the magic angle spinning (MAS) rate was 1 ~ 2 kHz.

3. Results and Discussion

At fixed temperature, the conversion of ice to hydrate is pressure-dependent process. Figure 2 shows the pressure effect of ice conversion at 1.0 ℃ and the consumed amount of gas molecules increased as the pressure increased. The rate of conversion gradually decreased near 60 min after hydrate nucleation. Higher conversion to hydrate (~92%) was obtained by keeping the pressure over 55 bar. At lower than 55 bar, ultimate amount of consumed gas molecules were lower than ideal amount. The hydrate sample was obtained after the conversion rate reached steady state at 55 bar. The ^{13}C CP/MAS spectrum of methane hydrate at 30.0 ℃ is shown in Figure 2. There are resonance line at 4.3656 and 6.7013 ppm, and as the large cages outnumber the small cages by a factor of 3 in structure I hydrate, the more intense upfield line can be assigned to methane in the large cages. The spectrum shown in Figure 2 is compared to reported results in the literature andpresent in Table 1. The absolute chemical shift values of the guests in the hydrate cages are different from literature values, but the chemical shift separation between a given pair of peak is about the same. The observed chemical shift differences may be due to external chemical shift referencing differences.

Table 1. ^{13}C chemical shift of CH_4 in sI hydrate

	Ref. 1[3]	Ref. 3[4]	this work
sI small cage	- 2.84	- 4.0	- .3
sI large cage	- 5.21	- 6.1	- 6.7

The cross-polarization technique depends in solidlike behavior, that is, there must be some static nuclear dipolar coupling between 1H and ^{13}C nuclei. In rigid systems, such as pure solid hydrocarbons, polarization transfer can be complete in times on order of ~ 1 ms or less. The signal intensities of methane hydrate as a function of CP time are shown in Figure 3. The ^{13}C polarization reaches a maximum value around 2 ms. Therefore, Quantitative analysis of methane molecules captured into large and small cages was done at 2 ms. From the data in Figure 3, occupancy ratio can be determined as $\theta_s(CH_4)/\theta_L(CH_4)=0.8847$, where θ_L and θ_S are large and small cage occupancies.

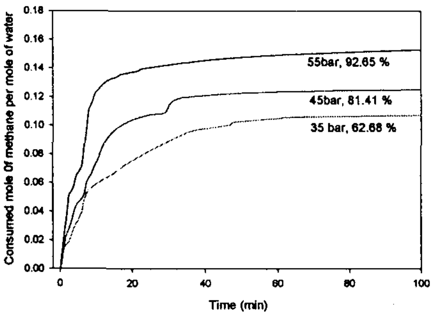

Fig. 2 Conversion of ice particle to CH_4 hydrate at 1.0℃

The chemical potential of the water molecules in structure I hydrate is given by

$$\mu_w(h)-\mu_w(h^\circ)=\frac{RT}{23}[3ln(1-\theta_L)-ln\theta_S] \quad (1)$$

When the hydrate is in equilibrium with ice, the left side of eq (1) becomes $\mu_w(ice)-\mu_w(h^\circ)=-\Delta\mu_w$, $\Delta\mu_w$ was determined to be 1297 J/mol. After allowing for the fact that there are 3 times as many large cages as small ones in structure I hydrate, the absolute occupancies $\theta_L=0.987$ and $\theta_S=0.873$. The hydration number n can then be found from $n=23/(3\theta_L+\theta_S)$, giving a value of 6.135. Other recent values for n, determined by using direct as well as indirect methods, are 6.05 and 6.03. Our results are in good agreement with the literature data.

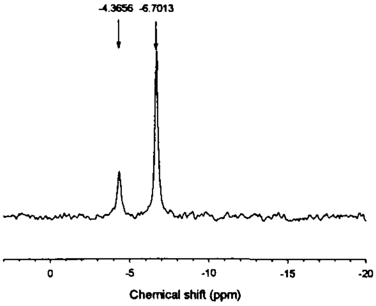

Fig. 3 ^{13}C CP/MAS NMR spectrum at -30℃

4. Conclusion

^{13}C NMR spectra were obtained for pure CH_4 hydrate in order to identify hydrate structure and cage occupancy of guest molecule. The NMR technique can provide both qualitative and quantitative hydrate characteristics. The moles of methane captured into pure CH_4 hydrate per mole of water were found to be similar to the full occupancy value. The overall results drawn from this study can be usefully applied to storage and transportation of natural gas.

References

[1] Ratcliffe CIJ, Ripmeester JA, 1986. "Proton and carbon-13 NMR studies on carbon dioxide hydrate", J. Phys. Chem., 90, 1259-1263.

[2] Cady GH, 1983. "Composltlon of Clathrate Gas Hydrates of H_2S, Xe, SO_2, CI_2, CH_3CI, CH_3Br, $CHCIF_2$, CCI_2F_2, and C_3Hs", J. Phys. Chem., 87, 4437-4441.

[3] Ripmeeste JA, Ratcliffe CIJ, 1998. "Low-temperature cross-polarization/magic angle spinning carbon-13 NMR of solid methane hydrates: structure. cage occupancy, and hydration number", J. Phys. Chem., 92, 337-339.

[4] Subramanian S, Kini RA, Dec SF, Sloan Jr ED, 2000. "Evidence of structure II hydrate formation from methane+ethane mixtures", Chem. Eng. Science, 55, 1981-1999.