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Phase behavior and structure transition of the mixed methane and nitrogen hydrates

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Abstract−Pure methane and nitrogen form structure I and II hydrate, respectively, and therefore the structure type of mixed gas hydrate was found to largely depend on their relative gas composition. In addition to the structural difference of size and shape, each hydrate structure shows different capacity to store the guest molecules. In this study, we investigated phase and structural behaviors according to the composition of methane+nitrogen gas mixture. Three-phase (H-L_w-V) equilibria of solid hydrate, water-rich liquid and vapor phase containing 25.24 mol%, 28.51 mol%, 31.23 mol% and 40.39 mol% of methane were determined at various temperatures (in the range from 273.30 K to 285.05 K) and pressures (from 8.325 MPa to 20.700 MPa). ^{13}C solid-state NMR spectroscopy and powder XRD method were performed to identify the formed structure of hydrate samples. The experimental results showed that gas hydrate of the methane+nitrogen mixture changes its structure from sI to sII between 25.24 mol% and 28.51 mol% of methane concentration. These results of phase behavior and structure identification for the mixed gas hydrates are expected to be very helpful in evaluating the feasibility of exploitation of methane gas from natural gas hydrate and the separation process using gas hydrate as a storage-media

Key words: Gas Hydrates, Methane, Nitrogen, Phase Equilibria, Spectroscopic Analysis

INTRODUCTION

Gas hydrates are crystalline compounds formed non-stoichiometrically under specific conditions, generally at high pressure and low temperature. Within the lattice structure, established by strong hydrogen bonds of water molecules (host), low molecular weight gases (guest) can be encaged so as to form gas hydrates as stable compounds. The guest molecules interact with the host molecules through van der Waals type dispersion forces [Sloan, 1998]. These compounds can be classified into three distinct categories, i.e. structure I (sI), structure II (sII) and structure H (sH), which contain different cages in both size and shape. The sI and sII hydrates consist of two types of cages called small and large, while the sH hydrate consists of three types of cages, small, medium, and large [McMullan and Jeffrey, 1965; Mak and McMullan, 1965; Ripmeester et al., 1987].

Initially, gas hydrates attracted particular interest in the area of petroleum industry. After the discovery of plugging problems in natural gas pipelines, many researchers have started to study the fundamentals of gas hydrates to resolve this drawback [Li et al., 1999]. These results have served as the basis for understanding the phase-equilibria and formation kinetics with inhibition and promotion of gas hydrates. Recently, huge amounts of deposit of natural gas hydrates were found both under the permafrost region and deep ocean sediments [Kim et al., 2005]. Because each volume of hydrate can contain as much as 160 volumes of gas for sI hydrate and 180 volumes of gas for sII hydrate at STP, naturally occurring gas hydrates in the earth containing mostly CH_4 are regarded as future energy sources. Also, this property can be applied to the utilizing of gas hydrates as a gas-storage medium [Seo et al., 2003].

To analyze these complex thermodynamic phenomena in extracting or storing natural gas, above all, the fundamental phase behavior of gas hydrates containing methane as a guest molecule should be investigated to understand the overall processing mechanism. In this respect, several related studies have been performed to examine hydrate equilibrium conditions of the methane and nitrogen mixture. Jhaveri and Robinson [1965] measured three-phase (H-L_w-V) equilibria for the methane, nitrogen and water mixture, which followed the discovery of the hydrates of nitrogen and oxygen by Van Cleeff and Diepen [1960]. They published the equilibrium temperatures and pressures of mixed gas hydrate at various compositions of gas mixture. They insisted that information gained from their study would be of value in determining the hydrate forming conditions in methane rich natural gas containing nitrogen. Mei et al. [1996] performed experimental and modeling studies on the hydrate formation of the methane+nitrogen gas mixture in the presence of aqueous electrolyte solutions. They measured the incipience of hydrate formation for the methane+nitrogen mixture in the presence of pure water and brines including a single salt and mixed salts of NaCl, $NaHCO_3$, $MgCl_2$, $CaCl_2$ and KCl. In all the above studies, however, multiple occupations by nitrogen molecules [van Klaveren et al., 2001] are not observed or suggested. The studies are mainly focused on the determination of equilibrium conditions for pure nitrogen or nitrogen+methane mixed gas hydrate. Until now, there have not been precise experimental works regarding the structure change including methane and nitrogen, although many physical properties would change in accordance with the formed hydrate structure. In this study, the equilibrium dissociation pressures for methane+nitrogen hydrates were measured in the CH_4 concentration range from 25.4 mol% to 40.39 mol%. To investigate the structure transition as a concentration of mixed gas changes and to analyze the microscopic

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properties of the formed hydrates, hydrate samples formed at various gas concentrations were analyzed by means of ^{13}C solid-state NMR spectroscopy and low-temperature X-ray diffraction (XRD) measurements.

EXPERIMENTAL SECTION

1. Materials

N_2 gas used in this study was supplied by World Gas (Korea) and had a stated purity of 99.99 mol%. CH_4 gas with a minimum purity of 99.95 mol% was supplied by Linde Gas UK Ltd. (UK). Water with ultra high purity was supplied from Merck (Germany). All materials were used without further purification.

2. Apparatus and Procedure

The apparatus for hydrate phase equilibria was specially constructed to measure accurately the hydrate dissociation pressures and temperatures. The equilibrium cell was made of 316 stainless steel and had an internal volume of about 130 cm^3. This equilibrium cell is contained in a bath whose temperature is maintained by an external PID temperature controller (JeioTech, MC-31) with ±0.1 K accuracy. The experiment for hydrate-phase equilibrium measurements began by charging the equilibrium cell with about 30 cm^3 of liquid water. After the equilibrium cell was pressurized to a desired pressure with mixed gas of methane and nitrogen, the whole system was slowly cooled to a sufficiently low temperature. When pressure depression due to hydrate formation reached a steady-state condition, the cell temperature was increased at a rate of about 0.1 K/h. The nucleation and dissociation steps were repeated at least two times in order to reduce hysteresis. The equilibrium pressure and temperature of three phases (hydrate (H) - water-rich liquid (L_w) - vapor (V)) were determined by tracing the P-T profiles from hydrate formation to dissociation. Gas chromatography was used to analyze the mixed gas composition in gas phase. To check the reliability of this experimental apparatus, pre-experiments using pure methane and methane+nitrogen mixture were performed, whose results showed a good agreement with the literature values.

To identify crystalline structure of formed gas hydrate, spectroscopic methods such as solid-state NMR (Bruker, 400 MHz) and XRD measurements were used in this study. The NMR spectra were recorded at 243 K by placing the hydrate samples within a 4 mm o.d. ZrO_2-rotor that was loaded into the variable temperature (VT) probe. All ^{13}C NMR spectra were recorded at a Larmor frequency of 100.6 MHz with magic angle spinning (MAS) at about 2-4 kHz. The pulse length of 2 μs and pulse repetition delay of 20 s under proton decoupling were employed when the radio frequency field strengths of 50 kHz corresponding to 5 μs 90° pulses were used. 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 acquisitions of signals were repeated until a further increase in peak intensities was not observed. XRD measurements were performed by using Rigaku D/max-RB with low-temperature equipment. This apparatus has a maximum capacity of 12 kW and can be operated up to 83 K. CuKα with wavelength of 1.54060 was used as light source, and the experiments were performed from 10.0° to 70.0° with 0.05° step. During the spectroscopic measurements, the experimental temperature was controlled to about 123 K to prevent the dissociation of gas hydrate.

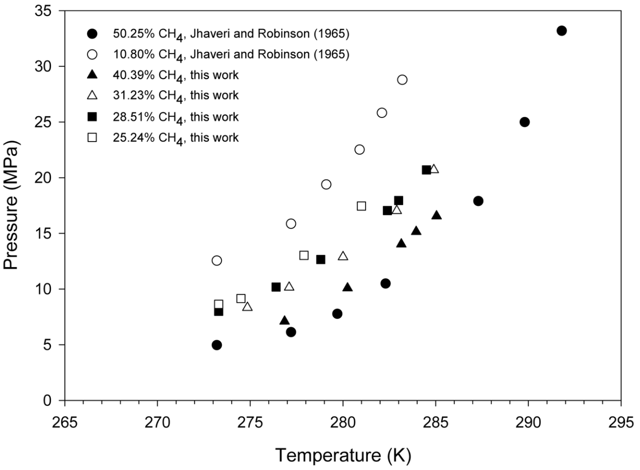

Fig. 1. Three-phase equilibria for the mixed methane+nitrogen gas hydrates at various gas compositions.

Table 1. Three-phase equilibria for the gas hydrate of the methane+nitrogen gas mixture

T, K	P, MPa	T, K	P, MPa
40.39 mol% CH_4		31.23 mol% CH_4	
285.05	16.550	284.90	20.700
283.95	15.150	282.90	17.025
283.15	14.025	280.00	12.875
280.25	10.075	277.10	10.150
276.85	7.100	274.85	8.325
28.51 mol% CH_4		25.24 mol% CH_4	
284.50	20.700	281.00	17.450
283.00	17.950	277.90	13.025
282.40	17.050	274.50	9.150
278.80	12.650	273.30	8.625
276.40	10.175		
273.30	80.000		

RESULTS AND DISCUSSION

It has been known that pure methane forms structure I hydrate and pure nitrogen forms structure II hydrate, respectively. Therefore, as the gas composition for the mixture of these two gas components changes, the formed hydrate structure is also expected to be changed. Fig. 1 and Table 1 show the three-phase (L_w-H-V) equilibria for the mixed methane+nitrogen gas hydrate. In this study, we expected that a structure change would occur below the 50 mol% methane of gas mixture, and three-phase equilibria for the mixed gas hydrate containing 40.39, 31.23, 28.51 and 25.24 mol% methane were measured. In Fig. 1, no significant difference according to gas composition was observed. However, as the concentration of methane increased, the equilibrium temperature also slightly increased at the constant pressure.

Because the experimental equilibrium data do not suggest any structural information for the mixed methane+nitrogen gas hydrate, microscopic methods such as NMR and XRD were used to identify and analyze the structural change. Fig. 2 shows the experimen-

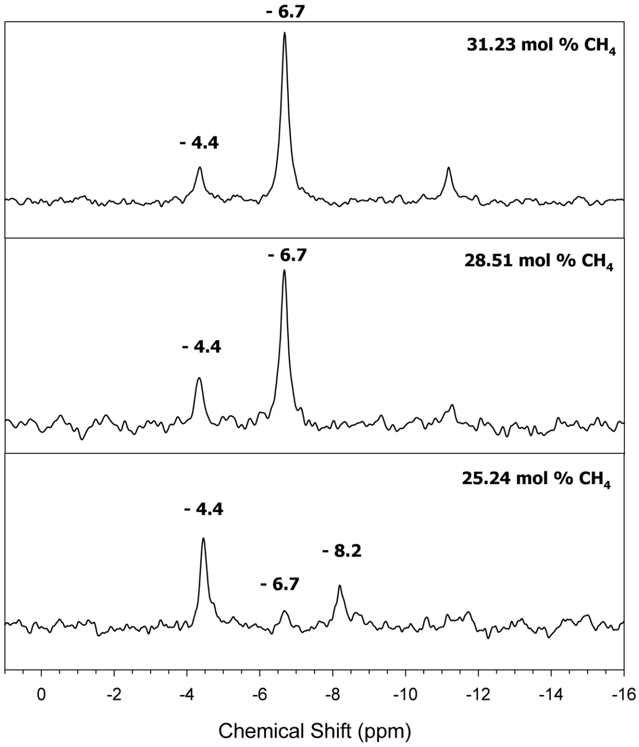

Fig. 2. NMR spectroscopy near the structure change region.

Table 2. Unit cell parameter and volume for mixed CH_4+N_2 gas hydrate samples

	Unit cell parameter	Unit cell volume
25.24 mol% CH_4 hydrate	16.87 Å	4,801 Å^3
28.51 mol% CH_4 hydrate	11.89 Å	1,680 Å^3
31.23 mol% CH_4 hydrate	11.88 Å	1,677 Å^3
40.39 mol% CH_4 hydrate	11.88 Å	1,677 Å^3

tal measurements of NMR spectroscopy for the mixed methane+nitrogen gas hydrate at three different compositions. As can be seen in this figure, a mixed gas hydrate of higher concentration of methane (up to 28.51 mol%) is formed as structure I, which is characterized by two distinct peaks (−4.4 ppm for methane molecules in small cages and −6.7 ppm for methane molecules in large cages). In case of the 25.24 mol % methane +74.76 mol% nitrogen mixed gas, the formed hydrate is mainly composed of structure II, which can be known by two characteristic peaks of −4.4 ppm for methane molecules in small cages and −8.2 ppm for methane molecules in large cages. To confirm the formed hydrate structure according to the gas composition, powder XRD method, which is the most powerful method to determine the solid crystal structure, was also used. From these experimental XRD data, lattice parameters for identifying the crystal structure can be obtained [McMullan and Jeffrey, 1965; Mak and McMullan, 1965]. Table 2 shows the unit cell parameters and volumes, which show very good agreement with the literature values of 12.00 Å for structure I and 17.00 Å for structure II. While the hydrate samples of mixed gas containing 31.23 mol% and 28.51 mol% methane were found to be structure I with a lattice parameter of 11.89 Å, hydrate sample of mixed gas containing 25.24 mol% methane was found to be structure II with a lattice parameter of 16.87 Å. As can be seen from Fig. 3, not only different lattice parameters calculated from the XRD measurements but also a noticeable change in the different diffraction patterns were

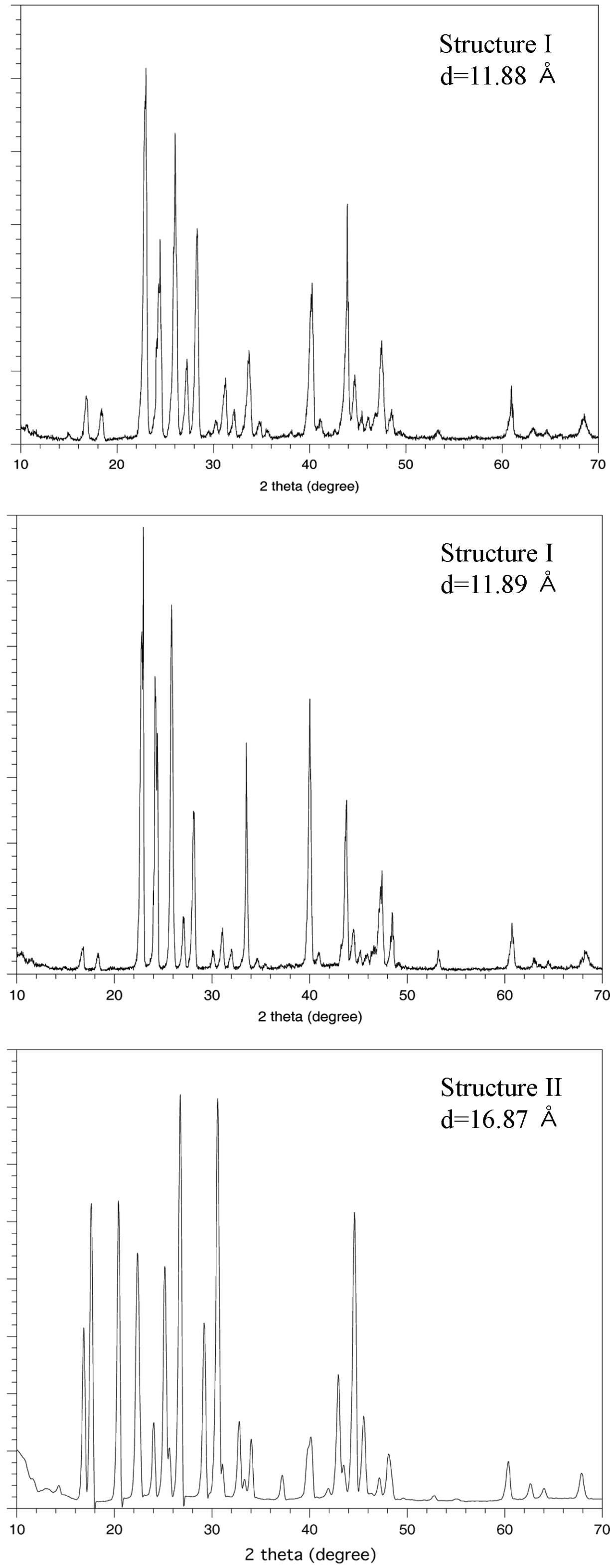

Fig. 3. XRD patterns and structure parameters near the structure change region.

observed in accordance with the different structure of the hydrate samples. This structural identification obtained by XRD experiments agrees with that of NMR spectroscopy.

CONCLUSIONS

Pure methane and nitrogen form structure I and II, respectively, and therefore the structure type of mixed gas hydrate was known to largely depend on their relative gas compositions. In this work, the hydrate structure change of nitrogen, methane and water mixture was measured by means of spectroscopic methods such as NMR and XRD. These spectroscopic measurements, in addition to the three-phase P-T equilibrium results, show that a structural change occurs in the range between 25.24 and 28.51 mol% of CH_4. Methane and nitrogen are found to be the main components in natural gas. Moreover, identification of two hydrate structures is critical in evaluating storage or separation capacities of gaseous guests. Therefore, the results obtained in this study can shed some light on the separation process by using natural gas hydrate as a storage-medium and the exploitation process of natural gas hydrate in the earth.

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