[Regular Paper]

Estimation of Gas Composition and Cage Occupancies in CH_4–C_2H_6 Hydrates by CP-MAS ^{13}C NMR Technique

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CP-MAS ^{13}C NMR measurements were carried out on mixed gas hydrates containing CH_4–C_2H_6. The changes in NMR chemical shift values for CH_4 and C_2H_6 clearly corresponded to the structural changes in the hydrate structure. The encaged gas compositions estimated by the integrated ^{13}C NMR signal intensities agreed well with the dissociated gas compositions measured by gas chromatography. Therefore, the gas composition in mixed gas hydrates can be directly estimated from the ^{13}C NMR spectra. The cage occupancies of the small and large cages of the hydrates were estimated from the ^{13}C NMR spectra on the basis of a statistical thermodynamic model. The large cages were almost fully occupied with guest molecules, whereas small cage occupancy decreased with increasing C_2H_6 concentration. Therefore, large cages are highly preferentially occupied by C_2H_6 molecules rather than CH_4 molecules.

Keywords
Gas hydrate, Natural gas, Gas composition, Cage occupancy, ^{13}C NMR

1. Introduction

Natural gas hydrates are expected to provide natural gas resources in the future. The scientific fundamentals and the technical developments relevant to gas hydrates were recently reviewed[1]. Gas hydrates are crystalline clathrate compounds which are stable under low-temperature and high-pressure conditions. The cages of natural gas hydrates mainly contain methane (CH_4). However, other hydrocarbons such as ethane (C_2H_6), propane (C_3H_8), and isobutane (i-C_4H_{10}) may be encaged together with CH_4[2]. Three crystallographic structures are known for gas hydrates, structure I (s**I**), structure II (s**II**), and structure H (s**H**)[1),3)]. Both C_2H_6 hydrate and CH_4 hydrate have the s**I** structure, in which the unit cell consists of 46 H_2O molecules (two small cages with twelve pentagonal faces (5^{12}), and six large cages with twelve pentagonal and two hexagonal faces ($5^{12}6^2$)). Mixed gas hydrates containing CH_4–C_2H_6 with appropriate gas compositions have the s**II** structure, in which the unit cell consists of 136 H_2O molecules (sixteen small cages with twelve pentagonal faces (5^{12}) and eight large cages with twelve pentagonal and four hexagonal faces ($5^{12}6^4$))[4].

The structure of natural gas hydrates is important to clarify for the estimation of the amount of natural gas, since the gas capacity in the hydrate crystal depends on the structure. The X-ray diffraction (XRD) method has been widely used to determine gas hydrate structures[2),3),5)]. ^{13}C NMR spectroscopy is also useful to determine hydrate structures containing hydrocarbons[2),4),6)].

The cage occupancy is defined as the ratio of (number of cages occupied by guest molecules)/(number of total cages), and is also important to estimate the amount of natural gas, since it depends on the conditions of the hydrate formation such as pressure and gas composition. In general, samples of synthesized gas hydrates and natural gas hydrates recovered from sea floor contain a certain amount of frozen water[5),7)]. Therefore, the cage occupancy is difficult to estimate from the amounts of water and gas obtained by dissociation of

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the sample. Raman spectroscopy has been used to estimate the cage occupancy in the case of the CH_4–C_2H_6 mixed system[4),8)], in which the values for the cage occupancies were calculated without considering the effect of the frozen water. However, Raman spectroscopy cannot easily distinguish the signals of CH_4 from those of other heavier hydrocarbons such as C_3H_8[9)]. Therefore, the establishment of techniques other than Raman spectroscopy is important to estimate the cage occupancies in natural gas hydrates.

^{13}C NMR (nuclear magnetic resonance) of s**II** natural gas hydrate containing hydrocarbons such as CH_4, C_2H_6, C_3H_8, and *i*-C_4H_{10} was found to distinguish the hydrocarbon molecules in different cages[2)]. Therefore, the cage occupancies could be estimated from the ^{13}C NMR data on the basis of the statistical thermodynamic model[6),10)]. Additionally, the ^{13}C NMR technique can be applied to more complex gas systems[11)]. Thus, the ^{13}C NMR technique may be effective for the determination of crystal structure and for the estimation of cage occupancies. However, suitable high quality spectra are difficult to obtain for natural gas hydrate samples because of the low natural abundance of ^{13}C and the low concentration of natural gas hydrate in the samples recovered from the sea floor[7)]. Therefore, the ^{13}C NMR measurement technique must be improved for the analysis of natural gas hydrate samples. The solid-state ^{13}C NMR method using the Cross Polarization and Magic Angle Spinning (CP-MAS) technique can effectively enhance the signal intensities[4),6),12),13)]. In addition, such enhancement in signal intensities is possible at lower temperatures, in contrast to previous ^{13}C NMR measurements of the hydrate samples which were usually carried out at 193-253 K[4),6)].

In the present study, CP-MAS ^{13}C NMR analyses of the mixed CH_4–C_2H_6 gas hydrate system were carried out at 163 K, and the cage occupancies of the guest molecules in mixed gas hydrates containing CH_4 and C_2H_6 were estimated.

2. Experimental

Pure CH_4 and C_2H_6 hydrates were prepared from ice particles and the corresponding hydrocarbon gases using a milling-type high-pressure vessel. Mixed CH_4–C_2H_6 gas hydrates were prepared in the same way using gas mixtures with the desired compositions. The preparation method was as follows. Small (0.5-1.0 mm) ice particles (30 g) were loaded into the high-pressure vessel (1×10^{-3} m^3) with two stainless steel rods for mixing, and the gas (1.5-1.8 MPa) was introduced into the vessel (gas composition analyzed by gas chromatography). The ice particles were milled by the stainless steel rods in the rotating vessel (*ca.* 50 rpm) in a cold room at 263 K. A decrease in pressure of 0.1-0.3 MPa was observed as a result of hydrate formation. The hydrate samples were recovered from the vessel at liquid N_2 temperature. A small portion of the sample was decomposed in a small vessel to analyze the dissociated gases by gas chromatography.

The ^{13}C NMR spectra of the hydrate samples were measured by an NMR spectrometer (JEOL model JNM-AL400, 100 MHz) equipped with a probe for solid samples (JEOL model SH40T6) at 163 K using cooled dry N_2 gas. Almost no appreciable decreases in the signal intensities were observed during the measurements at 163 K. The hydrate samples were introduced into a zirconia sample tube (JEOL; diameter: 6 mm, length: 22 mm) in liquid N_2. CP-MAS ^{13}C NMR measurement of hydrocarbon hydrates requires long contact time for the quantitative analysis[6)]. Therefore, the CP-MAS ^{13}C NMR measurements were carried out under the following conditions: contact time 10 ms, pulse delay time 50 s, number of acquisitions 40-400 (depending on the S/N ratio), and spinning rate 3.0-4.0 kHz at the magic angle. The values of the ^{13}C chemical shift were determined using adamantane as an external reference material with the methyl carbon peak at 298 K set at 29.472 ppm[14)]. ^{13}C single-pulse NMR measurements were carried out under the following conditions: ^{13}C pulse length 5.5 μs (90°), pulse delay time 50 s for complete relaxation of the samples, number of acquisitions 80 and 200 (depending on the S/N ratio), and spinning rate 3.8 kHz at the magic angle.

3. Results and Discussion

CP-MAS ^{13}C NMR spectra of pure CH_4 and pure C_2H_6 hydrates are shown in **Fig. 1 (a)** and **(e)**, respectively. The CH_4 hydrate was characterized by two peaks at chemical shifts of −4.14 ppm and −6.52 ppm, attributed to CH_4 molecules in the small and large cages of s**I**, respectively. The C_2H_6 hydrate was characterized by a single peak at 7.95 ppm, assigned to C_2H_6 molecules in the large cage of s**I** ($5^{12}6^2$), since C_2H_6 is too large for the small cage (5^{12}). The present peaks correspond to those already reported[4)].

In the mixed gas hydrates containing CH_4 and C_2H_6, the concentration of C_2H_6 in the hydrate phase (determined by gas chromatography and denoted as y_E^{GC}) was different from that in the initial feed mixed gas (denoted as x_E). For example, the mixed gas with $x_E = 1.1\%$ yielded a hydrate with $y_E^{GC} = 18\%$. The relationship between x_E and y_E^{GC} has been reported elsewhere[4),8)]. Typical CP-MAS ^{13}C NMR spectra of the mixed gas hydrates are also shown in **Fig. 1**. The crystallographic structure of the mixed gas hydrate with $y_E^{GC} = 18\%$ is s**II**[8)]. The spectrum **(b)** of this sample included three NMR peaks at 6.50 ppm, −4.04 ppm, and −7.88 ppm, which were attributed to C_2H_6 in $5^{12}6^4$, CH_4 in 5^{12}, and CH_4 in $5^{12}6^4$, respectively, on the basis of the previous study[4)]. Spectrum **(c)** of the sample with

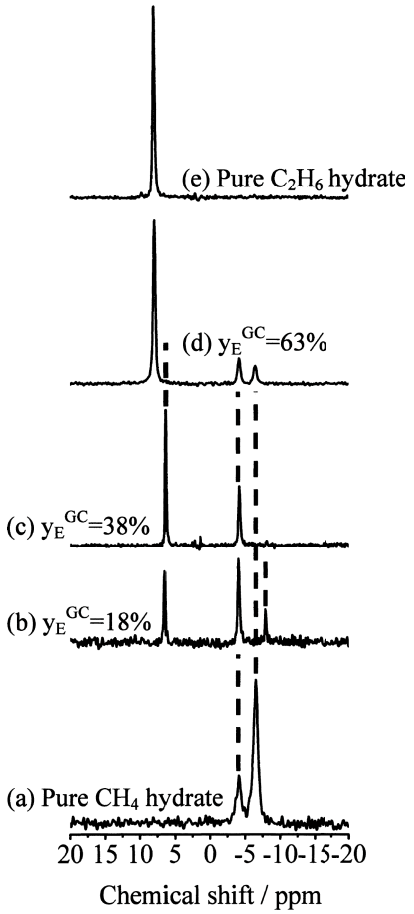


Fig. 1 CP-MAS ^{13}C NMR Spectra of Pure CH_4 Hydrate, Pure C_2H_6 Hydrate, and Mixed CH_4–C_2H_6 Hydrates at 163 K

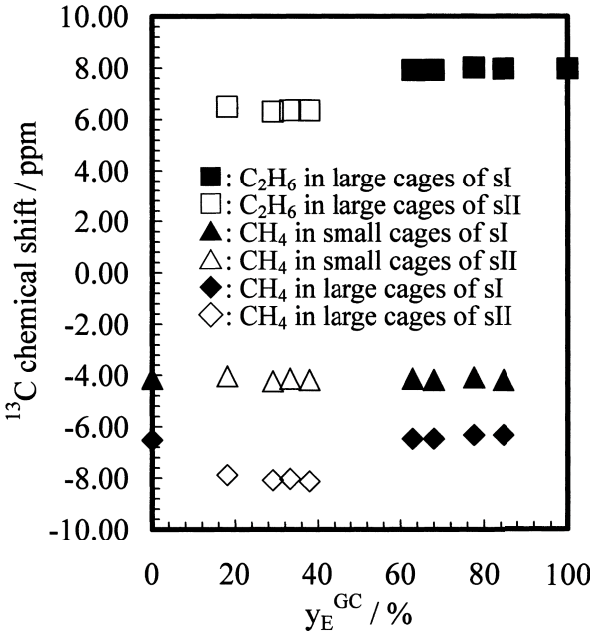


Fig. 2 Changes in ^{13}C Chemical Shifts in CH_4–C_2H_6 Hydrates with Dissociated C_2H_6 Concentrations Measured by Gas Chromatography (y_E^{GC})

$y_E^{GC} = 38\%$ ($x_E = 15\%$) showed three peaks at the same positions, indicating the s**II** structure. However, the peak intensity of CH_4 in $5^{12}6^4$ in spectrum **(c)** was much smaller than that in spectrum **(b)**. On the other hand, spectrum **(d)** showed the chemical shifts of the sample with $y_E^{GC} = 63\%$ ($x_E = 30\%$) were almost the same as those for pure CH_4 and C_2H_6 hydrates indicating the s**I** structure. In the present study, CP-MAS ^{13}C NMR measurements were carried out on eight samples in the range of $18 \le y_E^{GC} \le 85\%$. The observed chemical shifts are shown in **Fig. 2**. The changes in the chemical shifts for CH_4 and C_2H_6 in the large cages ($5^{12}6^2$ for s**I** and $5^{12}6^4$ for s**II**) clearly reflected the crystallographic changes according to the changes in the gas composition of the CH_4–C_2H_6 mixture. The observed structural changes associated with the C_2H_6 concentration were consistent with those already reported[4),5),8)].

Gas composition can be estimated from the ^{13}C NMR peak intensities assigned to CH_4 and C_2H_6 in the case of mixed gas hydrates containing CH_4–C_2H_6, without requiring the Cross Polarization (CP) technique. The concentration of C_2H_6 determined by ^{13}C NMR (denoted by y_E^{NMR}) can be evaluated by Eq. (1).

$$y_E^{NMR} = \frac{I_E}{I_M + I_E} \times 100 \quad (1)$$

I_M is the sum of the two integrated peak intensities of CH_4, and I_E is the half value of the integrated peak intensities of C_2H_6. ^{13}C single-pulse NMR spectra of two samples (b) (s**II**, $y_E^{GC} = 18\%$) and (d) (s**I**, $y_E^{GC} = 63\%$) are shown in **Fig. 3**. The C_2H_6 concentrations were calculated as 19% for (b) and 63% for (d) from the NMR spectra. Thus, C_2H_6 concentrations determined by the ^{13}C single-pulse NMR method agreed well with those estimated by gas chromatography (y_E^{GC}). However, sufficiently high quality spectra were difficult to obtain by the ^{13}C single-pulse method for samples with low concentrations of guest molecules. As shown in **Fig. 1**, high quality spectra could be obtained by the CP-MAS method for such samples. However, the CP efficiency depends on the type of molecule observed and measurement conditions. Therefore, y_E^{NMR} evaluated by Eq. (1) from the CP-MAS ^{13}C NMR data would not correspond to the real concentration if the CP efficiency for CH_4 was different from that for C_2H_6. **Figure 4** compares the C_2H_6 concentrations estimated from CP-MAS ^{13}C NMR spectra (y_E^{NMR}) with those estimated by gas chromatography (y_E^{GC}), and shows a good correlation (slope = 1.0055, correlation coefficient = 0.9988), implying that the CP efficiency for CH_4 is approximately the same as that for C_2H_6 in these hydrate structures. Although we did not study the difference in CP efficiency between CH_4 and C_2H_6 in detail, the results shown in **Figs. 3** and **4** indicate

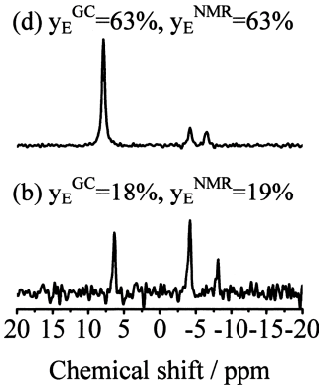
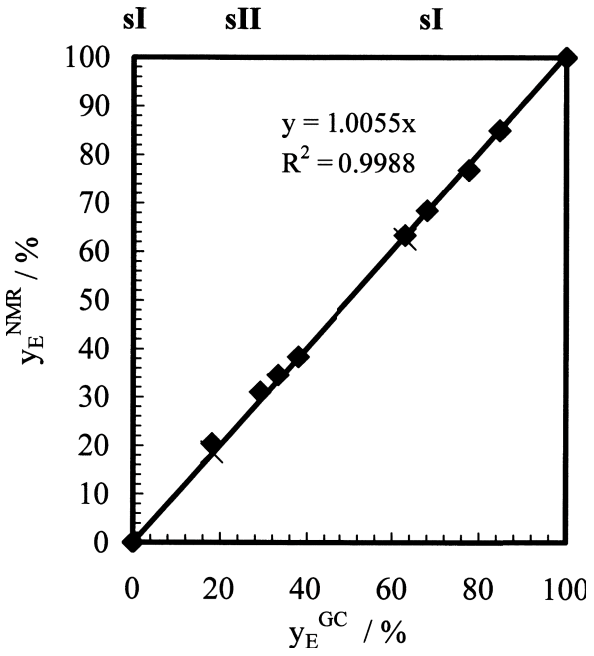


Fig. 3 ^{13}C Single-pulse NMR Spectra of Mixed CH_4–C_2H_6 Hydrates at 163 K

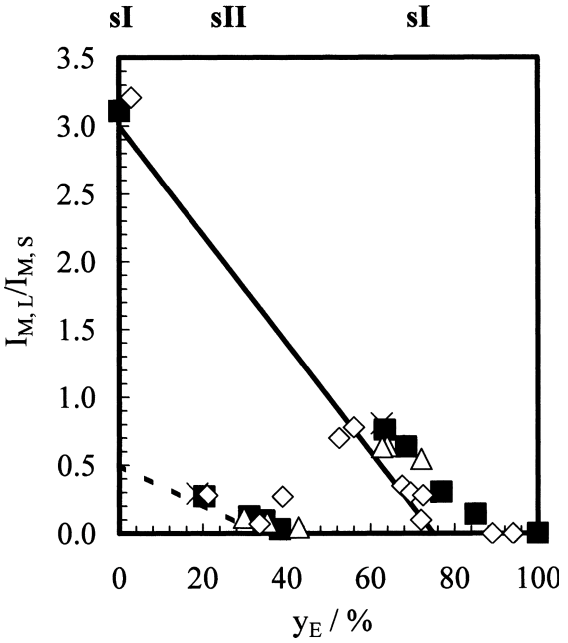


◆: CP-MAS ^{13}C NMR method, ×: ^{13}C single-pulse NMR method.

Fig. 4 Relationship between Encaged C_2H_6 Concentrations Estimated by ^{13}C NMR Spectra (y_E^{NMR}) and Dissociated C_2H_6 Concentrations Measured by Gas Chromatography (y_E^{GC})

that the compositions of CH_4 and C_2H_6 in the mixed gas hydrates can be directly determined from the CP-MAS ^{13}C NMR data. In contrast, studies using Raman spectroscopy determined the gas composition of the hydrate phase by gas chromatography. Consequently, CP-MAS ^{13}C NMR spectroscopy is much more convenient for the determination of hydrate structure and gas composition in the CH_4–C_2H_6 hydrates compared with Raman spectroscopy. Therefore, the C_2H_6 concentration evaluated by the CP-MAS ^{13}C NMR data will be simply expressed as y_E in the following discussion.

Figure 1 shows that both C_2H_6 and CH_4 molecules



■: CP-MAS ^{13}C NMR value, ×: ^{13}C single-pulse NMR value, △: Raman value[4], ◇: Raman value[8].
Solid line: full occupancy in s**I**, Dotted line: full occupancy in s**II**.

Fig. 5 Changes in the Relative Integrated Signal Intensities Ratio ($I_{M,L}/I_{M,S}$) with C_2H_6 Concentration in the Hydrate Phase (y_E)

in the different cages of the mixed gas hydrates can be distinguished by the ^{13}C NMR technique. Therefore, I_M in Eq. (1) can be divided into two peak intensities $I_{M,S}$ and $I_{M,L}$, which are the intensities of CH_4 in small and large cages, respectively. The ratio of $I_{M,L}/I_{M,S}$ may reflect the structures of the mixed gas hydrates. For pure CH_4 hydrate with the s**I** structure, $I_{M,L}/I_{M,S}$ should be 3 if all cages are fully occupied by CH_4. For pure CH_4 hydrate with the s**II** structure, $I_{M,L}/I_{M,S}$ should be 0.5. If all small cages are occupied by CH_4 and all large cages by CH_4 or C_2H_6, the changes in $I_{M,L}/I_{M,S}$ with y_E can be expressed by $(I_{M,L}/I_{M,S}) = 3–4y_E$ for s**I** and $(I_{M,L}/I_{M,S}) = 0.5–1.5y_E$ for s**II**. The changes in $I_{M,L}/I_{M,S}$ against y_E are shown in **Fig. 5**, where the solid line and the dotted line correspond to full occupancy in the s**I** and s**II** structures, respectively. The $I_{M,L}/I_{M,S}$ values estimated by the CP-MAS ^{13}C NMR technique for the samples with $20 \le y_E \le 38\%$ decreased with y_E along the dotted line for s**II**, and the $I_{M,L}/I_{M,S}$ values for the samples with $63 \le y_E \le 85\%$ decreased with y_E along the solid line for s**I**. The $I_{M,L}/I_{M,S}$ values estimated by the ^{13}C single-pulse NMR technique for the same samples were in good agreement. As shown in **Fig. 5**, the $I_{M,L}/I_{M,S}$ values obtained in the present study were greater than those assuming full occupancy for both structures, similar to the Raman spectroscopic findings reported previously[4]. Although a previous study showed almost full occupancy for the samples in this mixed gas system by Raman spectroscopy[8], the present

results indicate the presence of some vacant sites in the hydrates.

The present study attempted to estimate the cage occupancies of mixed gas hydrates from the CP-MAS ^{13}C NMR data using the statistical thermodynamic model[10]. This model has been already applied to estimation of the cage occupancy by the ^{13}C NMR and Raman techniques[4),6)]. The values of θ_S/θ_L in the CH_4–C_2H_6 system are given by Eq. (2) for s**I** and Eq. (3) for s**II**, where θ_S and θ_L represent the cage occupancies of the small cage and the large cage, respectively.

$$\frac{\theta_S}{\theta_L} = \frac{3I_{M,S}}{I_{M,L} + I_{E,L}}$$

$$\frac{\theta_S}{\theta_L} = \frac{I_{M,S}}{2\left(I_{M,L} + I_{E,L}\right)} \qquad (3)$$

Furthermore, $\theta_{M,S}$ (small cage occupancy by CH_4), $\theta_{M,L}$ (large cage occupancy by CH_4), and $\theta_{E,L}$ (large cage occupancy by C_2H_6) are given by Eq. (4) for s**I** and Eq.(5) for s**II**, respectively[6),10)].

$$\text{s}\mathbf{I}: -\Delta\mu_W^\circ(\text{I}) = \frac{RT}{46}\left[6\ln\left(1-\theta_{M,L}-\theta_{E,L}\right) + 2\ln\left(1-\theta_{M,S}\right)\right] \qquad (4)$$

$$\text{s}\mathbf{II}: -\Delta\mu_W^\circ(\text{II}) = \frac{RT}{136}\left[8\ln\left(1-\theta_{M,L}-\theta_{E,L}\right) + 16\ln\left(1-\theta_{M,S}\right)\right] \qquad (5)$$

$\Delta\mu_W^\circ$(I) and $\Delta\mu_W^\circ$(II) are the differences in chemical potentials between ice and the hypothetical empty hydrate lattices of s**I** and s**II**, respectively. The values of $\Delta\mu_W^\circ$(I) and $\Delta\mu_W^\circ$(II) used here were 1297 J/mol for s**I** and 937 J/mol for s**II**, respectively[15)]. R and T are the gas constant and temperature for hydrate formation, respectively.

The values for $\theta_{M,S}$, $\theta_{M,L}$, and $\theta_{E,L}$ in s**I** were calculated by Eqs. (2) and (4), and those in s**II** by Eqs. (3) and (5). In both structures, small cage occupancy (θ_S) corresponds to $\theta_{M,S}$, because the small cages can encage only CH_4. Large cage occupancy (θ_L) is the sum of $\theta_{M,L}$ and $\theta_{E,L}$, since the large cages allow inclusion of both guest molecules. The ratio of $\theta_{E,L}/\theta_{M,L}$ coresponds to $I_{E,L}/I_{M,L}$. The changes in θ_S and θ_L with y_E are shown in **Fig. 6**. For pure CH_4 hydrate, the cage occupancies were estimated as $\theta_S = 0.94$ and $\theta_L = 0.97$, which are almost consistent with those reported for artificial pure CH_4 hydrate ($\theta_S = 0.89$ and $\theta_L = 0.97$)[6)]. The present results show that more than 97% of large cages in both s**I** and s**II** are occupied by CH_4 and C_2H_6. However, θ_S decreases with increasing y_E ($\theta_S = 0.82$ at $y_E = 20\%$ and $\theta_S = 0.74$ at $y_E = 38\%$ in the region of s**II**, and $\theta_S = 0.77$ at $y_E = 63\%$ and $\theta_S = 0.45$ at $y_E = 85\%$ in the region of s**I**). Accordingly, the higher values of $I_{M,L}/I_{M,S}$ in **Fig. 5** reflects the decrease in θ_S with increase in y_E.

The changes in the guest molecule distribution in the large cages with increasing C_2H_6 concentration are shown in **Fig. 7**. The $\theta_{E,L}$ in the region of s**II**, $20 \le y_E \le 38\%$, increases with increasing y_E, whereas the $\theta_{M,L}$ decreases in this region. The values of $\theta_{M,L}$ and $\theta_{E,L}$ for the sample with $y_E = 38\%$ were 0.05 and 0.94, respectively, indicating that the large cages of s**II** in this sample were almost completely occupied by C_2H_6. At $y_E = 63\%$, the structure was s**I** and $\theta_{M,L}$ was 0.20. Then, $\theta_{M,L}$ decreases toward zero with increasing C_2H_6 concentration. Thus, the large cages in both s**I** and s**II** were preferentially occupied by C_2H_6. As can be seen from **Fig. 6**, θ_S rapidly decreased with increasing y_E in the region of s**II**. The pure C_2H_6 hydrate has the s**I** structure with $\theta_S = 0$, indicating that s**II** at the low level of θ_S is more unstable than s**I**. Therefore, excessive decrease in θ_S in s**II** might induce structural change from s**II** to s**I** at higher concentrations of C_2H_6.

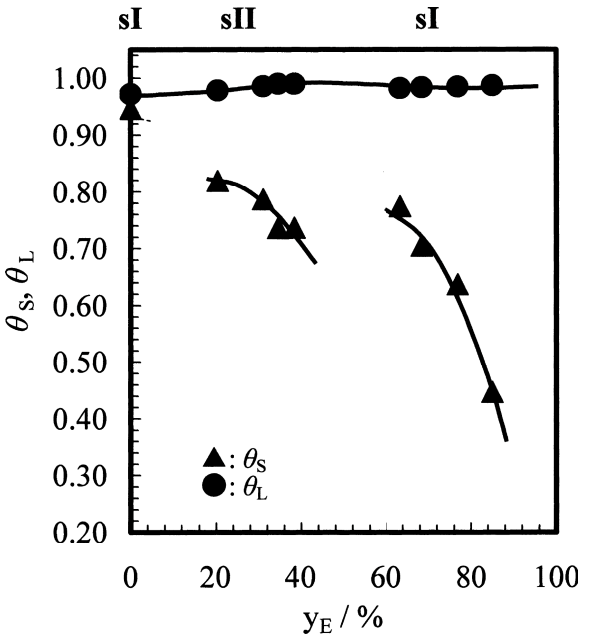


Fig. 6 Changes in the Occupancies of Small Cages (θ_S) and Large Cages (θ_L) with C_2H_6 Concentration in the Hydrate Phase (y_E)

4. Conclusions

The present study obtained high quality CP-MAS ^{13}C NMR spectra of mixed CH_4–C_2H_6 gas hydrates at 163 K without using ^{13}C-enriched gases. The changes in the NMR chemical shifts clearly corresponded to the structural changes in the hydrate structure (s**I** for pure CH_4 hydrate, s**II** in the range of $20 \le y_E \le 38\%$, and s**I** in the range $63\% \le y_E$), and agreed with the findings of other techniques such as the XRD method and Raman spectroscopy. The present study also clarified that the gas compositions estimated by the CP-MAS ^{13}C NMR spectra agreed well with the corresponding dissociated gases measured by gas chromatography and compo-

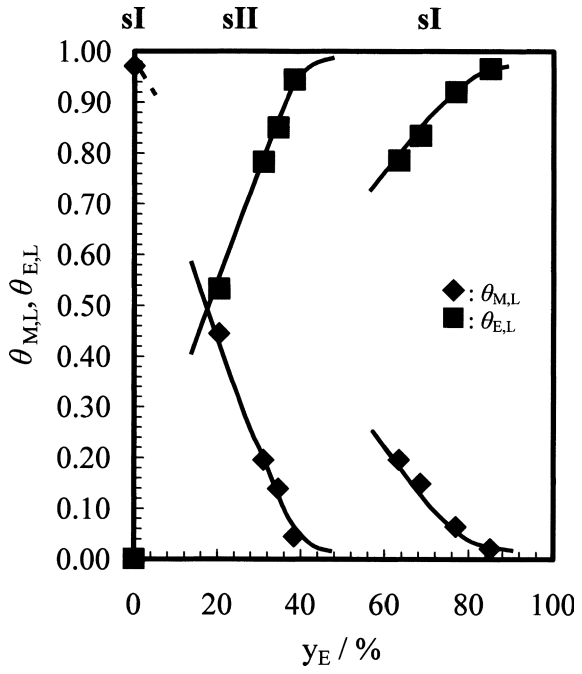


Fig. 7 Changes in the Guest Molecule Distribution in the Large Cages with C_2H_6 Concentration in the Hydrate Phase (y_E)

sitions estimated by the ^{13}C single-pulse NMR spectra, indicating that the gas composition in the mixed gas hydrates can be directly estimated from the CP-MAS ^{13}C NMR spectra. The occupancies of small cages and large cages were evaluated from the ^{13}C NMR data based on the statistical thermodynamic model, which showed that the occupancies of small cages decreased with increasing C_2H_6 concentration in both s**I** and s**II** structures, whereas the occupancy of large cages was unchanged through a wide range of C_2H_6 concentrations at almost the full occupancy level.

Acknowledgment

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要　　旨

CP-MAS ^{13}C NMR 法によるメタン-エタン混合ガスハイドレートのガス組成およびケージ占有率評価

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本研究では，メタン－エタン混合ガスハイドレートの CP-MAS ^{13}C NMR 測定を行った。得られたメタンとエタンの ^{13}C ケミカルシフト値はハイドレート構造の変化に対応した。包接ガス組成は得られた ^{13}C NMR シグナルの積分強度比から見積もられ，ガスクロマトグラフィーによって見積もられた分解ガス組成と良い一致を示した。このことから，混合ガスハイドレート中のガス組成は ^{13}C NMR スペクトルによって直接算出可能である。得られた ^{13}C NMR スペクトルおよび統計熱力学モデルに基づき，ハイドレートの小ケージおよび大ケージ占有率を算出した。その結果，大ケージはガス組成によらずほぼゲスト分子によって占有されているのに対して，小ケージ占有率はエタン組成増加に伴い減少することが示された。さらに，大ケージはメタン分子よりエタン分子によって優先的に占有されることが示唆された。

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