Structure and Guest Distribution of the Mixed Carbon Dioxide and Nitrogen Hydrates As Revealed by X-ray Diffraction and $^{13}$C NMR Spectroscopy

Yu-Taek Seo and Huen Lee*

Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, 373-1 Gusaeng-dong, Yuseong-gu, Daejeon 305-701, Korea

Received: April 28, 2003; In Final Form: September 25, 2003

In this contribution, X-ray diffraction and $^{13}$C NMR spectroscopy were used to identify structure and guest distribution of the mixed $\text{N}_2 + \text{CO}_2$ hydrates. X-ray diffraction results of the mixed $\text{N}_2 + \text{CO}_2$ hydrates confirmed that the unit cell parameter was \( \sim 11.8 \) Å over the gas mixture composition range of 3–20 mol % $\text{CO}_2$ and the formed hydrates were identified as structure I. When the composition of the gas mixture was reduced to 1 mol % $\text{CO}_2$, the structure of the mixed hydrate was transformed to structure II showing the unit cell parameter of 17.26(2) Å. $^{13}$C cross-polarization (CP) NMR spectroscopy was used to examine the distribution of carbon dioxide molecules in small \( 5^{12} \) and large \( 5^{12}6^2 \) cages of structure I. From NMR spectra of the mixed $\text{N}_2 + \text{CO}_2$ hydrate formed from gas mixture of 20 and 10 mol % $\text{CO}_2$, powder patterns having chemical shift anisotropy of \(-54.5\) and \(-53.8\) ppm were observed, respectively. There was no clear isotropic line indicating carbon dioxide molecules in the small \( 5^{12} \) cages of structure I. These NMR spectra showed that the carbon dioxide molecules occupied mainly the large \( 5^{12}6^2 \) cages of structure I when the mixed $\text{N}_2 + \text{CO}_2$ hydrate was formed at a vapor-phase composition range of 10–20 mol % $\text{CO}_2$. In addition, from the analysis of the gases collected from a dissociating hydrate sample, the amount of carbon dioxide in the mixed $\text{N}_2 + \text{CO}_2$ hydrates increased greatly with a small increase of carbon dioxide in the vapor phase. Accordingly, the carbon dioxide molecules seemed to occupy both the small and large cages of structure I above the vapor-phase composition of 33.3 mol % $\text{CO}_2$.

Introduction

Gas hydrates are a general class of crystalline compounds formed by the physically stable interaction between water and relatively small guest molecules.\(^1\) Under suitable temperature and pressure conditions, water molecules are connected by hydrogen bonding and form polyhedral cages. Low-molecular-weight gas molecules such as methane, carbon dioxide, and nitrogen could be contained in these cages. Although gas guest molecules are physically enclosed within the cages, no actual chemical union exists between the guest and host water molecules. These nonstoichiometric crystalline compounds are divided into three distinct structures, I, II, and H, which differ in cavity size and shape.\(^2\) Besides these three structures, structure T, a more complex structure, containing two unusually shaped cages, was also newly observed in the presence of dimethyl ether.\(^3\) It is clear that many of the physical attributes of gas hydrates remain unknown and thus have to be identified in more detail.

Gas hydrates are of particular interest in energy and environmental fields because of the emerging possible applications of hydrates in the storage of natural gas,\(^4\) sequestration of carbon dioxide on the ocean floor,\(^5\) and separation of greenhouse gas from flue gas.\(^6\) The literature contains a number of experimental and theoretical works to understand the macroscopic phase behavior and structural characteristics\(^7-10\) of pure and mixed hydrates. In particular, recently, a powerful hydrate equilibrium prediction program called as CSMGem was developed by the Colorado School of Mines, which basically incorporates the hydrate fugacity model with the Gibbs energy minimization techniques.\(^11\) However, only a few studies have been focused on the mixture of carbon dioxide and nitrogen despite its industrial importance in greenhouse gas separation. Kang et al.\(^5\) developed the basic concept for separating carbon dioxide from power plant flue gas using the mixed hydrate formation of nitrogen and carbon dioxide. They measured hydrate equilibrium conditions of the mixed hydrates and analyzed hydrate phase compositions to verify the feasibility of a hydrate-based gas separation process; however, they did not provide any precise experimental results revealing the structure of the mixed hydrate and distribution of guest molecules in the hydrate cages. Thus, in the present study, X-ray diffraction was used to confirm the structure of mixed $\text{N}_2 + \text{CO}_2$ hydrates, and NMR spectroscopy was used to identify the distribution of carbon dioxide in both small and large hydrate cages. In addition, the corresponding hydrate phase compositions were also measured as macroscopic approaches to complement the NMR spectroscopic results.

Experimental Section

The X-ray powder diffraction pattern was recorded at 113 K on a Rigaku Geigerflex goniometer diffractometer, using graphite monochromatized Cu $K\alpha$ radiation ($\lambda = 1.5406$ Å) in the $2\theta/\theta$ scan mode. Samples were scanned over a range of $10^\circ < 2\theta < 60^\circ$, with a scan speed of 0.5° per minute at an increment of 0.05° in 2$\theta$, rendering a total acquisition time of approximately 2 h for each sample.

The $^{13}$C cross-polarization (CP) NMR spectra were recorded on a Bruker DSX 400 NMR spectrometer at a Larmor frequency of 100.6 MHz. The powder samples were placed in a 4 mm
Results and Discussion

**CO₂ Dynamics in Hydrate Cages.** X-ray diffraction was adopted as one of the fundamental approaches to determine the crystal structure of gas hydrates. The guest dynamics in hydrate cages was determined by the NMR spectroscopic analysis of hydrate samples, so it is imperative to establish the mutual consistency between the structures by X-ray diffraction and the dynamics by NMR spectroscopy to obtain the structural characteristics of pure and mixed hydrates. Therefore, for the preliminary reference, these two powerful methods were used to analyze polycrystalline samples of pure CO₂ hydrates, which provide the unit cell parameters and more importantly the guest dynamics of carbon dioxide molecules in the small and large cages of structure I.

Figure 1a represents the X-ray diffraction pattern of pure CO₂ hydrate at 113 K, which was known to form structure I, along with the calculated angles of structure I. All of the diffraction lines of pure CO₂ hydrate were attributed to structure I and assigned as Miller indices at corresponding angles. It has been noted that the (110), (200), (210), and (211) diffraction peaks appearing at low angle ranges showed weak relative intensities compared to other peaks appearing from 25° to 60°. From these Miller indices and 20 values, the unit cell parameter for the polycrystalline sample of pure CO₂ hydrates that formed structure I was 11.89(3) Å. With the results of other structure I samples, all of the values were compared and confirmed to be in a high level of agreement.

The knowledge of molecular dynamics in small and large cages of structure I could be obtained from the analysis of the ¹³C NMR spectral shape of a pure CO₂ hydrate. If carbon dioxide molecules were isolated, it shows no chemical shift anisotropy, and therefore, gaseous carbon dioxide molecules contribute to the isotropic shift. For carbon dioxide enclathrated into hydrate cages, a chemical shift anisotropy has been induced by asymmetry in the immediate environment of the molecules making the chemical shift anisotropy a very sensitive probe of guest distribution in hydrate cages. The ¹³C CP NMR spectrum of pure CO₂ hydrate is shown in Figure 1b. Since the small ⁵¹² cages of structure I produced pseudospherical symmetry, causing the molecular motions to be isotropic, only a sharp line at the isotropic chemical shift of 123.1 ppm was observed. For carbon dioxide in the large ⁵¹⁶ cages of structure I, the powder pattern was observed due to the asymmetric shape of the ⁵¹⁶ cages and reflected the anisotropic motions of carbon dioxide molecules. The chemical shift anisotropy could be defined as \[ \Delta = \delta_{\text{iso}} - \delta_{zz} \] where \( \delta_{\text{iso}} \) is the isotropic chemical shift and \( \delta_{zz} \) is the \( zz \) component of the chemical shift tensor; then the observed chemical shift anisotropy value was 53.3 ppm. The symmetry
of small $5^{12}$ and large $5^{12}6^4$ cages of structure II was contrary to that of the structure I cages.

To investigate the CO$_2$ molecular dynamics in the cages of structure II, the mixed CO$_2$ + C$_3$H$_8$ hydrate was formed from 80 mol % CO$_2$ and a balanced propane gas mixture, where the structure of the mixed hydrate was known to be structure II. The resulting $^{13}$C CP NMR spectrum of the mixed CO$_2$ + C$_3$H$_8$ hydrate is shown in Figure 2. Although the carbon dioxide spectrum in Figure 2 is similar to the spectrum observed for structure I, there are clear differences in chemical shift data. The isotropic line observed at a chemical shift of 124.6 ppm indicates that carbon dioxide molecules occupy the pseudo-spherical large $5^{12}6^4$ cages. The powder pattern was associated with carbon dioxide molecules in small $5^{12}$ asymmetric cages, and the observed chemical shift anisotropy was $-42.2$ ppm, slightly lower than that of large cages of structure I. The two propane $^{13}$C resonance lines are not resolved and are observed as a single peak at 16.8 ppm. The $^{13}$C NMR spectra shown in Figures 1 and 2 clearly suggest that the cage symmetry could be used as an effective indicator for determining the guest distribution in hydrate cages. Thus, with cross-exploration of X-ray diffraction and the $^{13}$C CP NMR spectra, it becomes possible to elucidate the structure and guest distribution of mixed hydrates containing carbon dioxide.

Structure and Guest Distribution of the Mixed N$_2$ + CO$_2$ Hydrates. Nitrogen is one of the smallest formers of gas hydrate when existing as a single guest. Davidson et al.

To investigate the CO$_2$ molecular dynamics in the cages of structure II, the mixed CO$_2$ + C$_3$H$_8$ hydrate was formed from 80 mol % CO$_2$ and a balanced propane gas mixture, where the structure of the mixed hydrate was known to be structure II. The resulting $^{13}$C CP NMR spectrum of the mixed CO$_2$ + C$_3$H$_8$ hydrate is shown in Figure 2. Although the carbon dioxide spectrum in Figure 2 is similar to the spectrum observed for structure I, there are clear differences in chemical shift data. The isotropic line observed at a chemical shift of 124.6 ppm indicates that carbon dioxide molecules occupy the pseudo-spherical large $5^{12}6^4$ cages. The powder pattern was associated with carbon dioxide molecules in small $5^{12}$ asymmetric cages, and the observed chemical shift anisotropy was $-42.2$ ppm, slightly lower than that of large cages of structure I. The two propane $^{13}$C resonance lines are not resolved and are observed as a single peak at 16.8 ppm. The $^{13}$C NMR spectra shown in Figures 1 and 2 clearly suggest that the cage symmetry could be used as an effective indicator for determining the guest distribution in hydrate cages. Thus, with cross-exploration of X-ray diffraction and the $^{13}$C CP NMR spectra, it becomes possible to elucidate the structure and guest distribution of mixed hydrates containing carbon dioxide.

Structure and Guest Distribution of the Mixed N$_2$ + CO$_2$ Hydrates. Nitrogen is one of the smallest formers of gas hydrate when existing as a single guest. Davidson et al.

To investigate the CO$_2$ molecular dynamics in the cages of structure II, the mixed CO$_2$ + C$_3$H$_8$ hydrate was formed from 80 mol % CO$_2$ and a balanced propane gas mixture, where the structure of the mixed hydrate was known to be structure II. The resulting $^{13}$C CP NMR spectrum of the mixed CO$_2$ + C$_3$H$_8$ hydrate is shown in Figure 2. Although the carbon dioxide spectrum in Figure 2 is similar to the spectrum observed for structure I, there are clear differences in chemical shift data. The isotropic line observed at a chemical shift of 124.6 ppm indicates that carbon dioxide molecules occupy the pseudo-spherical large $5^{12}6^4$ cages. The powder pattern was associated with carbon dioxide molecules in small $5^{12}$ asymmetric cages, and the observed chemical shift anisotropy was $-42.2$ ppm, slightly lower than that of large cages of structure I. The two propane $^{13}$C resonance lines are not resolved and are observed as a single peak at 16.8 ppm. The $^{13}$C NMR spectra shown in Figures 1 and 2 clearly suggest that the cage symmetry could be used as an effective indicator for determining the guest distribution in hydrate cages. Thus, with cross-exploration of X-ray diffraction and the $^{13}$C CP NMR spectra, it becomes possible to elucidate the structure and guest distribution of mixed hydrates containing carbon dioxide.
behavior reflects the anisotropic motion of carbon dioxide molecules in asymmetric 51262 cages of structure I. There was no clear isotropic line identifying carbon dioxide molecules in pseudospherical 512 cages of structure I. Both X-ray diffraction and the 13C NMR spectrum indicate that structure I forms from a 20 mol % CO2 gas mixture, and carbon dioxide molecules occupy mainly the large 51262 cages of structure I.

Subsequently, the mixed N2 + CO2 hydrate was formed in a 10 mol % CO2 and balanced N2 gas mixture. As evident in Figure 4a, the obtained X-ray diffraction represents that the mixed hydrates of structure I only form from the binary gas mixture of carbon dioxide and nitrogen in the composition range of 10–20 mol % CO2. The 13C NMR spectrum is shown in Figure 4b. The powder pattern having a chemical shift anisotropy of –53.8 ppm was obtained for the mixed N2 + CO2 hydrate formed from a 10 mol % CO2 gas mixture, and there was no isotropic line of carbon dioxide molecules. It might be possible that the powder pattern of carbon dioxide in the large 51262 cages overwhelmed the low intensity isotropic line of carbon dioxide in the small 512 cages because of a relatively low concentration of carbon dioxide in the small 512 cages. However, the recent NMR spectroscopic results clearly suggest that when the mixed N2 + CO2 hydrate is formed from the gas mixture of 10 and 20 mol % CO2, carbon dioxide molecules primarily occupy the large 51262 cages of structure I. The 13C

TABLE 1: 13CO2 Chemical Shift Data of Pure and Mixed Hydrates

<table>
<thead>
<tr>
<th>System</th>
<th>Hydrate structure type</th>
<th>Δ&lt;sup&gt;13&lt;/sup&gt;C (ppm)</th>
<th>Δ&lt;sup&gt;1&lt;/sup&gt; (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure CO2</td>
<td>structure I</td>
<td>123.1</td>
<td>0</td>
</tr>
<tr>
<td>CO2 + C6H6 (80 mol % CO2)</td>
<td>structure II</td>
<td>127.8</td>
<td>-55.3</td>
</tr>
<tr>
<td>N2 + CO2 (20 mol % CO2)</td>
<td>structure I</td>
<td>128.3</td>
<td>-42.2</td>
</tr>
<tr>
<td>N2 + CO2 (10 mol % CO2)</td>
<td>structure I</td>
<td>124.6</td>
<td>0</td>
</tr>
</tbody>
</table>

TABLE 2: Hydrate Phase Compositions of the Mixed N2 + CO2 Hydrates Measured at the Corresponding Vapor Phase Compositions

<table>
<thead>
<tr>
<th>Formation condition (K, bar)</th>
<th>Vapor phase composition (mol % of CO2)</th>
<th>Hydrate phase composition (mol % of CO2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>272.1, 145</td>
<td>1.2</td>
<td>9.0</td>
</tr>
<tr>
<td>272.1, 130</td>
<td>3.3</td>
<td>14.6</td>
</tr>
<tr>
<td>272.1, 105</td>
<td>9.9</td>
<td>46.5</td>
</tr>
<tr>
<td>272.1, 77</td>
<td>18.4</td>
<td>58.8</td>
</tr>
<tr>
<td>272.1, 50</td>
<td>33.3</td>
<td>73.4</td>
</tr>
<tr>
<td>272.1, 41</td>
<td>49.9</td>
<td>85.9</td>
</tr>
<tr>
<td>272.1, 35</td>
<td>66.5</td>
<td>93.9</td>
</tr>
<tr>
<td>272.1, 32</td>
<td>84.7</td>
<td>96.5</td>
</tr>
</tbody>
</table>

CO2 chemical shift data for different hydrate cages are summarized in Table 1.

At this moment, it is uncertain whether the structure II mixed hydrates should be formed from gas mixtures of carbon dioxide and nitrogen. The careful X-ray diffraction analysis was carried out at lower compositions of 6 and 3 mol % CO2. The resulting diffraction patterns indicated that the mixed hydrates formed structure I, showing unit cell parameters of 11.81(1) and 11.78-(1) Å, respectively. However, in the case of the 1 mol % CO2 gas mixture, the structure II hydrates eventually formed, showing a unit cell parameter of 17.26(2) Å under the conditions of our experiments. These results suggest that the stabilization of hydrate cages is mainly governed by carbon dioxide molecules occupying the large cages of structure I in compositions above 3 mol % CO2. It must be noted, however, that below 1 mol % CO2 the structure II hydrate was formed and stabilized by nitrogen molecules.

The previous microscopic approaches for hydrate phase analysis using X-ray diffraction and NMR spectroscopy provide valuable information on hydrate structure and carbon dioxide distribution in hydrate cages. However, the exact compositions of carbon dioxide and nitrogen occupying the hydrate cages could not be obtained because it is difficult to simultaneously analyze individual molecular distributions of carbon dioxide and nitrogen directly from the NMR spectra. Apparently, a macroscopic approach must be introduced to determine the guest compositions in hydrate cages. Thus, the compositions of gases collected from the dissociating hydrate samples were analyzed to determine the relative amount of carbon dioxide and nitrogen occupying the hydrate cages. Table 2 lists the resulting carbon dioxide compositions of the hydrate phase at the corresponding compositions of vapor phase and, as can be expected, shows a trend of increasing the carbon dioxide amount with the increase of carbon dioxide in the vapor phase. At a low carbon dioxide composition in the vapor phase of 1.2 mol % CO2, the amount of carbon dioxide occupying the hydrate cages appeared to be 9.0 mol % CO2. Accordingly, nitrogen molecules might be expected to occupy most of the small and large cages, while carbon dioxide molecules occupy only a small amount of large cages. However, the amount of CO2 in the hydrate phase greatly
increased by changing the hydrate structure from II to I above 3 mol % CO₂ in the vapor phase as listed in Table 2. The cross evaluations of both the macroscopic and microscopic results obtained from the X-ray diffraction, NMR spectra, and hydrate phase compositions make the specific analysis of the guest distribution in the hydrate cages possible. From the X-ray diffraction analysis, the mixed N₂ + CO₂ hydrate was found to form structure I at compositions above 3 mol % CO₂ in the vapor phase. If we consider the ideal occupation of nitrogen and carbon dioxide molecules in small and large cages in the vapor phase, it was demonstrated that the carbon dioxide molecules occupied mainly the large cages of structure I. There was no clear isotropic line indicating the carbon dioxide molecules in small cages of structure I. The analysis of the gases collected from dissociating hydrate samples complements the NMR spectroscopic analysis and provides the carbon dioxide distribution in hydrate cages from the fact that the amount of carbon dioxide in mixed N₂ + CO₂ hydrates increased greatly with a small increase of carbon dioxide in the vapor phase. As the amount of carbon dioxide in the vapor phase increased, the role of stabilizing both small and large cages was transformed from nitrogen to carbon dioxide molecules, which is likely to prefer to stabilize the small and large cages of structure I.

Acknowledgment. This work was supported by Energy Technology R&D funded by the Ministry of Commerce, Industry and Energy of Korea and also partially supported by the Brain Korea 21 Project. In particular, we thank Dr. John A. Ripmeester, National Research Council of Canada, for his helpful discussions and valuable advice.

References and Notes