Identification of Structural Change of Tertiary Butylamine + Methane Mixed Hydrate Using Spectroscopy

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ABSTRACT

The tertiary butylamine hydrate, 16(CH3)3CNH2•156H2O, with type VI structure is a true clathrate (Jeffrey, 1984); there is no evidence of hydrogen-bonding between the amine molecule and the water framework. In this work, the mixed hydrate formation and structure were measured using spectroscopic methods such as NMR and XRD. These two spectroscopic measurements made it sure that P-T equilibrium results were show good agreement with hydrate structure. So these data can be very helpful to understand the basic phase behavior of gas hydrate. In results, it was confirmed that the tertiary butylamine molecules occupied the large cages when pure tertiary butylamine hydrate was formed and methane molecules were captured in the small cages of tertiary butylamine hydrate was formed, respectively from the NMR result. To confirm the hydrate structure formed, XRD data were obtained and calculated to get a structure parameter. The tertiary butylamine molecules act as a strong promoter in gas hydrate formation. Methane is main component in the natural gas, so these results also can be used to separation process by using natural gas hydrate.

KEYWORDS
Hydrate, tert-butylamine, methane, Phase Equilibria, 13C NMR, XRD

INTRODUCTION

The hydrate inclusion compounds are non-stoichiometric solid crystalline materials formed in mixtures of water and relatively small guest molecules. Under specific temperature and pressure conditions, water molecules are connected by hydrogen bonding and form into polyhedron cages. The guest molecules such as low molecular weight gases or volatile liquids can be captured in these cages. Although the guest molecules are physically enclosed within the cages, there does not exist actual chemical union between host water molecules and guest molecules. Especially, the clathrate hydrate, commonly called the gas hydrate, have had the most attention and have been investigated from several different points of view (Jeffrey, 1984). Clathrate hydrates are potentially important media for sate storage and transportation of natural gas, because each volume of clathrate hydrate can contain as much as 184 volumes of gas (STP) (Sloan, 1998).

In general, clathrate hydrates can be divided into three distinct structural type I (sI), II (sII) and H (sH), which are different in their combination of cages of different size and shapes[1]. Though above three structures are well-known, there exist several clathrate hydrate structures such as structure T (sT) and type III--VII (Jeffrey, 1984). The tertiary butylamine (t-BuNH2) clathrate hydrate, 16(CH3)3CNH2•156H2O, with type VI structure is a true clathrate(Jeffrey, 1984); there is no proof of hydrogen-bonding between the host water molecule and guest amine molecule. The t-
BuNH₂ molecules occupy large cages representing complex 17-hedra with 4^{3}, 5^{3}, 6^{2}, 7^{3} and small cages (4^{4}5^{4}) remain empty (McMullan, et al., 1967). The voids are polar and the C-N bond is oriented along the polar axis of the polyhedron (McMullan, et al., 1967).

In this investigation, the novel mixed CH₄ + t-BuNH₂ clathrate hydrate three phase equilibria were measured and its structural characteristics were confirmed by using spectroscopic methods. Also, in order to compare the captured amount of CH₄ gas within the pure and mixed clathrate hydrate, we performed gas uptake measurements for each clathrate hydrate.

**EXPERIMENTAL**

**Materials**: CH₄ gas with a minimum purity of 99.95 mol% was supplied by Linde Gas UK Ltd. The water with ultrahigh purity was supplied from Merck and t-BuNH₂ ((CH₃)₃CNH₂) with purity of 99.5 mol% was purchased from Aldrich. All materials were used without further purification.

**Apparatus and Procedure**: A schematic diagram and detailed description of the experimental apparatus for clathrate hydrate phase equilibria was given in the previous papers (Seo¹, et al., 2001; Seo², et al, 2001) The apparatus was specially constructed to measure accurately the clathrate hydrate dissociation pressures and temperatures. The equilibrium cell was made of 316 stainless steel and had an internal volume of about 50 cm³. Two sapphire windows equipped at the front and back of the cell allowed the visual observation of phase transitions that occurred inside the equilibrium cell. The cell content was vigorously agitated by a magnetic spin bar with an external magnet immersed in a water bath.

The experiment for clathrate hydrate phase equilibrium measurements began by charging the equilibrium cell with about 30 cm³ of aqueous solutions containing various amount of t-BuNH₂. After the equilibrium cell was pressurized to a desired pressure with guest methane gas, the whole main system was slowly cooled to 268 K. When pressure depression due to clathrate hydrate formation reached a steady-state condition, the cell temperature was increased at a rate of about 0.5 K/h. The nucleation and dissociation steps were repeated at least two times in order to reduce hysteresis phenomenon. The equilibrium pressure and temperature of three phases (hydrate(H) – water-rich liquid(L) –vapor(V)) were determined by tracing the pressure - temperature (P - T) profiles from clathrate hydrate formation to dissociation.

To identify clathrate hydrate structure, a Bruker 400 MHz solid-state NMR spectrometer was used in this study. The NMR spectra were recorded at 243 K by placing the powdered clathrate hydrate samples within a 4 mm o.d. Zr rotor that was loaded into the variable temperature (VT) probe. All ¹³C 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 40 s under proton decoupling were employed when the radio frequency field strengths of 50 kHz corresponding to 5 µs 90° pulse were used. The downfield 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 clathrate hydrate sample for spectroscopic analysis was prepared from the clathrate hydrate-forming reactor, which was made of a type 316 stainless steel, with an internal volume of about 140 cm³. The magnetically driven mechanical stirrer was sued for uniform mixing during clathrate hydrate formation. The clathrate hydrate-forming reactor was kept in the water-ethanol mixture bath and its temperature was controlled by an externally circulating refrigerator/heater (JEIO TECH, RBC-20). The reactor was maintained at a constant pressure condition by using a microflow syringe pump (ISCO, model 260D) operated by the mode of constant pressure. About 50 cm³ of the aqueous solution was initially charged into the reactor. When clathrate hydrate formation process was completed, the formed clathrate hydrates were finely powdered in the liquid nitrogen.
vessel and sampled into Zr rotor immersed in liquid nitrogen to prevent any clathrate hydrate dissociation. This Zr rotor, having clathrate hydrate samples, was then inserted to the precooled MAS NMR probe.

RESULTS AND DISCUSSIONS

Phase Equilibria  In this study the liquid \textit{t}-BuNH\textsubscript{2} and CH\textsubscript{4} gas were used as guest molecules to form the mixed clathrate hydrate. Because \textit{t}-BuNH\textsubscript{2} is completely miscible with water, there exist three phase such as the mixed clathrate hydrate (H), \textit{t}-BuNH\textsubscript{2} solution (L) and CH\textsubscript{4} gas (V). The three phase equilibria (H-L-V) for the CH\textsubscript{4} + \textit{t}-BuNH\textsubscript{2} + water system were measured to determine a stable region of the mixed clathrate hydrate at the fixed \textit{t}-BuNH\textsubscript{2} concentration of 9.3 mol\%, and the overall result are shown in Figure 1. The overall phase behavior of the CH\textsubscript{4} + \textit{t}-BuNH\textsubscript{2} + water system revealed that the participation of \textit{t}-BuNH\textsubscript{2} molecules in forming the mixed clathrate hydrate could greatly reduce the dissociation equilibrium pressure at a specific temperature when compared with the corresponding condition of pure CH\textsubscript{4} clathrate hydrate. In the mixed CH\textsubscript{4} + \textit{t}-BuNH\textsubscript{2} clathrate hydrate, the \textit{t}-BuNH\textsubscript{2} molecules can only occupy the large cages because of their size, and guest gas molecules occupy the small cages resulting in stabilizing the structure frame. From the phase behavior of the CH\textsubscript{4} + \textit{t}-BuNH\textsubscript{2} + water system, we could indirectly and on the qualitative basis confirm the enclathration of \textit{t}-BuNH\textsubscript{2} and guest gas molecules in the mixed clathrate hydrate. To identify the formed clathrate hydrate structure and obtain the cage occupancies in the mixed CH\textsubscript{4} + \textit{t}-BuNH\textsubscript{2} clathrate hydrate, the spectroscopic method of NMR and XRD have been adopted as discussed in the later section.

Spectroscopic Analysis Spectroscopic analyses of the mixed \textit{t}-BuNH\textsubscript{2} clathrate hydrate containing CH\textsubscript{4} gas have been made to identify the structure of the mixed clathrate hydrate and determine the cage occupancies of guest molecules captured in the cages. Experimental identification has not yet been reported for structure type of the mixed CH\textsubscript{4} + \textit{t}-BuNH\textsubscript{2} clathrate hydrate using the spectroscopic observation. NMR spectroscopy has been recognized as a powerful tool for the identification of clathrate hydrate, their structure, and compositions, the determination of the guest and host dynamics and recently also processes such as clathrate hydrate formation (Ripmeester and Ratcliffe, 1999). Figure 2 shows a stacked plot of \textsuperscript{13}C MAS NMR spectra of pure \textit{t}-BuNH\textsubscript{2} clathrate hydrate and the mixed CH\textsubscript{4} + \textit{t}-BuNH\textsubscript{2} clathrate hydrate. The pure \textit{t}-BuNH\textsubscript{2} clathrate hydrate spectrum (Figure 2 - (a)) demonstrated two peaks at 47.6 ppm and 31.9 ppm. By the comparison of integrated peak area and structural formula, these peaks can be assigned to the central carbon of \textit{t}-BuNH\textsubscript{2} molecule and the carbons of three methyl groups (–CH\textsubscript{3}) bonded with
the central carbon, respectively. In the NMR spectrum for the mixed \( \text{CH}_4 + t-\text{BuNH}_2 \) clathrate hydrate (Figure 2 - (b)), two distinct resonance lines representing \( t-\text{BuNH}_2 \) molecules captured in the large cages exactly coincide with pure \( t-\text{BuNH}_2 \) clathrate hydrate, and moreover there is a single \( \text{CH}_4 \) resonance line at -4.7 ppm.

The stable clathrate hydrates in the \( \text{CH}_4 + \text{tetrahydrofuran (THF)} + \text{water} \) system had widely varying overall compositions, as \( \text{CH}_4 \) molecules occupied some of large, as well as small, cages (Seo et al., 2003). In order to determine this phenomenon for the \( \text{CH}_4 + t-\text{BuNH}_2 + \text{water} \) system, we followed two specific \( t-\text{BuNH}_2 \) concentrations, 9.3 and 3.0 mol%, during clathrate hydrate formation. As an indirect measurement of clathrate hydrate formation, the \( P - T \) trajectory (Sloan, 1998), which represents hydrate nucleation, growth, and dissociation stages, was measured experimentally and the resulting closed loop made by the clathrate hydrate formation and dissociation processes is shown in Figure 3. The mixed \( \text{CH}_4 + t-\text{BuNH}_2 \) clathrate hydrate started to form directly after going through the three-phase equilibrium boundary, and rapid pressure reduction occurred immediately upon complete transformation of the 9.3 mol% aqueous (16(CH₃)₃CNH₂•156H₂O) \( t-\text{BuNH}_2 \) solution to clathrate hydrate. The system pressure continued to decrease almost linearly with temperature, which indicates that further clathrate hydrate formation did not occur, even after passing the three-phase equilibrium boundary of pure \( \text{CH}_4 \) clathrate hydrate. As the temperature was again raised to approach the phase boundary of the mixed clathrate hydrate, the system pressure abruptly increased due to complete dissociation of formed clathrate hydrate. For structure identification, the \( ^{13}\text{C} \) NMR spectrum of the mixed \( \text{CH}_4 + t-\text{BuNH}_2 \) clathrate hydrate sample obtained at point A was measured and shown the Figure 2 - (b).

In particular, we found an unusual \( P - T \) trajectory when an aqueous 3.0 mol% \( t-\text{BuNH}_2 \) solution (thus considerably below the ideal stoichiometry of the mixed clathrate hydrate of 9.3 mol% (Jeffrey, 1984)) was cooled, as shown in Figure 4. The first pressure reduction, which represents that again the mixed \( \text{CH}_4 + t-\text{BuNH}_2 \) clathrate hydrate formed just below the expected phase

![Figure 2. ¹³C MAS NMR spectra of pure t-BuNH₂ and the mixed t-BuNH₂ + CH₄ hydrate](image-url)
boundary of the mixed clathrate hydrate, is similar to that for the 9.3 mol% t-BuNH₂ mixture shown in Figure 3. Subsequently, further cooling initiated the second pressure drop below the phase boundary of pure CH₄ clathrate hydrate, suggesting that pure CH₄ clathrate hydrate formed as well. Upon warming, a sudden pressure increase, because of clathrate hydrate dissociation, was observed near the phase boundaries of both the pure and mixed clathrate hydrates. The $P - T$ trajectory shown in Figure 4 has two stages of pressure reduction, and it may indicate that there coexist two different kinds of clathrate hydrates in low temperature region like the CH₄ + THF (3.0 mol%) + water system (Seo et al., 2003). To identify the clathrate hydrate structures formed before and after the second reduction, $^{13}$C NMR spectra were obtained for the mixed clathrate hydrate samples at point B and C, and there are shown in Figure 5, respectively. For the mixed clathrate hydrate formed at point B, the NMR spectrum is the same as that of previous sample obtained at point A (Figure 2-(b)). When the temperature was reduced to point C, the unforeseen spectral characteristics of CH₄ molecules appeared as two resonances at -6.8 and -8.3 ppm. These peaks identified as CH₄ molecules in the 5₁₂₆₂ cages of sI clathrate hydrate (Subramanian, et al., 2000) and in the large cages of mixed CH₄ + t-BuNH₂ clathrate hydrate, respectively. In the figure 5 - (b), we could not distinguish the resonance peak of CH₄ molecules captured in the 5₁² cages of sI clathrate hydrate because it overlapped with that of CH₄ molecules enclosed in the small cages of mixed CH₄ + t-BuNH₂ clathrate hydrate located at -4.7 ppm. Accordingly, it can be concluded from the $P - T$ trajectory and NMR data that pure CH₄ clathrate hydrate formed and coexisted with mixed CH₄ + t-BuNH₂ clathrate hydrate in the low temperature region, after passing through the phase boundary of pure CH₄ clathrate hydrate.

XRD (X-ray diffraction) is the most powerful method to determine the crystal structure of solid material. To confirm the hydrate structure formed, XRD data were obtained and calculated to get a structure parameter. These values were compared with existing literature data. Figure 6 shows the experimental measurements of XRD spectroscopy for the mixed CH₄ + t-BuNH₂ and pure t-BuNH₂ clathrate hydrate.
Figure 4. P-T Trajectory of Mixed t-BuNH₂(3.0mol%) + CH₄ Hydrate

NMR Spectrum at Point B

NMR Spectrum at Point C

Figure 5. ¹³C NMR spectra at Point B and C of P-T Trajectory of Mixed t-BuNH₂(3.0mol%) + CH₄ Hydrate
To examine the applicability of hydrate-based storage process for the CH$_4$ gas, the hydrate formation kinetics of the ternary CH$_4$ + water + $t$-BuNH$_2$ system was also determined at 276.15K and 70bar as the first attempt. The consumption rate of CH$_4$ gas became fast at the early time of the growth period, gradually decreased, and finally went to the complete hydration. An abrupt increase of the consumption rate at the initial stage might be considered due to the direct hydration of guest molecules with host water molecules. After the short period of time the increment CH$_4$ consumption rate became low and finally almost flat. In this experiment, the consumed amount of CH$_4$ gas increased with decreasing the concentration of $t$-BuNH$_2$ and it was observed that clathrate hydrate formed fast by $t$-BuNH$_2$.

CONCLUSIONS

In the mixed CH$_4$ + $t$-BuNH$_2$ clathrate hydrate, the $t$-BuNH$_2$ molecules can only occupy the large cages because of their size, and guest gas molecules occupy the small cages resulting in stabilizing the structure frame. From the phase behavior of the CH$_4$ + $t$-BuNH$_2$ + water system, we could indirectly and on the qualitative basis confirm the enclathration of $t$-BuNH$_2$ and guest gas molecules in the mixed clathrate hydrate.

From NMR results, it could be concluded that the structure of pure $t$-BuNH$_2$ clathrate hydrate changed when mixed CH$_4$ + $t$-BuNH$_2$ clathrate hydrate was formed. The different structure of mixed CH$_4$ + $t$-BuNH$_2$ clathrate hydrate was also confirmed from XRD result. It was considered that the new structure of mixed CH$_4$ + $t$-BuNH$_2$ clathrate hydrate came from CH$_4$ occupying the small cage of pure $t$-BuNH$_2$ clathrate hydrate.

Though usual one step forming mixed CH$_4$ + $t$-BuNH$_2$ clathrate hydrate was shown in $P$ - $T$ trajectory of 9.3 mol% $t$-BuNH$_2$ as CH$_4$ occupied the small cage of pure $t$-BuNH$_2$ clathrate hydrate,
$P - T$ trajectory of 3.0 mol\% $t$-BuNH$_2$ showed two step that pure CH$_4$ hydrate was formed after mixed CH$_4$ + $t$-BuNH$_2$ clathrate hydrate had been formed: coexistence of pure CH$_4$ hydrate and mixed CH$_4$ + $t$-BuNH$_2$ clathrate hydrate was proved by using NMR spectroscopy.

New structure of mixed CH$_4$ + 9.3 mol\% $t$-BuNH$_2$ clathrate hydrate was obtained by pure $t$-BuNH$_2$ and mixed CH$_4$ + 9.3 mol\% $t$-BuNH$_2$ clathrate hydrate observation using the useful tool XRD for the structural analysis.

It would be expected that this study could contribute to not only suggestion of spectroscopic analysis about $t$-BuNH$_2$ clathrate hydrate but also improvement of CH$_4$ storage and transportation with interest as the alternative energy sources.

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REFERENCES