Gas hydrates, or more generally clathrate hydrates, are a type of inclusion compound and take the form of nonstoichiometric solid crystalline materials formed from water and small guest molecules.[1] Under sufficient pressure of the guest material and at specific temperatures, 3D hydrate structures are formed by the stacking of polyhedral cages of hydrogen-bonded water molecules. Suitably sized guest molecules are enclathrated in cages and their presence stabilizes the compounds formed. Although the guest molecules are physically enclosed within the cages, there are no direct chemical bonds between host water molecules and guest molecules.

In general gas hydrates form three distinct structural families known as structure I (sI), structure II (sII), and structure T (sT).[3] It is clear that a variety of more complex clathrate hydrate structures, labeled as types III–VII[2] and structure T (sT).[3] It is important to note that hydrogen bonding between host water molecules and guest amine molecules, tBuNH₂ molecules occupy large complex cages with 17 sides (4(5)6(7)) while the small cages (4(5)8) remain empty.[14] It is noteworthy that for lowering the pressure of hydrate formation without significant reduction of the capacity to store CH₄, the use of sH hydrate was suggested.[7]

Many experimental and theoretical works to understand structural transition and tuning of tert-Butylamine Hydrate★★

Do-Youn Kim, Jong-won Lee, Yu-Taek Seo, John A. Ripmeester, and Huen Lee*

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Many experimental and theoretical works to understand macroscopic phase behavior and microscopic structural characteristics of the pure and mixed hydrates have been reported.[8–12] Most recently, we proposed a tuning mechanism to increase the storage capacity of hydrogen in double hydrogen hydrate.[13]

Herein, we report a structural transition of the simple amine hydrate to produce a novel double (CH₄ + tBuNH₂) hydrate as confirmed by using microscopic analytical methods. Powder X-ray diffraction (PXRD) was adopted as the primary method to identify the structure of the gas hydrates and to provide lattice parameters. More importantly, the distribution of guest molecules over the hydrate cages was investigated by NMR spectroscopy, as it is imperative to establish a mutual consistency between the structures from PXRD and the structure-specific chemical-shift signatures from NMR spectroscopy to obtain a more complete description of the hydrates. In addition, the corresponding hydrate compositions were determined from a quantitative analysis of the NMR spectroscopic results. We note that during sample preparation in a high-pressure vessel, the composition of the aqueous phase continuously changes. However, for this work we have focused only on the final equilibrium compositions that are spontaneously determined by the pressure of CH₄, gas, system temperature, and initial concentration of tBuNH₂.

The tBuNH₂ clathrate hydrate, 16(CH₃)₃CNH₂·156H₂O, which Jeffrey designated as a type VI structure,[2] is a true clathrate as there is no evidence of hydrogen bonding between host water and guest amine molecules. tBuNH₂ molecules occupy large complex cages with 17 sides (4(5)6(7)) while the small cages (4(5)8) remain empty.[14] Figure 1 represents the PXRD patterns of both pure tBuNH₂ and double (CH₄ + tBuNH₂) hydrate at 113.15 K. According to a previous report,[14] the structure of pure tBuNH₂ hydrate is cubic (space group Fd3m) with a unit cell dimension of 18.81 ± 0.02 Å. The PXRD patterns of pure tBuNH₂ hydrate samples are consistent with the reported single-crystal structure.[14] The slightly smaller unit cell dimension of 18.7117 ± 0.0019 Å arises from the different temperatures at which the parameter was measured. In Figure 1a, all of the observed reflections for pure tBuNH₂ hydrate were attributed to type VI structure,[2] as indexed by the Checkcell program.[15] However, it should be noted that there are clear structural differences when we compare the PXRD patterns for pure tBuNH₂ hydrate with those of the double (CH₄ + tBuNH₂) hydrate. The introduction of CH₄ molecules as guests changes the structure of the pure tBuNH₂ hydrate. Preliminary X-ray results suggested that the transformed structure is a cubic sII hydrate, 16S·8L·136H₂O, with space group Fd3m. Because the ideal mole ratio of liquid guest (tBuNH₂) is 5.6 when it completely fills the large cages of the host (water), we chose to prepare a double (CH₄ + 5.6 mol % tBuNH₂) hydrate to verify the structural transition. The collected PXRD patterns were indexed by using the Checkcell program,[15] and the unit cell dimension was determined to be 17.3060 ± 0.0033 Å (see Supporting Information). The resulting refined pattern (Figure 1b) agrees with the reported value for a face-centered-cubic sII hydrate with a = 17.31 ± 0.01 Å.[16]
Communications

7750 www.angewandte.org

formula. Figures 2b and c show the 13C NMR spectra of the chemical shifts of double (CH4 + tBuNH2) hydrate, which both have CH4 and tBuNH2 as guest molecules. The CH4 molecules occupy only the small cages of the double hydrate, as indicated by a single signal at about δ = −4.7 ppm. At the same time, tBuNH2 molecules are present in the large cages, which can be identified by two resonances (δ = 46.5 and 33.1 ppm). However, at these concentrations of tBuNH2, the pure tBuNH2 hydrate and the double (CH4 + tBuNH2) hydrate are found to coexist as the NMR signals characteristic of both hydrates appear downfield of the NMR spectrum. As the concentration of tBuNH2 decreases further, the relative amount of double hydrate increases so that the number of encaged CH4 molecules in the small cages also increases. When the concentrations of tBuNH2 were 5.6 or 4.5 mol% (Figures 2d and e), only the double hydrate was found, as just three peaks were obtained for the double (CH4 + tBuNH2) hydrate. In contrast, pure sI CH4 hydrate also formed in addition to the double hydrate (sII) when the concentration of tBuNH2 was lowered to 3.0 mol% and 1.0 mol% (Figures 2f and g).

The distribution of CH4 molecules throughout the cages in the pure CH4 hydrate and in the double hydrate was investigated for concentrations of tBuNH2 from 3.0 to 1.0 mol%; expanded NMR spectra are presented in Figure 3. In the 13C NMR spectra of the sII double hydrate, two CH4 resonances at δ = −4.7 (small cage) and −8.3 ppm (large cage) are present, and the resonance of CH4 molecules in a large cage is clearly seen below 3.0 mol% of tBuNH2. Moreover, the number of encaged CH4 molecules in the large cages of the double hydrate continues to increase as the concentration of tBuNH2 decreases down to 1.0 mol%. In this region, when the aqueous tBuNH2 solution was cooled below the phase boundary of pure CH4 hydrate, it was found that pure CH4 hydrate also formed as indicated by two resonances at δ = −4.3 and −6.7 ppm, which are characteristic of CH4 molecules trapped in small and large cages of sI hydrate, respectively. As the concentration of tBuNH2 decreases, the amount of pure CH4 hydrate formed becomes larger because the amount of water participating in the formation of the double hydrate decreases. In the case of 1.0 mol% of tBuNH2, four NMR signals indicate the presence of CH4 molecules enclathrated in each of the four hydrate cages of pure (sI) and double hydrate (sII). Therefore, Figure 3e precisely indicates the coexistence and guest distribution of CH4 molecules in pure sI CH4 hydrate and the sII double hydrate. In our experiments, the relative amount of sI and sII hydrate observed at low concentrations of tBuNH2 is a variable that depends on the amount of excess water present and the reaction time. For practical purposes, it is desirable to work at a pressure that is just below the point at which sI hydrate appears. Therefore, the appearance of the spectra is not necessarily characteristic of the equilibrium distribution of the various hydrates. Note that the signal intensity in Figure 2 and Figure 3 does not directly represent the absolute amount of formed hydrates.

For several concentrations of tBuNH2, the ratio of signal areas for CH4 molecules in large cages to that of small cages of the double hydrates is plotted in Figure 4. As described above, the CH4 molecules can occupy only the small cages of

One of the objectives of this work was to determine the guest distribution of the two types of guest molecules and to use this information to find the equilibrium composition of the double hydrate. Although the 512 cages are common to many hydrate structures, the symmetry and size of these small cages in the structures are somewhat different and their interactions with guest molecules are also different. Accordingly, encaged guest molecules show different chemical shifts in the NMR spectrum which were used for structural assignments and the identification of guest distribution in cages of pure tBuNH2 hydrate and double (CH4 + tBuNH2) hydrate that range from a concentration of tBuNH2 from 9.3 to 1.0 mol%. Figure 2 shows 13C magic-angle spinning (MAS) NMR spectra of pure tBuNH2 hydrate and double (CH4 + tBuNH2) hydrate, which were used to assign the chemical shifts of tBuNH2 molecules as well as those of CH4 molecules in the hydrate cages. The spectrum of pure tBuNH2 hydrate (Figure 2a) is consistent with the tBuNH2 molecules occupying the large cages of this hydrate, as attested by signals at δ = 47.3 (-C(CH3)i) and 31.6 ppm (-C(CH3)i); the signal intensities reflect the molecular formula. Figures 2b and c show the 13C NMR spectra of double (CH4 + tBuNH2) hydrate (tBuNH2 concentrations of 9.3 and 7.0 mol%, respectively), which both have CH4 and tBuNH2 as guest molecules. The CH4 molecules occupy only the small cages of the double hydrate, as indicated by a single signal at about δ = −4.7 ppm. At the same time, tBuNH2 molecules are present in the large cages, which can be identified by two resonances (δ = 46.5 and 33.1 ppm). However, at these concentrations of tBuNH2, the pure tBuNH2 hydrate and the double (CH4 + tBuNH2) hydrate are found to coexist as the NMR signals characteristic of both hydrates appear downfield of the NMR spectrum. As the concentration of tBuNH2 decreases further, the relative amount of double hydrate increases so that the number of encaged CH4 molecules in the small cages also increases. When the concentrations of tBuNH2 were 5.6 or 4.5 mol% (Figures 2d and e), only the double hydrate was found, as just three peaks were obtained for the double (CH4 + tBuNH2) hydrate. In contrast, pure sI CH4 hydrate also formed in addition to the double hydrate (sII) when the concentration of tBuNH2 was lowered to 3.0 mol% and 1.0 mol% (Figures 2f and g).

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For several concentrations of tBuNH2, the ratio of signal areas for CH4 molecules in large cages to that of small cages of the double hydrates is plotted in Figure 4. As described above, the CH4 molecules can occupy only the small cages of

Figure 1. Powder X-ray diffraction patterns: a) pure tBuNH2 hydrate, a = 18.7117 ± 0.0019 Å; b) double (CH4 + tBuNH2) hydrate, a = 17.3060 ± 0.0033 Å.
The double hydrate up to 4.5 mol% but occupy both small and large cages of the double hydrate below concentrations of 4.0 mol% of \( t \)BuNH\(_2\). The ratio of the integrated intensities for the two signals was 0.04 at 4.0 mol% but jumped to 0.294 at 1.0 mol% of \( t \)BuNH\(_2\). To check the actual amount of CH\(_4\) molecules stored in the hydrate phase, we measured the volume of CH\(_4\) gas released from the double hydrate samples. The samples were prepared at 70 bar and 283.65 K to eliminate the possible formation of pure CH\(_4\) hydrates that may result from a reaction between residual water and CH\(_4\) gas in the low concentration region of \( t \)BuNH\(_2\). The measured volume of CH\(_4\) gas was converted into moles by considering the compressibility factor of the CH\(_4\) molecule, and the resulting values are shown in Figure 4. A value of 1.46, the lowest mole ratio of CH\(_4\) to \( t \)BuNH\(_2\) found, indicates that about 75% of the small cages are occupied by CH\(_4\) molecules in the double hydrate; if all small and large cages encapsulate the CH\(_4\) and \( t \)BuNH\(_2\) molecules in the double hydrate, respectively, the mole ratio of CH\(_4\) to \( t \)BuNH\(_2\) becomes 2.0. As the concentration of \( t \)BuNH\(_2\) decreases, the number of CH\(_4\) molecules captured in cages increases. Based on the assumption that the occupancy of the small cage by CH\(_4\) molecules is 0.75 (according to the result obtained for 5.6 mol% of \( t \)BuNH\(_2\)), the remaining CH\(_4\) molecules should be confined in large cages of the double hydrate, which is about 31% of the large cages at 1.0 mol% of \( t \)BuNH\(_2\).[18]

Thus, the amount of CH\(_4\) in the sII double hydrate can be tuned by decreasing the concentration of \( t \)BuNH\(_2\).

The results reported in this study show for the first time that a structural transition occurs in \( t \)BuNH\(_2\) hydrate according to the initial concentration of \( t \)BuNH\(_2\) when small molecules such as CH\(_4\) are introduced. The structural transition was confirmed by PXRD and analysis of the solid-state NMR spectrum. At sufficiently low concentrations of \( t \)BuNH\(_2\), pure CH\(_4\) hydrate (sI) and double (CH\(_4\) + \( t \)BuNH\(_2\)) hydrate (sII) coexist when crossing the corresponding phase boundary so that there is a complex mixture of solid phases. Moreover, it is shown that the storage capacity of CH\(_4\) gas in the hydrate phase increases drastically as the initial concentration of \( t \)BuNH\(_2\) decreases. These results confirm that the gaseous distribution of guest molecules and the hydrate composition can be altered by adjusting the concent-

**Figure 2.** \(^{13}\)C MAS NMR spectra and structural diagrams of the pure and double hydrates: a) pure \( t \)BuNH\(_2\) hydrate; b) and c) both pure \( t \)BuNH\(_2\) hydrate and sII double hydrate coexisted (9.3 and 7.0 mol% \( t \)BuNH\(_2\), respectively); d) and e) only the sII double hydrate formed (5.6 and 4.5 mol% \( t \)BuNH\(_2\), respectively); f) and g) both pure sI CH\(_4\) hydrate and sII double hydrate coexisted (3.0 and 1.0 mol% \( t \)BuNH\(_2\), respectively). All samples, except for the pure \( t \)BuNH\(_2\) hydrate, were prepared for NMR analysis by using the same experimental procedure (see text, Experimental Section, and Supporting Information for details). Hydrogen atoms were omitted in the structural diagrams.

**Figure 3.** Expanded \(^{13}\)C MAS NMR spectra of double (CH\(_4\) + \( t \)BuNH\(_2\)) hydrates. Concentrations of \( t \)BuNH\(_2\): a) 5.6; b) 4.0; c) 3.0; d) 2.0; e) 1.0 mol%.

**Figure 4.** The area ratio (\( A_{CH_4} \)) of \(^{13}\)C MAS NMR signals for CH\(_4\) molecules occluded in large and small cages and the CH\(_4\)/\( t \)BuNH\(_2\) mole ratio (\( \bullet \)) in the double hydrate.
tration of the liquid guest. This “tuning mechanism” plays an important role in understanding the dynamics of hydrate cages and should be one of the strategies used to enhance the gas-storage capacity of double-hydrate systems, including a water-soluble liquid hydrate promoter for application to gas storage and transportation areas.

**Experimental Section**

The PXRD patterns were recorded at 113.15 K on a Rigaku Geigerflex diffractometer (D/Max-RB) by using graphite-monochromatized CuKα radiation (λ = 1.5406 Å) in the θ/2θ scan mode. The XRD experiments were carried out in step mode with a fixed time of 10 s and a step size of 0.05° for 2θ = 10–60°, thus rendering a total acquisition time of approximately 2 h for each hydrate sample.

To identify hydrate structure and guest distribution, a Bruker DSX 400 MHz solid-state NMR spectrometer was used. The powdered samples were placed in a zirconia rotor with an outer diameter of 4 mm, which was loaded into a variable temperature probe. The powdered samples were placed in a zirconia rotor with an outer diameter of 4 mm, which was loaded into a variable temperature probe. The initial temperature (T) and pressure (P) were 293.15 K and 70 bar, respectively, and then T was gradually reduced to 270.15 K. The pure tBuNH2 hydrate was made by freezing an aqueous solution of tBuNH2 (9.3 mol%, the ideal stoichiometric concentration of tBuNH2 hydrate) at 243.15 K. All 13C NMR spectra were recorded at a Larmor frequency of 100.6 MHz with MAS at about 3 kHz. A pulse length of 2 μs and pulse repetition delay of 40 s under proton decoupling were employed with a radio frequency field strength of 50 kHz, which corresponded to 5-μs 90° pulses. The downfield carbon resonance signal of adamantane, which was assigned a chemical shift of δ = 38.3 ppm at 300 K, was used as an external chemical shift reference. For the mixed hydrate samples, 13CH4 gas was used to obtain higher-intensity CH4 signals.

Received: July 8, 2005

**Keywords:** clathrates · host–guest systems · inclusion compounds · NMR spectroscopy · water chemistry

[18] In this case, by assuming that θCH4 = 0.75 and θ = θCH4 + θBuNH2 = 1 due to stability of sII hydrate, we could determine the number of moles of guest molecules, CH4, and tBuNH2, in small and large cages of double hydrate, which was in agreement with nCH4/nBuNH2 = 2.61. From the resulting values, it appears that the final composition of double hydrate is (12CH4)5[2.4CH4]0.75L·136H2O.