

CRITICAL GUEST CONCENTRATION AND COMPLETE TUNING PATTERN APPEARING IN THE BINARY CLATHRATE HYDRATES

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ABSTRACT

Previously we have suggested the concept of tuning hydrate compositions which makes it possible to increase the gas storage capacity of binary hydrates. Herein, we report for the first time the existence of a critical guest concentration (CGC) and establish the complete tuning pattern that appears to exist in binary hydrates, including the water-soluble hydrate formers (promoters) and water insoluble guests. The first attempt to verify the new features of clathrate hydrate compositions is executed on the binary hydrate of CH₄ + THF and involves a detailed examination of the guest distribution by spectroscopic methods. THF molecules by themselves form sII hydrate from a completely miscible aqueous solution, and in this structure, because of their size, THF molecules occupy only the large 5¹²6⁴ cages. The CGC value appears to depend

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largely on the chemical nature of the liquid guest component participating in the binary hydrate formation. The present experimental findings on the existence of critical guest concentration and the complete tuning phenomenon can be expected to make a meaningful contribution to both inclusion chemistry and a variety of hydrate-based fields.

Keywords: Clathrate hydrate, Critical guest concentration, THF, Tuning phenomenon, sII

NOMENCLATURE

A_L Area of peak from large cage
 A_S Area of peak from small cage
 MAS Magic Angle Spinning
 NMR Nuclear Magnetic Resonance
 P Pressure
 sII Structure-II
 T Temperature
 THF Tetrahydrofuran
 θ_L Cage occupancy in large cage
 θ_S Cage occupancy in small cage

INTRODUCTION

Clathrated hydrate, commonly named *Gas hydrates*, are stabilized by van der Waals interaction between a guest molecule and a host framework, and thus with their property, they have been implicated as a potential resource in the exploitation of natural gas hydrates [1], as a material for the sequestration of CO₂ [2,3] as a means of storage and transportation of natural gas [4], and very recently, hydrogen storage [5-7]. Clathrate hydrate research can be divided broadly into two categories that emphasize either macroscopic or microscopic approaches. However, these two approaches do need to be closely linked for a better understanding of the structures and processes involving both natural phenomena and hydrates for industrial processes. Even though many investigations were carried out to clarify thermodynamic and structural characteristics of clathrate hydrates, up to now, details on the molecular scale that concern the less usual properties of clathrate hydrates remain unknown.

Herein, we report for the first time the existence of a critical guest concentration (CGC) and establish the complete tuning pattern that occurs in the binary hydrates, including water-soluble hydrate formers (promoters) and water-insoluble guests, while we already suggested the concept of tuning phenomenon which could make it possible to increase the gas storage capacity of binary hydrate in the previous studies [7,8]. The first attempt to verify the new features of clathrate hydrate compositions is executed on the binary hydrate of CH₄ + THF and involves a detailed

examination of the guest distribution by spectroscopic methods. THF molecules by themselves form sII hydrate from a completely miscible aqueous solution, and in this structure, because of their size, THF molecules occupy only the large 5¹²6⁴ cages. Furthermore, the binary hydrate formed by THF and CH₄ guests also has been identified as an sII structure over the full range of THF to water ratios. In addition to binary hydrate of CH₄+THF, we also show the tuning phenomenon and CGC appearing in binary sII hydrate of CH₄+*t*-BuNH₂ (*tert*-butylamine, (CH₃)₃CNH₂).

EXPERIMENTAL PROCEDURES

Formation of the CH₄+THF binary hydrate

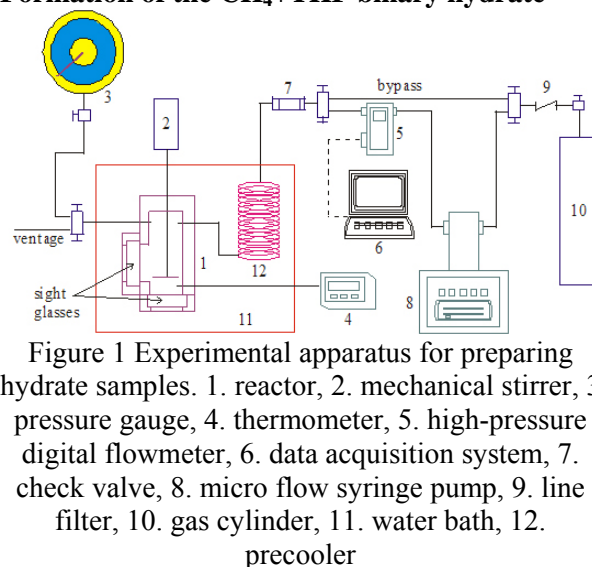


Figure 1 Experimental apparatus for preparing hydrate samples. 1. reactor, 2. mechanical stirrer, 3. pressure gauge, 4. thermometer, 5. high-pressure digital flowmeter, 6. data acquisition system, 7. check valve, 8. micro flow syringe pump, 9. line filter, 10. gas cylinder, 11. water bath, 12. pre-cooler

A schematic diagram of the experimental apparatus was given in the Figure 1. Preparation of binary hydrate samples were started by loading THF hydrate powder in a mechanically stirred reactor having internal volume of 150 cm³, which is pre-cooled to prevent the THF hydrate particles from melting. Before loading, THF hydrates, made from freezing THF solutions of various concentrations in a freezer at 253 K, were used to be pulverized to fine powder. After loading and assembling, the reactor was placed in a water-ethanol mixture bath at 268K and slowly

pressurized with a CH₄ gas up to 20 ~ 100 bar. Temperature of the bath and pressure of the reactor were controlled by an externally circulating refrigerator/heater (JEIO TECH, RBC-20) and a micro-flow syringe pump (ISCO, model 260D), respectively. A mechanical stirrer agitated the THF hydrate particles during the entire formation process to promote the formation of binary hydrates. When the binary hydrate formation process was completed, the formed hydrate was ground in the liquid nitrogen vessel again.

Formation of the CH₄+ *t*-BuNH₂ binary hydrate

The clathrate hydrate sample for spectroscopic analysis was prepared in a clathrate hydrate forming reactor, which was made of type 316 stainless steel with an internal volume of about 140 cm³. The magnetically driven mechanical stirrer was used for uniform mixing during clathrate hydrate formation. The clathrate hydrate-forming reactor was kept in a water ethanol bath and its temperature was controlled by an externally circulating refrigerator/heater (JEIO TECH, RBC-20). About 50 cm³ of the *t*-BuNH₂ aqueous solution was initially charged into the reactor and then pressurized with a CH₄ gas to a higher pressure than the corresponding three-phase equilibrium pressure at the same temperature. The initial *T* and *P* were 293.15 K and 70 bar, respectively, and then *T* was gradually reduced to 270.15 K. When the clathrate hydrate formation process was complete, the clathrate hydrates formed were finely powdered in a mortar and pestle in liquid nitrogen to prevent any clathrate hydrate dissociation.

NMR Spectroscopic measurements

The magic angle spinning (MAS) 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 diameter Zr-rotor loaded into a variable temperature probe. For the MAS NMR measurements, all spectra were recorded at 3 kHz under high-power proton decoupling (HPDEC). A pulse length 2 μs and pulse repetition delay of 20 s with radio-frequency field strengths of 50 kHz corresponding to 90° pulses of 5 μs duration 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.

RESULTS AND DISCUSSION

NMR measurement

The binary hydrates of CH₄+*t*-BuNH₂ were produced at 270.15 K and 70 bar. The distribution of CH₄ molecules between large and small cages in the pure CH₄ hydrate and in the binary hydrate was investigated for *t*-BuNH₂ concentration range 3.0~1.0 mol %. The NMR spectra of the binary hydrates are presented in Figure 2. In the ¹³C NMR spectra of the sII hydrate, two CH₄ resonances are shown at δ = -4.7 for small cage and -8.3 ppm for large cage, and the resonance of CH₄ molecules in the large cage is clearly seen below 3.0 mol % of *t*-BuNH₂. CH₄ resonance representing large cage continues to intensify until the concentration of *t*-BuNH₂ decreases down to 1.0 mol %. In this region, when the aqueous *t*-BuNH₂ solution was cooled below the phase boundary of pure CH₄ hydrate, it was observed that pure CH₄ hydrate is also formed as indicated by two resonances at δ = -4.3 and -6.7 ppm, corresponding characteristic of CH₄ molecules trapped in small and large cages of sI hydrate, respectively. As the concentration of *t*-BuNH₂ decreases, the amount of pure CH₄ hydrate formed increases because of reducing amount of the binary hydrate. In the case of 1.0 mol % of *t*-BuNH₂, 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 2e precisely indicates the coexistence and guest distribution of CH₄ molecules in pure sI CH₄ hydrate and the sII double hydrate.

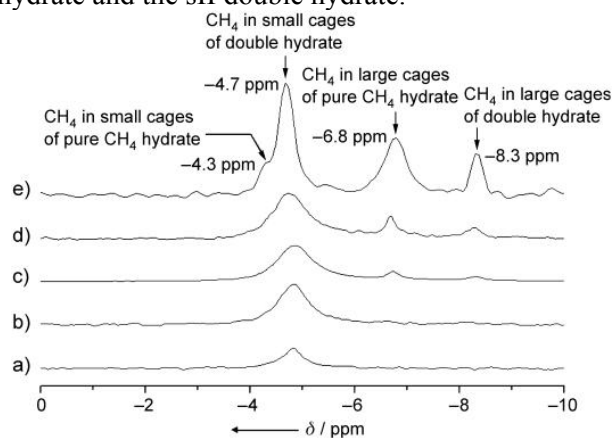


Figure 2 Expanded ¹³C MAS NMR spectra of double (CH₄ + *t*-BuNH₂) hydrates. Concentrations of *t*-BuNH₂: a) 5.6; b) 4.0; c) 3.0; d) 2.0; e) 1.0 mol %.

For several concentrations of *t*-BuNH₂, the ratio of signal areas for CH₄ molecules in large cages to

that of small cages of the binary hydrates is plotted in Figure 3. As described above, the CH₄ molecules can occupy only the small cages of 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*-BuNH₂. The ratio of the integrated intensities for the two signals was 0.04 at 4.0 mol % but increased with decreasing *t*-BuNH₂ until *t*-BuNH₂ reaches to 1.0 mol% showing the value of 0.294.

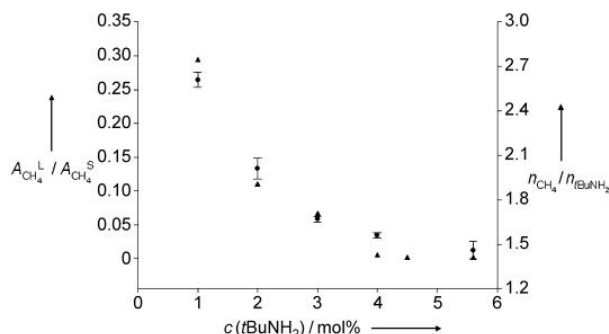


Figure 3 The area ratio (▲) of ¹³C MAS NMR signals for CH₄ molecules occluded in large and small cages and the CH₄/*t*-BuNH₂ mole ratio (■) in the double hydrate.

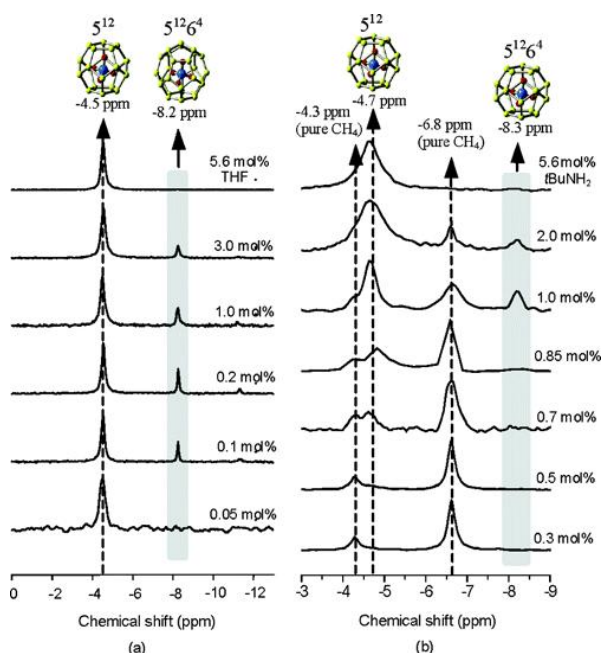


Figure 4 (a) ¹³C MAS NMR spectra of the CH₄+THF binary hydrates ranging from 5.6 to 0.05 mol % of THF. At THF concentrations higher than 5.6 mol %, the CH₄ molecules occupy only the small cages. (b) ¹³C MAS NMR spectra of the CH₄ + *t*-BuNH₂ binary hydrates ranging from 5.6 to 0.3 mol % of *t*-BuNH₂.

Next, to precisely investigate the CGC and tuning phenomenon, the temperature and pressure conditions were kept constant at 268 K and 20 bar to avoid any possible appearance of pure CH₄ hydrate. Thus CH₄ should appear only in the cages of binary sII hydrate over the entire THF concentration range in the specific *P-T* domain used in this study. Since the composition of pure THF hydrate is very nearly THF·17H₂O, the stoichiometry of THF solutions becomes 5.6 mol %, which is the highest host-to-guest ratio for forming a clathrate hydrate. As clearly indicated by the NMR signals [9], the CH₄ molecules occupy only the small cages of the binary hydrate at the stoichiometric THF concentration. Figure 4a shows the NMR spectra for hydrate samples prepared from 5.6-0.05 mol % at 268 K and 20 bar. When the THF concentration is lowered below the stoichiometric ratio, the CH₄ occupancy of sII large cages becomes possible, showing the tuning behavior of the clathrate composition. The cage occupancy ratio, $\theta_{L,\text{CH}_4}^{\text{sII}} / \theta_{S,\text{CH}_4}^{\text{sII}}$, can be obtained using experimental NMR peak areas in combination with the thermodynamic equation of van der Waals and Platteeuw. The value increases continuously until it reaches a maximum at a specific THF concentration of 0.2 mol % (Table 1). Hereafter, we refer to this unique concentration as the critical guest concentration (CGC) that becomes apparent when the water-soluble liquid guests are quite dilute in the crystalline hydrate lattice. Below the CGC, the amount of hydrate becomes very small and makes the spectroscopic detection of the captured gaseous molecules more difficult. Nevertheless, a more accurate exploration, particularly in the highly dilute liquid guest region, was attempted for understanding the tuning mechanism more completely. As THF concentrations become lower than the CGC, CH₄ molecules still occupy small cages but not the large cages. Accordingly, the large cages become quite deficient in CH₄ when THF concentrations approach this low concentration, and finally CH₄ molecules are no longer observed to occupy large cages below a certain threshold concentration. As shown in Figure 4a, the CH₄ peak representing the large cage population disappears completely at 0.05 mol % of THF. We confirmed that the general tuning patterns at two different pressures of 20 and 100 bar are found to be essentially the same, but we note that THF is likely to act as a specific inhibitor of sI hydrate in this *P-T* domain.

We may expect that the concentration of liquid guest involved in forming the sII binary hydrate plays an important role in the overall composition of hydrate, and also, CH₄ molecules are accommodated in cages of various types according to the concentration of liquid guest used to tune the composition. Therefore, it is necessary to investigate the behavior of CH₄ molecules in the lower concentration region with great care, especially below 1.0 mol % of *t*-BuNH₂. In Figure 4b, the ¹³C MAS NMR spectra are shown in the region of -3 to -9 ppm to focus on the CH₄ molecules that occupy the hydrate cages, which provide both qualitative and quantitative information such as structure type, distribution of CH₄ molecules, and absolute cage occupancies in each cage of the hydrate. However, in the present work, we focused on the especially chosen *P-T* trajectories and ¹³C MAS NMR measurements near and below the anticipated CGC. During enclathration, the CH₄ + *t*-BuNH₂ binary hydrates maintain sII structure, but pure CH₄ hydrate (sI) appears as well and coexists with the binary hydrate. After going through the structural transformation, the basic tuning pattern of the CH₄+*t*-BuNH₂ binary hydrate is quite similar to that of the CH₄+THF binary hydrate, and the corresponding CGC appears to be about 1.0 mol % of *t*-BuNH₂ with the absolute cage occupancies of $\theta_{S,CH_4}^{sII} = 0.7413$ and $\theta_{L,CH_4}^{sII} = 0.4359$. The CGC values for the binary hydrate appear to be unique, depending on the chemical nature of the participating liquid guest molecules and their interactions with the host lattices. At 0.85 mol % of *t*-BuNH₂, less than the CGC, the absolute cage occupancies of CH₄ molecules trapped in small and large cages are $\theta_{S,CH_4}^{sII} = 0.7628$ and $\theta_{L,CH_4}^{sII} = 0.1773$, which indicates that the θ_{L,CH_4}^{sII} value drops significantly at liquid guest concentrations below the CGC, while the θ_{S,CH_4}^{sII} values remain almost constant. Eventually, at the lower concentrations of 0.7 and 0.5 mol % of *t*-BuNH₂, the θ_{L,CH_4}^{sII} values become zero. However, we note that there is no variation of the θ_{S,CH_4}^{sII} values on going from the stoichiometric mole ratio of 5.6 to 0.5 mol % of *t*-BuNH₂. We further lowered the *t*-BuNH₂ concentration to 0.3 mol % and found that the *t*-BuNH₂ molecules no longer play an active role in forming the binary hydrate and failed to

form sII hydrate. Although *t*-BuNH₂ itself can form sII hydrates with CH₄ molecules, the tendency to the type IV structure from pure *t*-BuNH₂ inhibits the formation of both sI and sII hydrates by affecting the activity of water. However, at sufficiently high pressures, water molecules do react with CH₄ to form pure CH₄ hydrate as confirmed by the ¹³C MAS NMR spectrum. In the case of 0.3 mol % of *t*-BuNH₂ in Figure 4b, just two resonances, attributed to CH₄ molecules in sI hydrate, were observed at -4.3 and -6.8 ppm. The ratio of integral intensities of these peaks was determined to be $I_S/I_L = 0.2998$, which is close to the ideal stoichiometric ratio (1/3) of 5¹² to 5¹²6² cage of sI hydrate. The detailed cage occupancy of guest molecules is listed in Table 2.

So far, we closely checked two binary hydrate systems to identify the CGC existence and guest distributions in cages and found that the overall tuning pattern might be observed in most of the binary sII hydrate systems, as shown in Figure 5.

THF (mol%)	A_s of CH ₄ sII	A_L of CH ₄ sII	$\theta_{sII_L}/\theta_{sII_S}$
5.56	1.0000	0.0000	0.0000
3.00	1.0000	0.1325	0.2650
1.00	1.0000	0.2036	0.4072
0.20	1.0000	0.2451	0.4902
0.10	1.0000	0.1873	0.3746
0.05	1.0000	0.0000	0.0000

Table 1. Cage occupancy ratio of CH₄ in CH₄+THF binary hydrate formed at 20 bar and 268 K .

<i>t</i> BuNH ₂ (mol%)	$A_{L,sII}^{CH_4} / A_{S,sII}^{CH_4}$	$\theta_{L,sII}^{BuNH_2}$	$\theta_{L,sII}^{CH_4}$	$\theta_{S,sII}^{CH_4}$	$\theta_{L,sII}^{CH_4} / \theta_{S,sII}^{CH_4}$
5.6	0.0	0.9935	0.0	0.6986	0.0
2.00	0.113	0.8130	0.1751	0.7748	0.226
1.00	0.294	0.5553	0.4359	0.7413	0.588
0.7	0.0	0.9918	0	0.7312	0.0
0.5	0.0	0.9895	0	0.7630	0.0
0.3	none	-	-	-	-

Table 2. Absolute cage occupancy of guest molecules in CH₄+*t*-BuNH₂ binary hydrate.

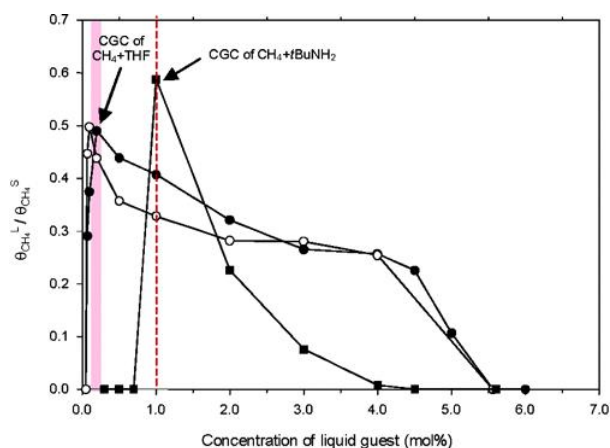


Figure 5 Complete tuning patterns and CGC appearing in the binary CH_4 +THF formed at 20 bar (\circ), CH_4 + THF formed at 100 bar (\square) and CH_4 + t -BuNH $_2$ (\blacksquare) hydrates at 70 bar.

Thermodynamic Measurements

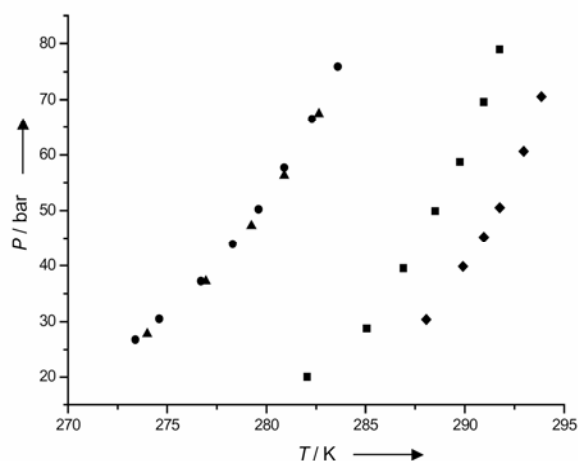


Figure 6 sII binary hydrate phase equilibria of the CH_4 + t -BuNH $_2$ +water system for three specific t -BuNH $_2$ concentrations. Binary hydrates are only stable in the above and left region of three-phase equilibrium line; \bullet , \blacktriangle , \blacksquare , and \blacklozenge represent the CH_4 +water, CH_4 +0.3 mol% t -BuNH $_2$ solution, CH_4 +2.0 mol% t -BuNH $_2$ solution [8], and CH_4 +5.6 mol% t -BuNH $_2$ solution [8], respectively.

t -BuNH $_2$ is completely miscible with water when forming the binary hydrate mixed with CH_4 gas so that there exist three phases of binary hydrate (H), t -BuNH $_2$ solution (L) and CH_4 gas (V) after the hydrate formation. The three-phase equilibria (H-L-V) for the CH_4 + t -BuNH $_2$ +water system were measured to determine a stable region of the binary hydrate at the specific t -BuNH $_2$ concentrations, each representing the characteristic region in the tuning mechanism. As the results of

overall phase behaviors of the CH_4 + t -BuNH $_2$ +water system (Figure 6), it is found that the participation of t -BuNH $_2$ molecules in forming the binary hydrate could greatly reduce the dissociation equilibrium pressure at a specific temperature compared with the corresponding condition of pure CH_4 hydrate. However, it should be noted that the secondary liquid guest does not play any significant role in stabilizing the structure frame when the t -BuNH $_2$ concentration reaches below 0.3 mol%. Hereafter, the molecular behavior of the binary hydrate in each characteristic region will be explained.

P - T trajectories of the hydrate formation were measured experimentally so as to infer the molecular behaviors of two guests in the hydrate sample [10]. The CH_4 + t -BuNH $_2$ binary hydrate started to form directly after going through the three-phase equilibrium boundary, and rapid pressure reduction occurred immediately upon complete transformation of the 5.6 mol% aqueous t -BuNH $_2$ solution to binary hydrate (Figure 7a). The system pressure continued to decrease almost linearly with temperature even after passing the three-phase equilibrium boundary of pure CH_4 hydrate, which indicates that further hydrate formation did not occur. As the temperature was again raised to approach the phase boundary of the binary hydrate, the system pressure abruptly increased due to the complete dissociation of formed hydrates. The ^{13}C MAS NMR spectrum (Figure 7b) of binary hydrate sample shows a single peak at -4.7 ppm representing that CH_4 molecules only occupy the 5^{12} cage of binary hydrate [8]. On the other hand, t -BuNH $_2$ molecules reside in the $5^{12}6^4$ cage, as identified by the two resonances at 46.5 ($-\text{C}(\text{CH}_3)_3$) and 33.1 ppm ($-\text{C}(\text{CH}_3)_3$).

Different pattern of P - T trajectory was observed for an aqueous 2.0 mol% t -BuNH $_2$ solution which is considerably below the ideal stoichiometry of binary hydrate was cooled, as shown in Figure 8a. In this case, after the first pressure reduction due to the formation of the binary hydrate, second pressure drop was occurred with further cooling, which leads us to think that the residual water molecules reacted with CH_4 gas to form pure CH_4 hydrate as well [9]. This phenomenon was previously suggested for CH_4 +THF binary hydrate [9], so the coexistence of sI and sII binary hydrate including the liquid guest molecules might be a general phenomenon appearing at the moderate concentration of liquid guest molecule. The ^{13}C

MAS NMR spectrum, obtained at point A and shown in Figure 8b, is also supporting this elucidation. When the temperature was reduced at point A, the spectral characteristic of pure CH₄ hydrate appeared as two resonances at -4.3 and -6.8 ppm: these could be assigned to CH₄ molecules occluded in 5¹² cage and 5¹²6² cage of sl hydrate, respectively. After taking everything into consideration, it can be concluded that pure CH₄ hydrate is formed and coexists with CH₄+*t*-BuNH₂ binary hydrate in the low temperature region, after passing through the phase boundary of pure CH₄ hydrate.

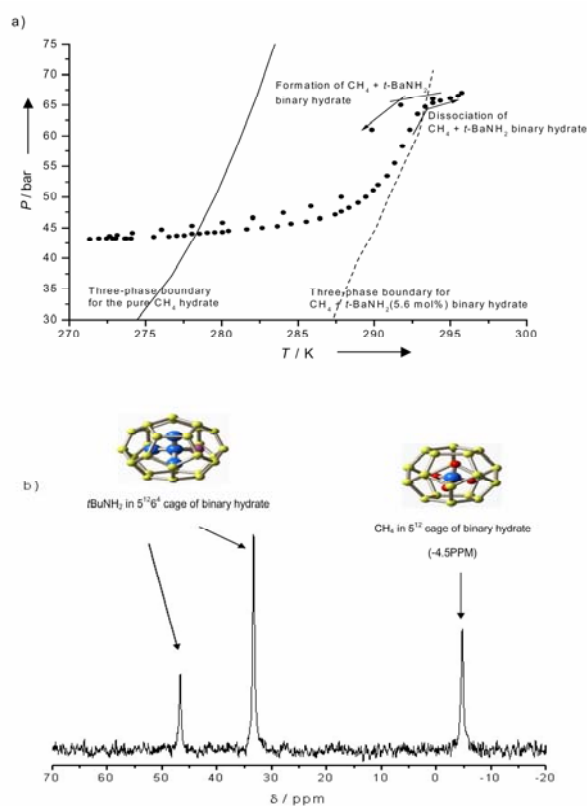


Figure 7 a) *P-T* trajectory representing one stage of hydrate formation and dissociation from 5.6 mol% *t*-BuNH₂ solution. b) ¹³C NMR spectrum of CH₄+*t*-BuNH₂ binary hydrate.

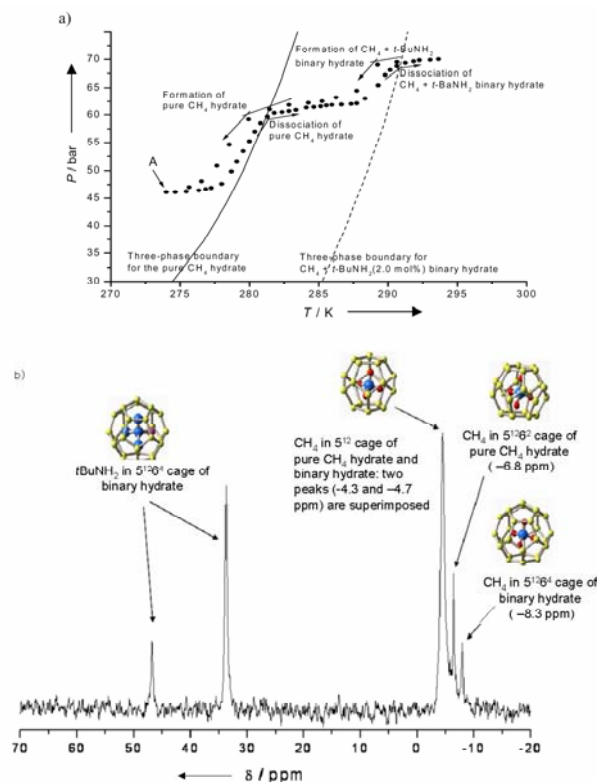


Figure 8 a) *P-T* trajectory representing two stages of hydrate formation and dissociation from 2.0 mol% *t*-BuNH₂ solution. b) ¹³C NMR spectrum of CH₄+*t*-BuNH₂ binary hydrate at point A.

Furthermore, the ¹³C MAS NMR spectrum of hydrate sample made from the dilute concentration of *t*-BuNH₂, 0.3 mol%, showed unexpected result as represented in Figure 9a. As the system temperature was reduced to point B, the pressure drop owing to hydrate formation occurred not around the phase boundary of binary hydrate, but below that of pure CH₄ hydrate. It means that the *t*-BuNH₂ molecules no longer derived the formation of binary hydrate due to an extremely small number of *t*-BuNH₂ molecules, and then the unreacted water molecules could only participate in forming the pure CH₄ hydrate. The ¹³C MAS NMR spectrum of sample obtained at point B reinforced the individual existence of pure CH₄ hydrate. In Figure 9b, just two resonances attributed to CH₄ molecules in sl hydrate were observed at -4.3 and -6.8 ppm.

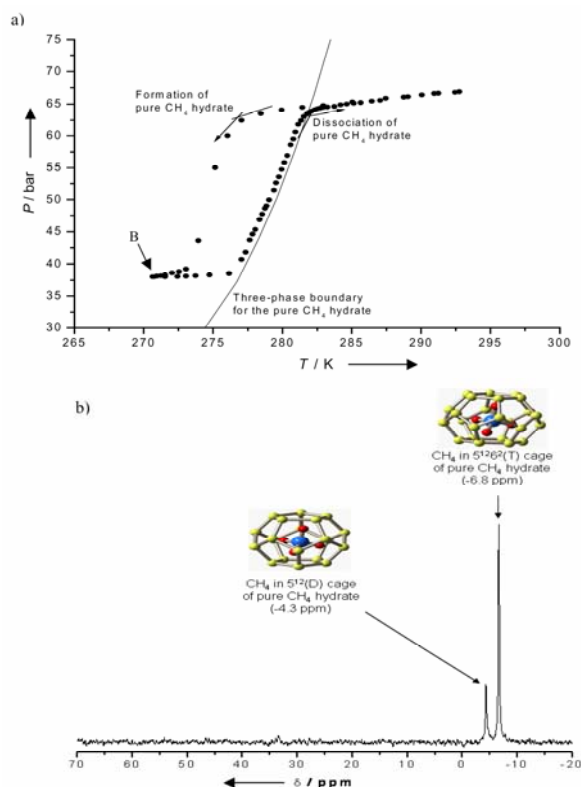


Figure 9 a) P - T trajectory representing one stage of hydrate formation and dissociation from 0.3 mol% t -BuNH₂ solution. b) ^{13}C NMR spectrum of pure CH₄ hydrate at point B.

CONCLUSION

The CGC value appears to largely depend on the chemical nature of a liquid guest component participating in the binary hydrate formation. The present experimental findings on the existence of critical guest concentration and complete tuning mechanism might be expected to make meaningful contributions to both inclusion chemistry and a variety of hydrate-based fields. In particular, further research on other complex hydrate structures and organic clathrates is in progress.

ACKNOWLEDGMENT

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