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Critical Guest Concentration and Complete Tuning Pattern Appearing in the Binary Clathrate Hydrates

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Clathrate hydrates constitute a class of inclusion compounds that have been implicated as a potential resource in the exploitation of natural gas hydrates,[1] as a material for the sequestration of CO_2,[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.

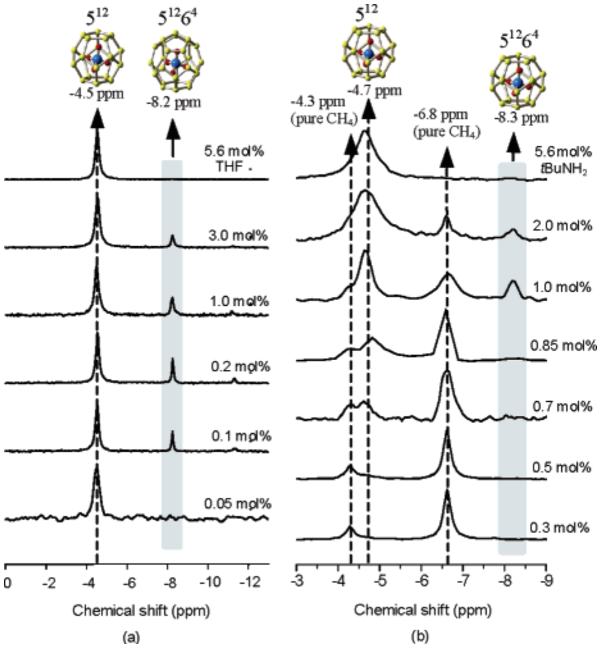

Figure 1. (a) ^{13}C MAS NMR spectra of the CH_4 + THF binary hydrates ranging from 5.6 to 0.05 mol % of THF. At THF concentrations higher than 5.6 mol %, the CH_4 molecules occupy only the small cages. (b) ^{13}C MAS NMR spectra of the CH_4 + *t*-$BuNH_2$ binary hydrates ranging from 5.6 to 0.3 mol % of *t*-$BuNH_2$.

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 CH_4 + 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 $5^{12}6^4$ cages. Furthermore, the binary hydrate formed by THF and CH_4 guests also has been identified as an sII structure over the full range of THF to water ratios. During sample preparation in a high-pressure vessel, the temperature and pressure conditions were kept constant at 268 K and 20 bar to avoid any possible appearance of pure CH_4 hydrate. Thus CH_4 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$\cdot$17H_2O, 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 CH_4 molecules occupy only the small cages of the binary hydrate at the stoichiometric THF concentration. Figure 1a 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 CH_4 occupancy of sII large cages becomes possible, showing the tuning behavior of the clathrate composition. The cage occupancy ratio, $\theta^{sII}_{L,CH_4}/\theta^{sII}_{S,CH_4}$, 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 %. 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, CH_4 molecules still occupy small cages but not the large cages. Accordingly, the large cages become quite deficient in CH_4 when THF concentrations approach this low concentration, and finally CH_4 molecules are no longer observed to occupy large cages below a certain threshold concentration. As shown in Figure 1a, the CH_4 peak representing the large cage population disappears completely at 0.05 mol % of THF. We confirmed that the general

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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.

For more definite and comprehensive evidence, we also examined the binary hydrate of CH_4 + *tert*-butylamine (*t*-$BuNH_2$, $(CH_3)_3CNH_2$) through the structural transition.[8] The *t*-$BuNH_2$ is completely miscible with water under the P, T conditions where the three phases of binary hydrate (H), *t*-$BuNH_2$ solution (L_w), and CH_4 gas (V) coexist. We measured the $H-L_w-V$ phase boundaries to determine a stable region of the binary hydrate at several *t*-$BuNH_2$ concentrations and to identify adequate hydrate-forming routes for sample preparation. For the CH_4 + *t*-$BuNH_2$ binary hydrate, the *t*-$BuNH_2$ molecules only occupied the $5^{12}6^4$ cages, while CH_4 molecules were included in the 5^{12} cages, or both $5^{12}6^4$ and 5^{12} cages, depending on *t*-$BuNH_2$ concentration.[8] From the preliminary macro/microscopic results (see Supporting Information), 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, CH_4 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 CH_4 molecules in the lower concentration region with great care, especially below 1.0 mol % of *t*-$BuNH_2$. In Figure 1b, the ^{13}C MAS NMR spectra are shown in the region of −3 to −9 ppm to focus on the CH_4 molecules that occupy the hydrate cages, which provide both qualitative and quantitative information such as structure type, distribution of CH_4 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 ^{13}C MAS NMR measurements near and below the anticipated CGC. During enclathration, the CH_4 + *t*-$BuNH_2$ binary hydrates maintain sII structure, but pure CH_4 hydrate (sI) appears as well and coexists with the binary hydrate. After going through the structural transformation, the basic tuning pattern of the CH_4 + *t*-$BuNH_2$ binary hydrate is quite similar to that of the CH_4 + THF binary hydrate, and the corresponding CGC appears to be about 1.0 mol % of *t*-$BuNH_2$ with the absolute cage occupancies of $\theta^{sII}_{S,CH_4} = 0.7413$ and $\theta^{sII}_{L,CH_4} = 0.4359$. 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*-$BuNH_2$, less than the CGC, the absolute cage occupancies of CH_4 molecules trapped in small and large cages are $\theta^{sII}_{S,CH_4} = 0.7628$ and $\theta^{sII}_{L,CH_4} = 0.1773$, which indicates that the θ^{sII}_{L,CH_4} value drops significantly at liquid guest concentrations below the CGC, while the θ^{sII}_{S,CH_4} values remain almost constant. Eventually, at the lower concentrations of 0.7 and 0.5 mol % of *t*-$BuNH_2$, the θ^{sII}_{L,CH_4} values become zero. However, we note that there is no variation of the θ^{sII}_{S,CH_4} values on going from the stoichiometric mole ratio of 5.6 to 0.5 mol % of *t*-$BuNH_2$. We further lowered the *t*-$BuNH_2$ concentration to 0.3 mol % and found that the *t*-$BuNH_2$ molecules no longer play an active role in forming the binary hydrate and failed to form sII hydrate. Although *t*-$BuNH_2$ itself can form sII hydrates with CH_4 molecules, the tendency to the type IV structure from pure *t*-$BuNH_2$ 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 CH_4 to form pure CH_4 hydrate as confirmed by the ^{13}C MAS NMR spectrum. In the case of 0.3 mol % of *t*-$BuNH_2$ in Figure 1b, just two resonances, attributed to CH_4 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 5^{12} to $5^{12}6^2$ cage of sI hydrate.

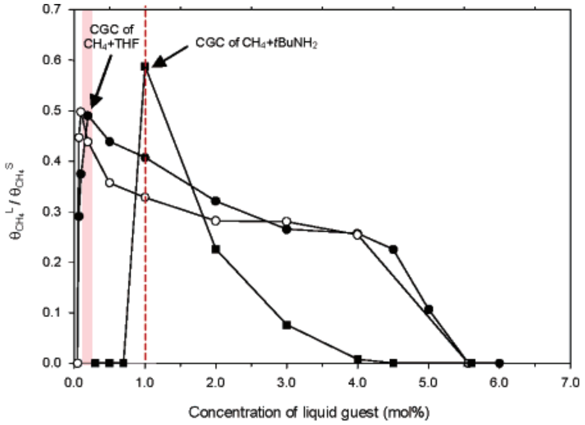

Figure 2. Complete tuning patterns and CGC appearing in the binary CH_4 + THF formed at 20 bar (●), CH_4 + THF formed at 100 bar (○) and CH_4 + *t*-$BuNH_2$ (■) hydrates at 70 bar.

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 2. 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.

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Supporting Information Available: Experimental procedure, NMR spectroscopic measurement, thermodynamic measurement, and cage occupancy ratio details. This material is available free of charge via the Internet at http://pubs.acs.org.

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