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STRUCTURE AND TUNING PATTERN IN THE IONIC DOUBLE CLATHRATE HYDRATES

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ABSTRACT

A number of notable studies on pure ionic clathrate hydrates have utilized their unique ionic characteristics for electric applications, including their use as an electrolyte for nickel-metal hydride batteries. Although quaternary ammonium salt hydrates have recently been applied to gas separation and storage areas with the expectation of the small co-guest occupancy in empty cages, most of the researches have been oriented to macroscopic approaches based on hydrate phase equilibria and many other process variables. On the other hand, spectroscopic analyses for identifying the structure transition of ionic clathrate hydrates together with a comprehensive consideration of their complex phase patterns have not yet been reported in spite of their importance to the energy and environmental fields. Accordingly, in this study, we present the report of an extraordinary structural transition accompanying the occurrence of more than two coexisting clathrate hydrate phases and channel-induced tuning pattern in ionic double hydrate systems. In particular, the tuning observation uniquely occurring in the ionic clathrate hydrates is quite surprising, even though the tuning behavior is more commonly observed in the non-ionic hydrate systems. The remarkable feature of this work is that the icy ionic hydrate materials can be effectively used in energy devices. Moreover, the microscopic analyses of ionic clathrate hydrates for identifying the physicochemical characteristics are expected to provide new insights into a variety of inclusion chemistry fields.

Keywords: ionic hydrates, structure transition, NMR

INTRODUCTION

Unlike general clathrate hydrates stabilized by van der Waals interaction between a host lattice and guest molecule [1], ionic clathrate hydrates are a type of inclusion compound in which an ionic interaction exists between a cation or an anion and the surrounding host network [2]. Various ionic molecules such as HPF_6, HBF_4, and alkyl ammonium salts are known to form ionic clathrate hydrates [2-4]. Many remarkable studies on pure ionic clathrate hydrates have utilized their unique ionic characteristics for electric applications such as serving as the electrolyte for nickel-metal hydride batteries [5,6]. Pure or mixed non-ionic clathrate hydrates have meanwhile been examined mainly for versatile energy and environmental applications such as future energy resources, gas storage, and carbon dioxide sequestration [7-10]. Although the quaternary ammonium salt hydrates have recently been applied to gas separation and storage with the expectation of small co-guest occupancy in empty cages, most research has been oriented to macroscopic approaches based on hydrate phase equilibria and process variables [11,12]. The ionic guests strongly interacting with the water cage framework make the resulting clathrate hydrate structure more complex than the hydrate structure of non-ionic guests. Moreover, several different crystalline phases of ionic clathrate hydrates are generally observed over the

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entire range of water concentrations [4]. Thus far, the spectroscopic analyses for identifying the structure transition of ionic clathrate hydrates together with a comprehensive consideration of their complex phase patterns have not yet been reported in spite of urgent need for inclusion chemistry fields.

In this study, an extraordinary structural transformation and tuning pattern occurring in cage-like as well as channel-like host frameworks of the double (CH_4 + tetramethyl ammonium hydroxide (Me_4NOH)) and (H_2 + Me_4NOH) ionic clathrate hydrates are reported. The Me_4NOH hydrate has been the subject of some research, primarily owing to its peculiar structural characteristics, which are strongly influenced by the water concentration and temperature. Me_4NOH • n H_2O has been reported to have eight different crystalline hydrate phases according to its hydration number and temperature. Among these phases, β forms of Me_4NOH • 7.5 H_2O (β-7.5 hydrate) and Me_4NOH • 5 H_2O (β-5 hydrate) are true ionic clathrate hydrates composed of an encaged Me_4N^+ cationic guest and a water host lattice in which the anions are incorporated by hydrogen-bonding. The α-form hydrates also have a clathrate-related structure, but some of the oxygen atoms are not fully connected. Given that β-form hydrates appear at a higher temperature as compared to α-form hydrates, genuine clathrate hydrates do not exist at low temperatures below 279 K [2,4]. The unusual structure patterns of ionic clathrate hydrates were identified from solid-state NMR Spectra.

EXPERIMENTAL PROCEDURES

Reagents

The CH_4 and H_2 gases with a minimum purity of 99.95 mol% used in this study were supplied by Special Gas (Korea). The $^{13}CH_4$ gas with a minimum purity of 99.0 % was supplied by Cambridge Isotope Laboratories, Inc. Water of ultrahigh purity was supplied by Merck, and the tetramethylammonium hydroxide pentahydrate was supplied by SIGMA-ALDRICH Inc. The tetramethylammonium hydroxide solutions were frozen at 203 K for at least 1 day and were then ground to a fine powder (~ 200 μm). The powdered solid hydrate was placed in the two pressurized cells each with a volume of 20 cm^3 and was then exposed to CH_4 or H_2 gas at a constant pressure of 120 bar and temperature of 203 K for 48 h. After the hydrate formation process was completed, the formed hydrate was finely powdered in the liquid nitrogen vessel.

Experimental Measurement

A Bruker (Bilerica, MA) AVANCE 400 MHz solid-state NMR spectrometer was used in this study. The powdered samples were placed in a 4 mm o.d. zirconia rotor loaded into a variable temperature probe. The ^1H NMR spectra of the (CH_4 + Me_4NOH) samples were recorded with magic angle spinning (MAS) at approximately 5 kHz and the proton resonance peak of tetramethylsilane (TMS), assigned a chemical shift of 0 ppm at 298K, was used as an external chemical shift reference. The ^1H NMR spectra of the (H_2 + Me_4NOH) samples were recorded with MAS at approximately 12 kHz to obtain sharper signals from the H_2 hydrates. All ^{13}C NMR spectra were recorded at a Larmor frequency of 100.6 MHz with MAS at approximately 5 kHz. A pulse length of 2 μs and a pulse repetition delay of 10 s under proton decoupling were employed with a radio frequency field strength of 50 kHz, corresponding to 5 – μs 90° pulses. The downfield carbon resonance peak of adamantine was assigned a chemical shift of 38.3 ppm at 298 K and was used as an external chemical shift reference. The cross-polarization (CP) NMR spectra were also obtained to identify gas and the liquid phase signal from the high-power decoupling (HPDEC) NMR spectra. For the mixed hydrate samples, $^{13}CH_4$ was mixed to obtain higher-intensity CH_4 signals.

RESULTS AND DISCUSSION

Figure 1 represents the ^1H and High-Power Decoupling (HPDEC) ^{13}C NMR spectra of double (CH_4 + Me_4NOH) ionic clathrate hydrates at several different water concentrations at a temperature of 203 K. The proton signals from the host lattice at all water concentrations are in Figure 1a. The ^{13}C signal from CH_4 is presented in Figure 1b. A remarkable peak shifting appears in both the ^1H and ^{13}C NMR spectra of the 16.0 H_2O sample in Figure 1. In Figure 1a, the host lattice signal at δ = 7.1 ppm shifts to δ = 6.7 ppm around the 16.0 H_2O at which the CH_4 signal shifts from δ = -4.0 ppm to δ = -4.5 ppm, leading to a structural transformation of double (CH_4 + Me_4NOH) ionic hydrates. At water concentration higher than 16.0 H_2O most of the β-7.5 ionic clathrate hydrate transforms to the sI. Here, it should be noted that this converted sI is the double ionic, rather than

the pure CH_4 clathrate hydrate simply formed by only water and methane.

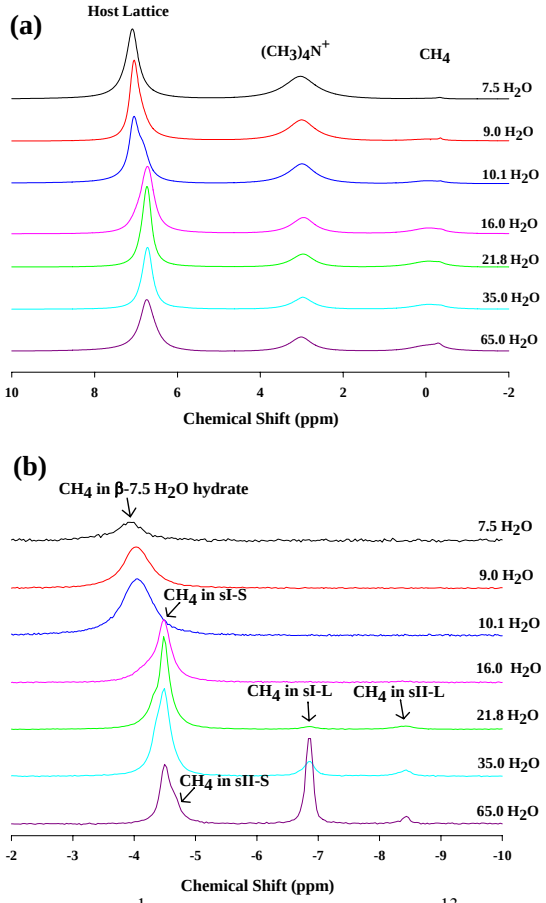

Figure 1. (a) ^{1}H MAS and (b) HPDEC ^{13}C NMR Spectra of ionic double (CH_4 + Me_4NOH) hydrate system at 203K and 5kHz spinning rate

From the ^{13}C NMR spectra (Figure 1b) it is confirmed that nearly complete conversion to the structure-I (sI) is achieved at water concentrations higher than 16.0 mol H_2O per 1.0 mol Me_4NOH (16.0 H_2O). Significantly, small signals of CH_4 in large cages of sI (sI-L, δ = -6.9 ppm) and sII hydrates (sII-L, δ = -8.4 ppm), compared to ideal distributions of CH_4 in sI and sII cages, imply that Me_4N^+ is enclosed in both sI-L and sII-L at a higher water concentration (Figure 1b; 16 H_2O, 21.8 H_2O, and 35 H_2O). However, the CH_4 signal at δ = -4.0 ppm (Figure 1; 7.5 H_2O, 9.0 H_2O, and 10.1 H_2O) cannot be assigned by solely NMR spectra. This peak, which is located at a more de-shielded region than CH_4 in small cages of sI (sI-S, δ = -4.5 ppm) and sII (sII-S, δ = -4.7 ppm), indicates that CH_4 is enclosed in a smaller cage than sI-S and sII-S. Considering that only β-7.5 hydrate has an empty cage (4^25^8) that not only can be occupied by a CH_4 molecule but also is smaller than sI-S or sII-S among the eight crystalline phases of $Me_4NOH \bullet n\ H_2O$, β-7.5 hydrate is the most likely structure for low water concentration hydrates [4,13].

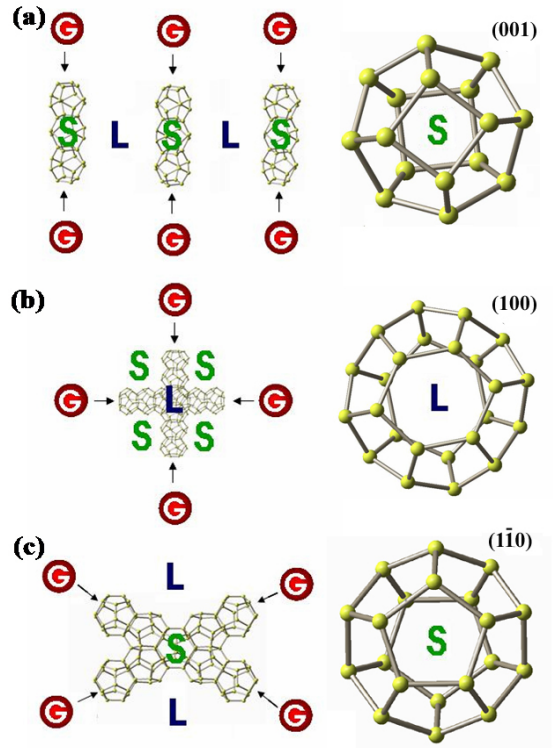

Figure 2. Channel patterns of guest diffusion pathways composed by like-cage stacking. The surrounding cages adjacent to the channels are irregularly arranged. (a) 4^25^6 channel in the β – 7.5 clathrate hydrate and 4^25^6 channel entrance, (b) $5^{12}6^2$ channel in the sI clathrate hydrate and $5^{12}6^2$ channel entrance, (c) 5^{12} channel in the sII clathrate hydrate and 5^{12} channel entrance (G: guest, L: large cage, S: small cage).

Another remarkable observation in the (CH_4 + Me_4NOH) clathrate hydrate system is the tuning phenomenon (Figure 1b). As seen in Figure 1b, a unique tuning phenomenon is clearly observed at the chemical shift of -8.4 ppm where relatively small gaseous CH_4 molecules partly occupy the sII-L cages, pulling out large cationic Me_4N^+ that is considered to be strongly bounded with the surrounding host lattices. Such a small and non-polar guest inclusion into sII-L cages of the ionic clathrate hydrate is a surprising feature in from the viewpoint of inclusion chemistry [10,14]. First, it can be thought that the relatively small critical radii of sII-S channels restrict the uptake of small

guest molecules. More significantly, the irregular and disordered sII-L polyhedral cages encompass the sII-S channels without any ice phase appearance when the mixed hydrate is formed at a stoichiometric proportion. However, even at the excess water concentration, only a small amount of pure ice phase can coexist because most of the ice phase must be structurally transformed to pure methane clathrate hydrate. This sI structure naturally provides of continuous small guest diffusion openings through intersecting sI-L channels, thus enabling small guest molecules to attack the cations encaged in sII-L through the windows of sI-L polygonal faces and eventually occupy the sII-L cages. Accordingly, such an unusual tuning mechanism is likely to be better understood through simultaneous consideration of channel-like as well as cage-like host framework characteristics. In a specific intra-crystalline clathrate hydrate structure, guest molecules of a suitable size and shape may be readily accessible to the resulting patterns of channels and cages, as observed in zeolite inclusion complexes. In Figure 2 three different channel patterns are shown for β-7.5, sI, and sII. The β-7.5 channels are all parallel and thus no cross-connecting openings for guest molecules to cross from one channel to adjacent channels exist, and only one-dimensional diffusion takes place. The polygonal faces provide the windows essential for creating continuous diffusion paths for guest molecules or for exchangeable cations. Thus far, although the vacant channels formed by the linkage of specific cages have not received any attention in the inclusion phenomena of clathrate hydrates, it is essential to realize that these channels can play an important role in guest diffusion pathways and occupancy occurring in a complex clathrate hydrate matrix. Apparently, the presence of guest molecules in the nearly immobile host frameworks is capable of inducing the crystalline structure to transform to a more stable structure by lowering the chemical potential of the fresh host lattice formation.

A similar structural pattern was observed in the double (H_2 + Me_4NOH) ionic clathrate hydrates as shown in Figure 3. The incipient signal shift of the host lattice is observed in the 9.0 H_2O sample, which appears to be slightly lowered as compared with that of the (CH_4 + Me_4NOH) clathrate hydrate. The H_2 peaks representing sI-S (δ = 4.1 ppm) first appear, but under more hydrated surroundings the H_2 peaks representing sII-S (δ = 4.3 ppm) [8,15] are newly detected, confirming the coexistence of two different sI and sII double (H_2 + Me_4NOH) ionic clathrate hydrates.

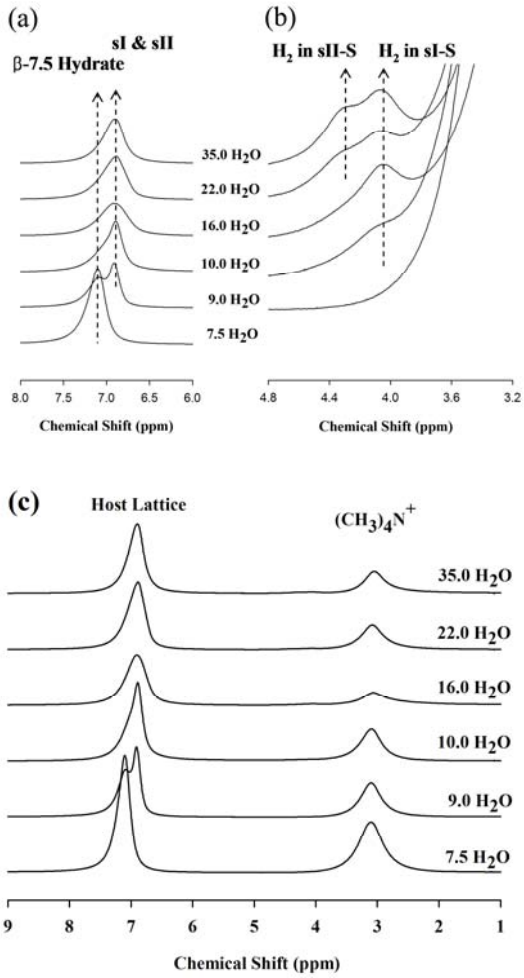

Figure 3. ^1H MAS NMR spectra of the double (H_2 + Me_4NOH) ionic clathrate hydrate measured at 203 K and a 5 kHz spinning rate; (a) the region of the host lattice signal (b) the region of the H_2 signal; (c) the entire ^1H NMR spectra. Because H_2 peaks are too small compared with Me_4N^+ signal, H_2 signals are not seen in these spectra.

Again, it is important to that the sI phase only contains the double ionic clathrate hydrate, eliminating any possible formation of the pure hydrogen clathrate hydrate under the present experimental condition. At excess water concentrations, most water molecules that do not participate in forming the ionic hydrate remain in the pure ice phase, hindering the creation of open windows through which hydrogen molecules must pass. As a result, one of the possible channels for approaching the sII-L cage does not exist in the (H_2 + Me_4NOH) hydrate system. The β-7.5

structure does not sufficiently provide potential cages or channels, which prevents H_2 molecules from migrating and becoming entrapped. This implies that the guest molecules with incongruent sizes and shapes become scarcely accessible and distributed to the empty confined space.

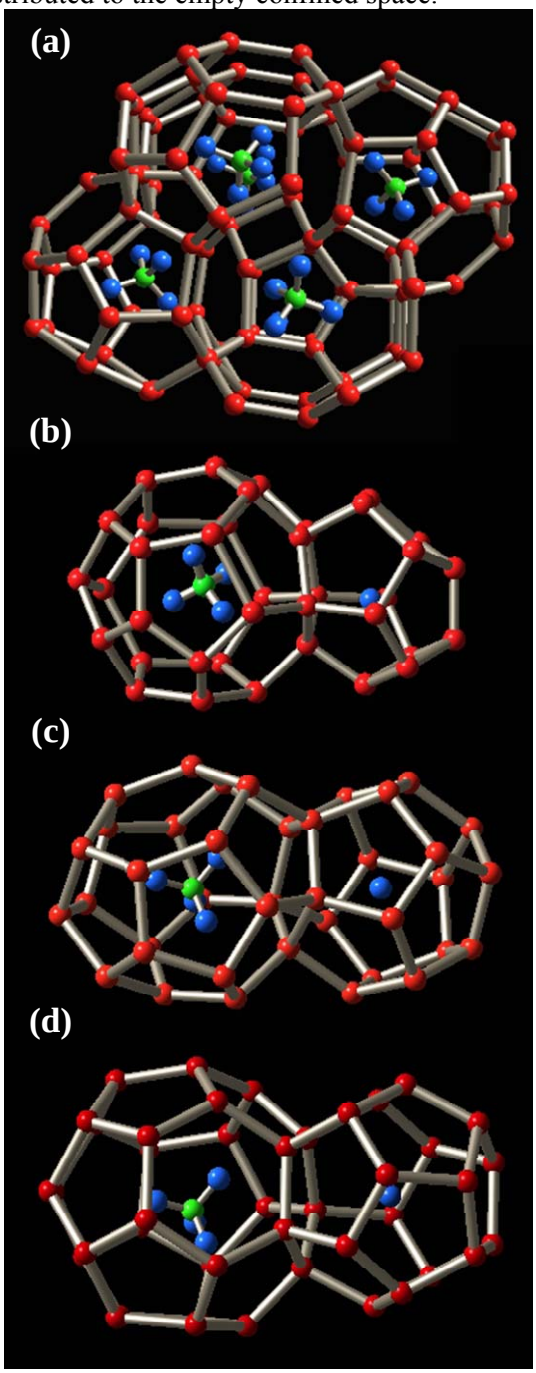

Figure 4. The structure of clathrate hydrate phases (a) α-7.5 hydrate[4] (b) β-7.5 hydrate (c) double (Me_4NOH + CH_4) sI hydrate (d) double (Me_4NOH + CH_4) sII hydrate. Methane guest is represented by a single blue ball and Me_4N^+ guest by the blue and green balls.

Through the complex nature of this structural transformation, it can be observed that the four solid hydrate phases of α-7.5, β-7.5, sI, and sII coexist (each structure is represented in Figure 4). It is noted from the ^{13}C NMR spectrum of the 65.0 H_2O sample in Figure 1b and from the ^{1}H NMR spectrum of the 35.0 H_2O sample in Figure 3b that the CH_4 and H_2 peak intensities representing sII-S increase. Close examination of the HPDEC ^{13}C and ^{1}H NMR spectra reveals that the type-II structure of the double (CH_4 + Me_4NOH) and (H_2 + Me_4NOH) ionic clathrate hydrates increase according as the water concentration becomes higher. However, at water concentrations slightly higher than 10.0 mol H_2O per 1.0mol Me_4NOH (10 H_2O), sI appears to be dominant and gradually transforms to sII in proportion to the water concentration. This unusual structure transformation implies that the cationic and spherical-like Me_4N^+ guest is best incorporated in sII-L.

CONCLUSION

In this study, the effects of cations, anions, and water host molecules on the structural transformation and tuning pattern of double ionic clathrate hydrates occurring in confined cages as well as open channels were examined. However, macroscopic and microscopic approaches must be linked together in order to obtain a complete understanding of the guest dynamic behavior and host-guest interactions in the solid ionic state. It must be clearly understood that the inclusion phenomena and structural patterns of ionic clathrate hydrates are to a certain extent different from conventional non-ionic patterns, and thus distinctive features due to ionic contributions must be taken into account. In particular, intracrystalline channel patterns created in complex ionic host-guest networks are considered to play an important role in providing pathways and windows for small guest diffusion and sorption. Although several key structural and dynamic characteristics occurring in crystalline clathrate hydrate matrix were addressed, further extensive works should be done for versatile ionic clathrate hydrates with specific functions including ionic liquids and ionic surfactants [16] in order to promote a wider range of practical applicability. Furthermore, microscopic analyses of ionic clathrate hydrates that seek to identify physicochemical characteristics are expected to provide new insights into inclusion chemistry fields.

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