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Structure Transition and Swapping Pattern of Clathrate Hydrates Driven by External Guest Molecules

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Numerous hydrate studies, covering both macroscopic and microscopic approaches, have recently been conducted for a variety of purposes[1−3] and with some notable successes. Sloan et al.[4,5] reported the sI to sII transition of clathrate hydrates formed from binary gas mixtures of CH_4 and C_2H_6 observed through spectroscopic analysis and also examined the complex hydrate-phase behavior of the corresponding binary gas mixtures in contact with water. Halpern et al. performed in situ neutron powder diffraction studies to observe a transition of sII argon hydrate to sI hydrate achieved by exposing sII argon hydrate to liquid CO_2.[6] Ota et al. conducted replacement experiments of CH_4 hydrate with liquid CO_2 using an in situ Raman analysis.[7] In a previous study we have also explored a replacement mechanism of CH_4 hydrate with gaseous CO_2 using the solid-state NMR. It was determined that a replacement of CO_2 with CH_4 hydrate appears to be fairly different from a reverse one of CH_4 with CO_2 hydrate.[8]

In the present study, the swapping phenomenon observed between external and internal guests is initially examined. In addition, the physicochemical basis of the dominance of an external guest phase that directly affects and reestablishes the complex hydrate structures to the most favorable host−guest network, causing their crystal lattices and cages to transform, is addressed. Second, as real phenomena reflecting this unique swapping pattern, the structure transition observed during the replacement between external (pure CH_4) and internal (CH_4-rich + C_2H_6 or isopentane/methylcyclohexane) guests is examined, and spectroscopic evidence is put forth that establishes the preponderant occurrence of sI over sII and sH in natural methane hydrate deposits. To realize the swapping mechanism between the enclathrated guest in a cage and the externally approaching gaseous guest, sII and sH hydrates are synthesized, and their structures are confirmed through spectroscopic analysis. These hydrate samples are exposed to gaseous methane surroundings under specified temperature and pressure conditions. For more precise information regarding the guest distribution of CH_4 and C_2H_6 guests, the high-power decoupling ^{13}C NMR spectra and corresponding chemical shifts of CH_4 and C_2H_6 molecules occupying the sI and sII cages were obtained before and after the CH_4 replacement.

The mixed $CH_4 + C_2H_6$ hydrate formed from 10 mol % C_2H_6 balanced CH_4 (Figure 1a) has peaks from CH_4 in both sII-L and sII-S at chemical shifts of −8.3 and −4.5 ppm, respectively, and from C_2H_6 in the sII-L at 5.793 ppm.[9−11] For this sample, the hydrate-phase composition was 70.25% CH_4 and 29.48% C_2H_6 according to a GC analysis. When the mixed $CH_4 + C_2H_6$ hydrate was exposed to CH_4 at 25 bar and 274.15 K, the resulting spectrum was found to be the same as the intact sII hydrate without any guest exchange.

However, at a pressure condition of 117 bar, the hydrate structure was transformed from sII to sI, as clearly seen from the CH_4 at −6.7 ppm (sI-L) and −4.3 ppm (sI-S). It is important to note that the C_2H_6 peak completely disappears after 3 days of exposure to CH_4, which is also crosschecked by the GC that analyzes the directly dissociated gas amount of the replaced hydrate samples. Additionally, a higher concentration of 20 mol % C_2H_6 is used for the sII hydrate formation owing to the decisive role C_2H_6 plays in making the sII lattices. As shown in Figure 1b, the mixed sII $CH_4 + C_2H_6$ hydrate represents three resonances at −8.3 ppm (CH_4, sII-L), −4.5 ppm (CH_4, sII-S), and 5.763 ppm (C_2H_6, sII-L).

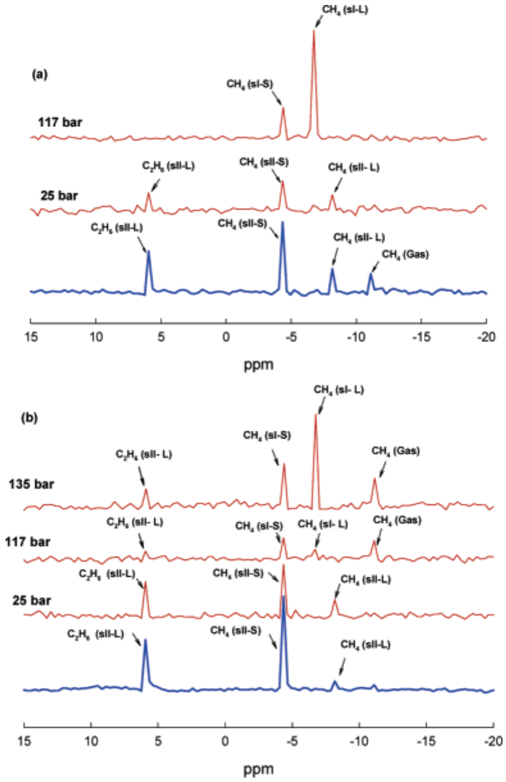

Figure 1. ^{13}C NMR spectra of the mixed $CH_4 + C_2H_6$ hydrate replaced by CH_4: blue line, before replacement; red line, after replacement. Part a shows the mixed $CH_4 + C_2H_6$ hydrate formed from 10 mol % C_2H_6 balanced CH_4 (272.15 K, 55 bar) and hydrate replaced by 25 bar CH_4 and 117 bar CH_4 at 274.15 K. Part b shows the mixed $CH_4 + C_2H_6$ hydrate formed from 20 mol % C_2H_6 balanced CH_4 (272.15 K,55 bar) and hydrate replaced by 25 bar CH_4, 117 bar CH_4, and 135 bar CH_4 at 274.15 K for 3 days.

When compared to the CH_4 (sII-L) in Figure 1a, the corresponding intensity was slightly lower, as a relatively large amount of C_2H_6 from the binary guests is expected to occupy the sII-L. The hydrate-phase composition was found to be 59% CH_4 and 41% C_2H_6 from the GC. Again, the mixed sII $CH_4 + C_2H_6$ hydrate formed from 20 mol % C_2H_6 is replaced by CH_4 at three different pressures of 25, 117, and 135 bar at 274.15 K. At a low pressure of 25 bar, no structure transition occurs, but at 117 and 135 bar the chemical shifts of methane in sII are shifted to −6.7 ppm (CH_4,

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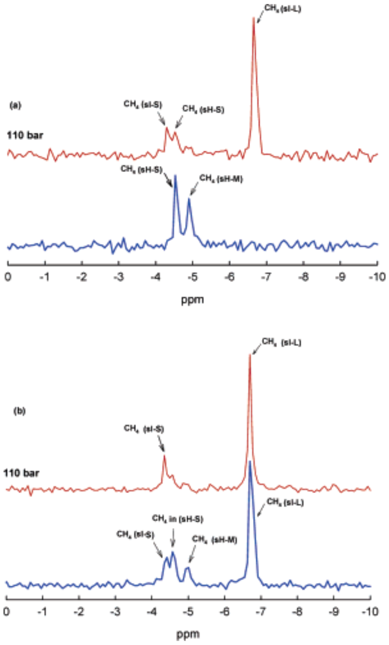

Figure 2. ^{13}C NMR spectra of MCH (or isopentane) + CH_4 hydrate replaced by CH_4: blue line, before replacement; red line, after replacement. Part a shows the [MCH (2.8 mol %) + CH_4] hydrate (272.15 K, 50 bar) and the hydrate replaced by 110 bar CH_4 at 274.15 K. Part b shows the [isopentane (2.8 mol %) + CH_4] hydrate (272.15 K, 50 bar) and the hydrate replaced by 110 bar CH_4 at 274.15 K for 3 days.

sI-L) and small −4.3 ppm (CH_4, sI-S). It was also noted that, even at a high pressure of 135 bar, a substantial amount of ethane remains in the sII-L of −5.793 ppm, and two sI and sII structures coexist. According to the structure patterns observed from Figure 1b, it was expected that most of the sII hydrates would eventually be converted to sI hydrates in a pressure region higher than 135 bar. In particular, this progressive structure change strongly implies from a geophysical viewpoint that the sII methane hydrates deposited in very deep-ocean sediments readily transform to sI methane hydrates because of the highly CH_4−rich surroundings. In a shallow region, however, a large amount of sII methane hydrates remains intact, coexisting with the converted sI.

For the sH hydrate, the same approaches attempted for sII hydrate was taken, including proper spectroscopic measurements. The inclusion of large hydrocarbons induces a hydrate forming condition to be more favorable by lowering pressure and raising temperature for forming the mixed hydrate when compared with the corresponding condition of pure CH_4 hydrate (Figure S4, Supporting Information (SI)). The ^{13}C NMR spectrum before replacement on the sH hydrate of the MCH (2.8 mol %) + CH_4 in Figure 2a indicates that methane molecules exist in both sH-S and sH-M, but not in sH-L, where the chemical shifts are −4.5 ppm and −4.9 ppm, respectively. A CH_4 introduction at 110 bar causes a structural transition of sH to sI. As confirmed in Figure 2a, the intensities of the CH_4 trapped in sH-S and sH-M mostly decrease, while simultaneously the new sI-S and sI-L peaks appear and increase. To better understand the influence of the molecular characteristics on the structure, isopentane, which reveals the peculiar pattern of sH formation, was utilized. Unlike MCH, the sH hydrate containing isopentane coexists with pure sI CH_4 hydrate, caused by its dissimilar molecular size and shape. The hydrate sample conditions maintained at 273.6 K and 50 bar and the resulting ^{13}C NMR spectra are shown in Figure 2b. Isopentane forms a sH hydrate having two resonance lines at −4.5 ppm and −4.9 ppm, indicating that methane molecules are absorbed only in small and medium-sized cages. At the same time, the pure sI, including methane molecules of both sI-L (−6.7 ppm) and sI-S (−4.3 ppm), coexists with the sH of the mixed isopentane + CH_4 (Figure 2b). At a high pressure of 110 bar, the coexistence of sI and sH shifts to the preponderant sI owing to the highly CH_4-rich surroundings. In addition to the NMR, Raman spectroscopy was also used to crosscheck the structural aspects of hydrate samples before and after the CH_4 swapping, as shown in SI Figure S2. Interestingly, it was further confirmed that CH_4 can replace the most stabilized sH-forming guest molecules.

Simply judging from the hydrate stability region based on the equilibrium PT behavior, the sII and sH appear to be more stable than the sI in most of the mixed hydrate systems. Thus, it may be concluded that the sII and sH methane hydrates are more abundant compared to those that can be discovered at the present level. However, from the actual experiments of the guest swapping scenario, it is confirmed that most of the sII and sH methane hydrates ultimately transform into sI under free methane-rich surroundings sealed by an overlying impermeable hydrate layer, which explains presumably the preponderance of sI among the complex structures of naturally occurring methane hydrates. More importantly, it is noted that the unique and cage-specific swapping pattern of multiguests is expected to provide new insights for a better understanding of the inclusion phenomena of clathrate materials.

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Supporting Information Available: Experimental procedure, X-ray diffraction, high-power decoupling ^{13}C NMR spectroscopy, Raman spectroscopy, and phase stability conditions details. This material is available free of charge via the Internet at http://pubs.acs.org.

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