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# sI 천연 메탄하이드레이드의 존재 : 결정구조 변화의 분광학적 분석

연 순화, 설 지웅, 이 흔

# Preponderant Occurrence of sI natural methane hydrates: Spectroscopic analysis of crystalline structure transition

Sun-Hwa Yeon, Jiwoong Seol, Huen Lee

**Key words** : Methane (메탄), sI hydrate (sI 하이드레이트), sH hydrate (sH 하이드레이트), Crystalline structure (결정구조)

**Abstract** : We report here that under strong attacksof external $CH_4$ guest molecules the sII and sH methane hydrates are structurally transformed to the crystalline framework of sI, leading to favorable change of the lattice dimension of the host-guest networks. The High Power Decoupling $^{13}C$ NMR and Raman spectroscopies were used to identify structure transitions of the mixed $CH_4$+$C_2H_6$ hydrates (sII) and hydrocarbons (methylcyclohexane, isopentane) + $CH_4$ hydrates (sH). The resulting spectra indicate that most of the synthesized sII and sH hydrates were transformed to methane hydrate of sI under 110 bar and particularly the coexistence of sI with sII or sH appear according to the surrounding methane-rich gas conditions. The present findings might be expected to provide rational evidences regarding the preponderant occurrence of naturally-occurring sI methane hydrates in marine sediments.

## 1. Introduction

The most abundant methane hydrate discovered in nature has a crystalline structure of sI that is deposited in continental slope sediments such as the Gulf of Mexico and many other basins dominated by methanogentic process such as bacterial methane [1, 2]. On the other hand, the sII hydrate that forms owing to the influence of thermogenic hydrocarbon and mainly includes the oil-related $C_1$-$C_4$ hydrocarbons isdiscovered at shallow depth in sea floor sediment in a few sites such as the Gulf of Mexico outside of the Caspian Sea [3]. Simultaneously, the occurrence of the sH that is identified as a new structure by Ripmeester et al. through laboratory experiments [4, 5], has not been identified in nature, but the coexistence of sII with sH containing 2-methylbutane(isopentane) is presented on Bush Hill of the Gulf of Mexico continental slope [6, 7]. Furthermore, in many places, the anomalous phenomena on methane have been raised that higher concentrations of methane than normally found in bottom seawaters occur in deep seawaters through fluid migration of the methane which might be generated from the fermentative decomposition of organic matter and bacterial $CO_2$ reduction [8, 3]. From this generation and migration of methane, we can expect that plenty of methane might be collected into the deep sediment from beneath the sea floor, and hence the most of the sediment pressure having several tens of MPa arestrongly influenced by the methane composition. The dominance of this methane atmosphere will open great possibilities to transform the structure, sII and sH, of the previously formed oil-related natural gas hydrate at shallow depth in sea floor sediment

Herein, we examine the geophysical reasons why the sI occurs preponderantly over the sII and sH in natural methane hydrate deposits. The free methane gas existing below the methane hydrates sealed in by the overlying impermeable hydrate layer might attack the sII and sH hydrates already existing in marine sediments.

## 2. Experimental

To realize the replacement between sII and sH hydrates and externally approaching methane gas we first synthesized the sII ($CH_4$ + $C_2H_6$) and sH (isopentane/methylcyclohexane + $CH_4$) hydrates and confirmed their structures through spectroscopic analysis. These hydrate samples are exposed to gaseous methane surroundings at the specified temperature and pressure conditions. For more precise information regarding the guest distribution of $CH_4$ and $C_2H_6$ guests we obtained the $^{13}C$ NMR spectra and corresponding chemical shifts of $CH_4$ and $C_2H_6$ molecules occupied in sI and sII cages before and after $CH_4$ replacement.

## 3. Results and Discussion

The mixed $CH_4$+$C_2H_6$ hydrate formed from 10 mol % $C_2H_6$ and balanced $CH_4$ (Figure 1(a)) has peaks from $CH_4$ in both the sII-L and sII-S atchemical shifts of 8.3 and -4.5 ppm, respectively, and from $C_2H_6$ in the sII-L at 5.793 ppm [9, 10, 11]. For this sample, the hydrate-phase composition was 70.25 % $CH_4$and 29.48 % $C_2H_6$ from the GC. When the mixed $CH_4$+$C_2H_6$ hydrate was exposed to $CH_4$ at 25 bar and 274.15K, the resulting spectrum was found to be the same as the intact sII hydrate without any guest exchange. But, under the deep-ocean floor pressure condition of 117 bar the hydrate structure was transformed from sII to sI as clearly seen from $CH_4$ at -6.7 ppm (sI-L) and -4.3 ppm (sI-S). We note that the $C_2H_6$ peakcompletely disappears after 3 days 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 because of the decisive role of $C_2H_6$ in making the sII lattices. As shown in Figure 1(b), 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).

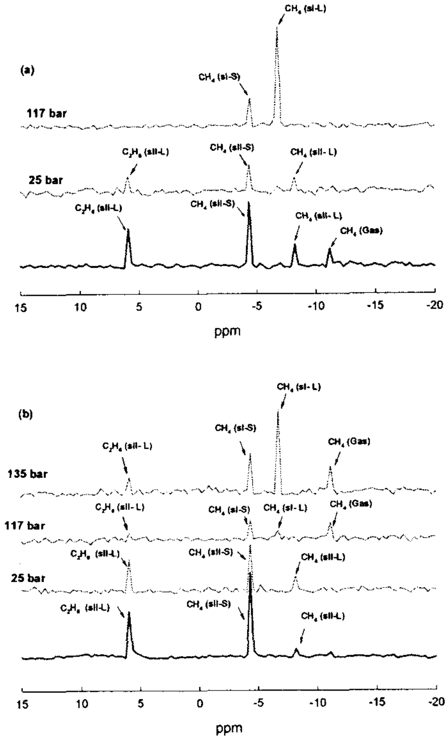

Figure 1. $^{13}C$ NMR spectra of the mixed $CH_4$+$C_2H_6$ hydrate replaced by $CH_4$: blue line -before replacement, red line - after replacement. (a) the mixed $CH_4$+$C_2H_6$ hydrate formed from 10 mol% $C_2H_6$ balanced $CH_4$ (272.15 K, 55 bar) andhydrate replaced by 25 bar $CH_4$, 117 bar $CH_4$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

When compared to $CH_4$ (sII-L) of Figure 1(a), the corresponding intensity was a little lowered because a relatively large amount of $C_2H_6$ from the binary guests is expected to occupy the sII-L. The hydrate-phase composition is found to be 59 % $CH_4$ and 41 % $C_2H_6$ from the GC.

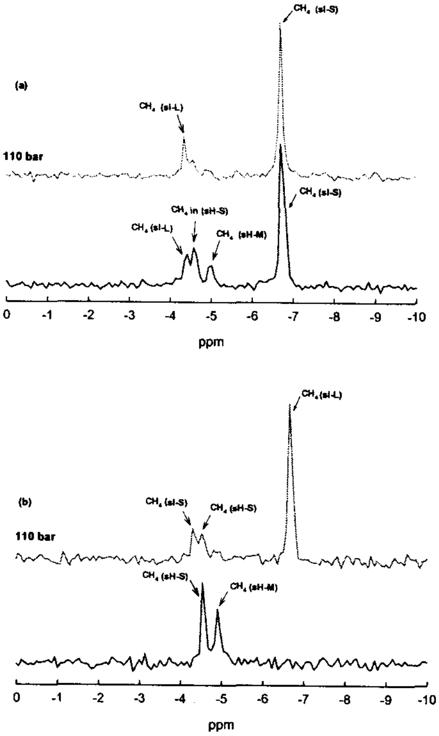

Figure 2. $^{13}C$ NMR spectra of MCH (or isopentane) + $CH_4$ hydrate replaced by $CH_4$: blue line - before replacement, red line - after replacement. (a) the [MCH (2.8 mol%) + $CH_4$] hydrate (272.15 K, 50 bar) and the hydrate replaced by 110 bar $CH_4$ at 274.15 K. (b) the [isopentane (2.8 mol%)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

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 bars and 274.15K. At 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 ($CH_4$, sI-L) and small -4.3 ppm ($CH_4$, sI-S). We note that, even at a high pressure of 135 bar, a substantial amount of ethane still remains in sII-L of -5.793 ppmand two sI and sII structures coexist. According to structure patterns observed from Figure 1(b) we expect that most of sII will be eventually converted to sI in the higher pressure region than 135 bar. This progressive structure change might suggest that the sII methane hydrates deposited in the very deep-ocean sediments readily transform to sI methane hydrates due to gaseous $CH_4$attack, but in the shallow region a large amount of sII methane hydrates still remains intact coexisting with the converted sI.

For sH hydrate we make the same approaches attempted for sII hydrate, including the proper spectroscopic measurements. The PT stability conditions of hydrates indicate that the sH forms at the milder state than sI (Figure S3). The inclusion of large hydrocarbons such as isopentane, methylcyclohexane and methylcyclopentane in sH-L induces the formed hydrates to be readily stabilized even at the low pressure and high temperature region. The $^{13}C$ NMR spectrum before replacement in Figure 2 (a) 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. At low pressure of 27 bar the sH hydrate of the MCH (2.8 mol %) + $CH_4$ maintains the same structure even after replacement. But, the $CH_4$ introduction at110 bar causes the structural transition of sH to sI. As confirmed in Figure 2 (a), the intensities of $CH_4$ trapped in sH-S and SH-M mostly decrease and simultaneously the new sI-S and sI-L peaks appear and increase. To better understand the influence of molecular characteristics on structure we choose isopentane that reveals the particular pattern of sH formation. Unlike MCP the sH hydrate containing isopentane coexists with the pure sI $CH_4$ hydrate, caused by its dissimilarmolecular size and shape. The hydrate sample conditions maintained at 273.6 K and 50 bar and the resulting $^{13}C$ NMR spectra were shown in Figure 2 (b). Isopentane forms thesH hydrate having two resonance lines at -4.5 ppm and -4.9 ppm, indicating that methane molecules are only absorbed 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 sH of the mixed isopentane + $CH_4$ (Figure 2 (b)).

At high pressure of 110 bar the coexistence of sI and sH shifts to the preponderant sI by $CH_4$ attack. Besides the NMR, the Raman spectroscopy is also used to crosscheck the structural aspects of hydrate samples before and after $CH_4$ replacements, as shown in Figure 3.

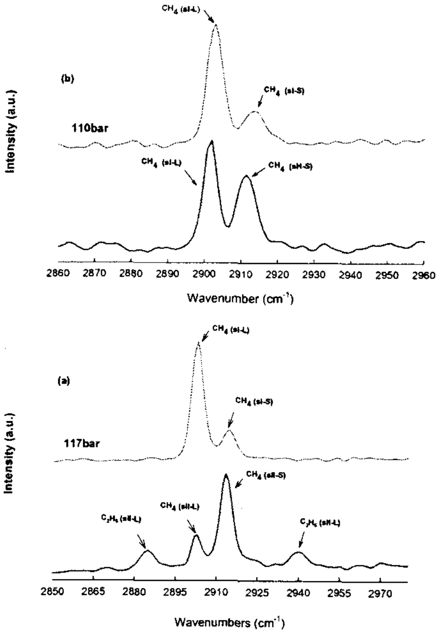

Figure 3. Raman spectra of the mixed hydrates: blue line - before replacement, red line - after replacement. (a) the mixed $CH_4$+$C_2H_6$ hydrate formed from 10 mol% $C_2H_6$ balanced $CH_4$( 272.15 K, 55 bar) and hydrate replaced by 117 bar $CH_4$ at 274.15 K. (b) the [isopentane (2.8 mol%) + $CH_4$] hydrate (272.15 K, 50 bar) and hydrate replaced by 110 bar $CH_4$ at 274.15 K

## 4. Conclusion

From these spectroscopic results we suggest that most of the sII and sH methane hydrates ultimately transform to the sI, which presumably explain the preponderance of sI among complex structures of naturally-occurring methane hydrates. Furthermore, the present findings provide the important implications for understanding the unique molecular distributions under strong attacks of external guest molecules to the existing cages, and are possibly extended to various hydrate-based fields and inclusion chemistry.

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