

COMPLEX COEXISTENCE BEHAVIOR OF STRUCTURE I AND H HYDRATES

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ABSTRACT

¹³C NMR spectroscopic analysis was carried out to clarify the formed hydrate structure in specific conditions on hydrate phase diagram of ternary methane, neohexane, and water system. The obtained NMR spectra at three different conditions suggested that both structure I and H were formed simultaneously and coexisted at 273.6 K and 50 bar. But, for both conditions of 273.6 K, 25 bar and 283.1 K, 50 bar the formed hydrate was identified as structure H only. These results showed that the pure CH₄ hydrate of structure I was formed and coexisted with mixed CH₄+neohexane hydrate of structure H in low temperature and high pressure region after passing through the phase boundary of pure CH₄ hydrate. We have examined the structure coexistence at 273.6 K and 50 bar with other structure H formers of isopentane, methylcyclopentane, and methylcyclohexane. In case of isopentane, the obtained NMR spectrum showed that structure I and H coexisted and the amount of methane molecules in structure I was two times as many as in cages of structure H. However, there were no resonance lines of structure I when methylcyclohexane formed structure H with methane molecules.

Keywords: Structure coexistence, phase equilibrium, structure H, methane, neohexane

INTRODUCTION

Gas hydrates are crystalline materials formed by a physical interaction between host water molecules and relatively light guest molecules [1]. At high pressure and low temperature conditions water molecules are connected by hydrogen bonds and form various cavities capable of entrapping guest molecules. Those non-stoichiometric crystalline compounds are divided into three distinct structures I, II and H, which differ in cavity size

and shape [2]. Although the hydrate structures were usually known to be determined by the largest guest molecule in hydrate forming system, the complex structural characteristics indicating the occurrence of metastable structure II Xe hydrate have been reported [3] when a THF hydrate was exposed to hyperpolarized Xe. Recently, we have reported the heterogeneous state of mixed CH₄+THF hydrate and liquid water from microimaging observation to follow water

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consumption [4]. The heterogeneous mixture was transformed to solid mixture of pure CH₄ and mixed CH₄+THF hydrate when the temperature was decreased to low region of the phase boundary of pure CH₄ hydrate. Such issues of complex processes that led to unexpected hydrate structure are of considerable importance, suggesting the requirement of cross exploration through phase equilibrium determination and spectroscopic analysis of hydrate structures. This study had been considered to explore the structural characteristics depending on the hydrate equilibrium conditions of ternary methane, neohexane, and water system. Although normally a single structure is expected to be stable in such systems, here we report the coexistence of structure I and H at different conditions of hydrate formation. Furthermore the similar experiment with other structure H formers showed the effect of molecular shape on determining the distribution of hydrate structures.

EXPERIMENTS

To identify hydrate structure, a Bruker 400 MHz solid-state NMR spectrometer was used. Spectra were recorded at 243 K by placing samples within a 4 mm o.d. Zirconia rotor loaded into variable temperature probe. All ¹³C NMR spectra were recorded at a frequency of 100.6 MHz with magic angle spinning (MAS) at about 2 kHz. The radio frequency field strengths of 70 kHz corresponding to 5 μs 90° pulses were used. The adamantane that assigned a chemical shift of 38.3 ppm at 300 K was used as an external chemical shift reference. A detailed method capable of resolving hydrate structures using NMR spectroscopic analysis can be found in literature [5, 6].

The hydrate samples were prepared in a mechanically stirred reactor. The reactor maintained at a constant temperature was filled with the liquid mixtures of water and neohexane, and then subsequently pressurized with pure CH₄ gas to higher pressure than the corresponding hydrate equilibrium pressure at the same temperature. By stirring aqueous mixture solid hydrate formation was proceeded through induction, nucleation, and growth periods, successively. When hydrate formation process was completed, the formed hydrates were sampled by keeping both the cell and Zr-rotor immersed in liquid nitrogen to prevent any hydrate dissociation or distortion. This Zr-rotor having hydrate samples was then inserted to the solid-state NMR.

RESULTS AND DISCUSSION

In general, the phase equilibrium of pure CH₄ hydrate was represented as three-phase equilibrium, H-L_w-V, curve and it meant the limit condition for formation and stable existence of hydrate phase. The presence of organic hydrocarbons clearly makes a drastic difference in phase behavior. Figure 1 showed the comparison of hydrate equilibrium conditions for pure CH₄ and mixed CH₄+neohexane hydrates. The pure CH₄ hydrate could be formed at lower temperature and higher pressure conditions than the H-L_w-V curve (region I) and the formed hydrate was known to be structure I composed of 5¹² and 5¹²6² cages. The addition of neohexane induced 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 CH₄ hydrate. The equilibrium condition of mixed CH₄+neohexane hydrate was represented as four-phase equilibrium, H-L_w-L_{hc}-V, curve because neohexane was immiscible to liquid water phase. At lower temperature and higher pressure conditions than the H-L_w-L_{hc}-V curve (region H), the formed mixed CH₄+neohexane hydrate was known to be structure H composed of 5¹², 4³5⁶6³, and 5¹²6⁸ cages [7].

It is noted that the formation condition of pure CH₄ hydrate assigned as region I was included into the formation condition of mixed CH₄+neohexane hydrate assigned as region H. Accordingly, it is possible to think that the formation of structure I and H should compete each other for better occupation of guest molecules and stabilization of hydrate structure if we consider the hydrate formation in region I of Figure 1. To investigate the relationship between hydrate structure and phase equilibrium, we have formed the hydrate at three different conditions of point A, B, and C as seen in Figure 1. First the hydrate was formed at 273.6 K and 25 bar (point A, region H) to observe the spontaneous formation of structure H hydrate. Secondly, the hydrate was formed at 273.6 K and 50 bar (point B, region I), which was considered as possible region for simultaneous formation of structure I and H. Finally, to investigate the effect of changing the formation region the hydrate was formed again at condition of point B and then the temperature was increased to 283.1 K (point C, region H) after the hydrate formation reaction reached steady-state.

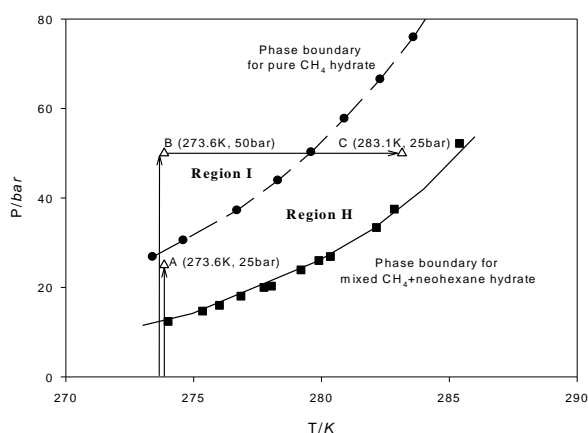


Figure 1. Hydrate phase boundary of pure CH₄ (structure I, assigned as dotted line) and mixed CH₄+neohexane (structure H, assigned as solid line) hydrates. Point A, B, and C represents sample obtaining conditions for ¹³C NMR spectroscopy.

Figure 2 represented a stacked plot of three ¹³C NMR spectra obtained at each point, which were used to identify the formed hydrate structures. Neohexane was showed as four distinct resonance lines because it was composed of six carbons and each resonance line was attributed to the individual functional group. However, in this study, ¹³C NMR spectra was showed from 0 to 10 ppm to focus on the methane molecules occupying the hydrate cages, which provide the structural information of hydrate samples such as structure type and guest distribution in hydrate cages. Figure 2 (a) representing ¹³C NMR spectrum of hydrate sample formed at point A indicate that the methane molecules are enclathrated into both 5¹² and 4³5⁶6³ cages of structure H at -4.5 and -4.9 ppm, respectively. The stoichiometric ratio of 5¹² and 4³5⁶6³ cages appears to be 3 : 2 in the unit cell of structure H [5]. The relative integrated intensities of NMR spectrum directly gave the value of occupancy ratio of methane molecules in 4³5⁶6³ cages to those in 5¹² cages, $\theta_{M,CH_4} / \theta_{S,CH_4} = 1.22$, confirming the fact that methane molecules in 5¹² cages was more abundant than those in 4³5⁶6³ cages. The NMR spectrum provides no evidence of methane molecules occupying the 5¹²6⁸ cages, which was known to only accommodate the structure H formers, i.e. neohexane. This result suggested that the spontaneous formation of structure H was possible without an initiating medium to create hydrogen bonding in aqueous phase. However, the

hydrate sample formed at point B showed different structural characteristics.

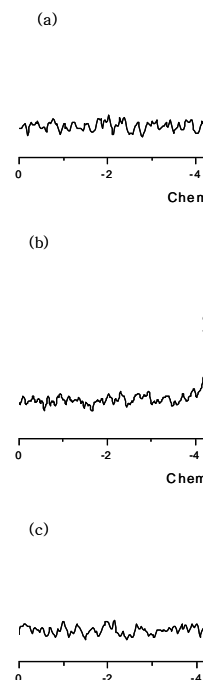


Figure 2. Stacked plot of ¹³C NMR spectra for ternary methane, neohexane, and water system. (a) structure H at point A (b) coexistence of structure I and H at point B (c) structure H at point C.

The ¹³C NMR spectrum in Figure 2 (b) showed two resonance lines at -4.5 and -4.9 ppm, which were identified as methane molecules in 5¹² and 4³5⁶6³ cages of structure H, respectively. The occupancy ratio of $\theta_{M,CH_4} / \theta_{S,CH_4} = 1.22$ was obtained from relative integrated intensities of both resonance lines. In addition, two more resonance lines were also detected at -4.3 and -6.7 ppm. Our previous work[8] revealed that both resonance lines came from pure CH₄ hydrate because the methane molecules captured into 5¹² and 5¹²6² cages of structure I was showed peaks at -4.3 and -6.7 ppm, respectively. The occupancy ratio appears to be $\theta_{L,CH_4} / \theta_{S,CH_4} = 1.16$ and the corresponding intensity ratio of $I_{L,CH_4} / I_{S,CH_4} = 3.49$ is analogues to the stoichiometric ratio of 5¹² and 5¹²6² cages in structure I. This result strongly suggested that mixed CH₄+neohexane hydrate was formed at point B and simultaneously pure CH₄ hydrate was also formed and coexisted with mixed hydrate.

The ^{13}C NMR spectrum obtained in point C as shown in Figure 2 (c) represents a change of structural characteristics in hydrate phase. There are only two resonance lines identified as methane molecules in 5^{12} and $4^35^66^3$ cages of structure H at -4.5 and -4.9 ppm, respectively. The occupancy ratio was $\theta_{M,CH_4}/\theta_{S,CH_4} = 1.36$, which meant that the occupancy of methane in 5^{12} cages decreased slightly than corresponding occupation in point A and B. It is noted that from the NMR spectrum both structure I and H coexisted at point B, but upon warming to point C the structure I was totally dissociated while structure H remained largely intact. Accordingly, it can be concluded from the NMR analysis based on equilibrium conditions that the pure CH_4 hydrate formed and coexisted with mixed CH_4 +neohexane hydrate in low temperature and high-pressure region after passing through the phase boundary of pure CH_4 hydrate.

At this moment, it must be resolved whether the distribution of hydrate structure should be observed for other hydrocarbons forming structure H with methane molecules. We chose three specific structure H formers of isopentane, methylcyclopentane (MCP), methylcyclohexane (MCH) in order to observe the effect of molecular size and shape. For ternary system of selected hydrocarbon, methane, and water the hydrate sample was formed at 273.6 K and 50 bar, same condition of point B. The obtained ^{13}C NMR spectra for three different structure H formers were shown in Figure 3. Isopentane was known to be one of alkane hydrocarbon to form structure H and as seen in Figure 3 (a) two resonance lines at -4.5 and -4.9 ppm revealed the formation of structure H hydrate, which indicate the methane molecules in 5^{12} and $4^35^66^3$ cages. In addition, as discussed in Figure 2 (b), two resonance lines of methane molecules in 5^{12} and $5^{12}6^2$ cages of structure I also came from pure CH_4 hydrate coexisting with mixed CH_4 +isopentane hydrate. The amount of methane molecules occupying the cages of structure I was two times as many as methane molecules in cages of structure H, while in case of neohexane the ratio of methane molecules of structure I to H was 0.9. Based on these spectra, there must be preferential distribution of structure I and H in ternary system containing methane and alkane hydrocarbons that could selectively participate in forming both hydrate structures.

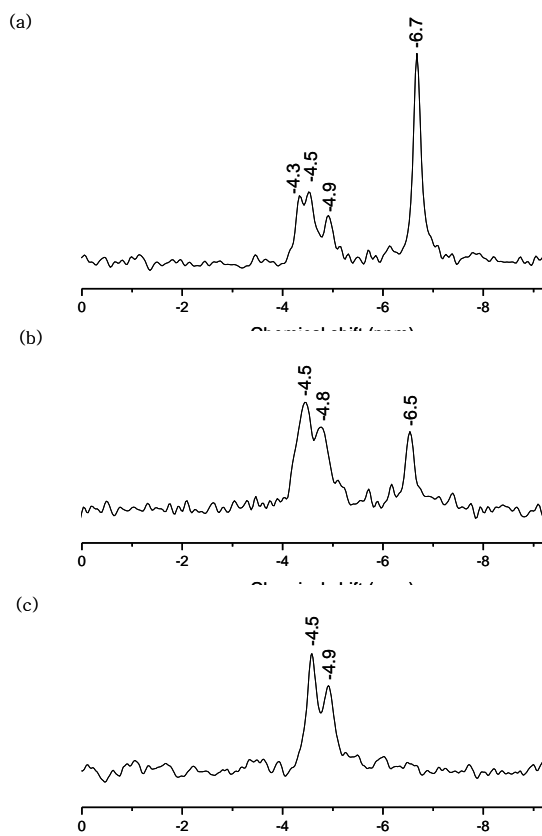


Figure 3. (a) ^{13}C NMR spectra of coexisting pure CH_4 and mixed CH_4 +isopentane hydrates formed at 273.6 K and 50 bar for ternary methane, isopentane, and water system. (b) ^{13}C NMR spectra of mixed CH_4 +MCP hydrate containing small amount of pure CH_4 hydrate formed at 273.6 K and 50 bar for ternary methane, MCP, and water system. (c) ^{13}C NMR spectra of mixed CH_4 +MCH hydrate formed at 273.6 K and 50 bar for ternary methane, MCH, and water system representing the overall hydrate phase was structure H.

However, following spectroscopic results of cycloalkane represent the different structural characteristics, suggesting the importance of molecular shape of hydrocarbons.

Figure 3 (b) was ^{13}C NMR spectrum of hydrate sample for ternary methane, MCP, and water system. The methane molecules occupying the 5^{12} and $4^35^66^3$ cages of structure H were represented as two resonance lines at -4.5 and -4.8 ppm, respectively, while there was only one resonance line indicating methane molecules in $5^{12}6^2$ cages of structure I at -6.5 ppm. The ratio of methane molecules of structure I to H was 0.3, suggesting the hydrate phase was largely structure H and

there exist only small amount of structure I even though the resonance line of methane molecules in 5^{12} cages of structure I might superimposed to resonance line of methane molecules in 5^{12} cages of structure H. When the hydrate was formed in ternary system of methane, MCH and water, ^{13}C NMR spectrum, Figure 3 (c), showed only two resonance lines of methane molecules occupying 5^{12} and $4^35^66^3$ cages of structure H at -4.5 and -4.9 ppm respectively. There were no resonance lines of methane in cages of structure I. Accordingly, the overall hydrate phase could be identified as structure H. Figure 3 (b) and (c) suggested that the structure H was abundant during the hydrate formation process if cycloalkane hydrocarbons participated in the formation of structure H. The methane molecules played a role as help gas to form mixed hydrate with hydrocarbons and didn't initiate the formation of structure I. Comparing with the results of linear alkane hydrocarbon, it is possible to suggest that cycloalkane is more preferable compounds to form structure H than linear alkane because the shape of cycloalkane is more available to fill and stabilize the $5^{12}6^8$ cages of structure H.

CONCLUSIONS

In this contribution, we observed the particular phenomena of simultaneous formation of two different hydrate structures and effect of molecular shape on formation process. Stable coexistence of structure I and H must be considered to develop the exploitation process of natural gas from marine sediments of Gulf of Mexico because the natural gas hydrate deposit was known to be structure H by powder X-ray diffraction studies.

Moreover, in the petrochemical processes containing structure H formers, the developing kinetic inhibitors will have to prevent the both hydrate structures of I and H. Although the structural characterization has been carried out for important systems with natural gas components, many of the physical attributes of hydrate structure still remain unknown and need to be identified in detail. More precise and considerable amount of work needs to be done in order to resolve the formation rate of hydrate structures and interaction between two coexisting hydrate structures.

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