

Inhibition of Natural Gas Hydrates in the Presence of Liquid Hydrocarbons Forming Structure H

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Received: November 17, 2009; Revised Manuscript Received: March 29, 2010

The effects of LMGS (large molecule guest substance) amount on the thermodynamics of natural gas hydrates, as well as structural characteristics of mixed hydrates of LMGS and natural gas, have been studied. The addition of 1.7 wt % neohexane (NH) to water induced inhibition of natural gas hydrates, and this inhibition effect increased with increased addition of NH up to 7.8 wt %. However, the hydrate equilibrium condition changed slightly when the concentration of NH further increased from 7.8 to 14.5 wt %. Investigations on structural characteristics were carried out by analyzing ^{13}C NMR spectra of mixed hydrates formed from the mixture of natural gas and NH. They indicate that two hydrate structures of II and H coexist simultaneously, and the ratio of structure H to II decreased from 0.97 to 0.43 when the NH concentration decreased from 14.5 to 7.8 wt %. In addition, it was confirmed that ethane, propane, and iso-butane gas molecules do not participate in the formation of structure H and only enclathrated in large cages of structure II. These results indicate the existence of multiple hydrate structures, which must be considered in many industrial applications when mixed hydrates are formed from multicomponent gas mixtures and liquid hydrocarbons.

Introduction

Gas hydrates, known as nonstoichiometric crystalline compounds,¹ are classified into three structural families: cubic structure I (sI), cubic structure II (sII), and hexagonal structure H (sH). The discovery of sH² marked a starting point for comprehensive research on large molecule guest substances (LMGS) that can be accommodated into large cages of sH. Its discovery also led to research on the effect of sH formers on the flow assurance in the petroleum industry. Initial studies focused on the effect of sH formation on the thermodynamics of reservoir fluid.³ Although there was the opinion that sH was likely to form in real reservoir fluids with high concentrations of intermediates, thermodynamic modeling suggested that sII was the most stable hydrate structure for up-to-date investigated reservoir fluid conditions.⁴ The use of sH for natural gas storage was also proposed with the expectation of enabling a rather high gas storage capacity at lower pressure than that required for forming sI methane hydrate.⁵ The optimum gas storage capacity of sH varied with the LMGS used and was approximately 20–40% less than that of sI methane hydrate according to characterization with spectroscopic methods.⁶ Additionally, it

has been suggested that sH would show a 40% increase in the amount of hydrogen stored by weight compared with sII.⁷ Recently, there was evidence from natural gas hydrate samples recovered from the Cascadia margin, Canada, that sII and sH coexist in a natural environment.⁸

A large number of studies have been carried out to identify phase equilibrium conditions, formation kinetics, and structural characteristics of sH.^{3–8} However, a weak point in much of these works is that sH was formed from pure methane or nitrogen gas with the addition of excess amounts of LMGS rather than the stoichiometric composition against water, which can be calculated from the structure of sH, $3\text{S} \cdot 2\text{M} \cdot 1\text{L} \cdot 34\text{H}_2\text{O}$, and the premise of 100% occupation of large cages with LMGS molecules.⁹ Natural gas is a mixture of hydrocarbons and a few non-hydrocarbons. Each of these components has their own hydrate equilibrium and structural characteristics; however, it is considered to form sII hydrate when natural gas composed of hydrocarbons from methane, ethane, propane, and butane contacts water at high pressure and low temperature conditions. Higher hydrocarbons (+C6) that mostly occur in the liquid condensate phase form sII with natural gas, e.g., cyclohexane and cyclopentane.^{4,13} However, in the case of methylcyclohexane and neohexane, they form sH with methane.¹ Since natural gas

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is composed of many gaseous hydrocarbons and has been produced with liquid condensate phase containing higher hydrocarbons (+C6), the thermodynamics and structural characteristics of hydrate in a multicomponent system have to consider the possibility of multiple hydrate structures. Moreover, the effect of the LMGS amount on the thermodynamic equilibrium of natural gas hydrates has not been completely understood yet. In the present study, we show that sH can coexist with sII under certain temperature and pressure conditions, and the decrease of LMGS amount has led to a change of structure ratio. Here, natural gas is defined as the hydrocarbon gas mixture of methane, ethane, propane, and iso-butane and higher hydrocarbons forming sH with methane is defined as LMGS.

Experiments

The apparatus and procedure for thermodynamic measurements has been described in detail in our previous works;^{10,11} hence, only the procedures are summarized here. About 30 g of HPLC grade water was introduced into a high pressure cell that was carefully evacuated in advance. Neohexane (NH, 2,2-dimethylbutane) was selected as a LMGS and added to the cell with a concentration variation from 1.7 to 14.5 wt % in water. The cell was then pressurized to desired pressures with synthetic natural gas that is composed of methane 89.86, ethane 6.40, propane 2.71, and iso-butane 1.03 mol %. It was then cooled slowly to 263.1 K at a rate of 0.1 K/h. Once the pressure reached a steady state while maintaining a temperature of 263.1 K, the temperature started to increase at a rate of 0.1 K/h. The equilibrium pressure and temperature of the four phases (hydrate (H)–water-rich liquid (L_w)–LMGS-rich liquid (L_{LMGS})–vapor (V)) were determined by tracing the P – T profile from hydrate formation to dissociation. The crossing point between the pressure inclination line by hydrate dissociation and the pressure increase line by thermal expansion was chosen as the equilibrium condition.

Hydrate samples for ^{13}C NMR experiments were prepared by a similar method for the thermodynamic measurements described above. After completing the formation of hydrate that could be evidenced by stabilization of system pressure, the temperature was maintained for at least 48 h. The hydrate samples were obtained from the high pressure cell and then transported to the ZrO_2 rotor that was inserted into the precooled NMR probe. The sample preparation and NMR analysis at each hydrate formation condition were repeated at least three times to confirm the analysis results. The procedures for NMR analysis were presented in our previous work.¹¹ For determining hydrate structure and guest distribution over hydrate cages, ^{13}C magic angle spinning (MAS) NMR spectra were recorded at 230.1 K by placing the hydrate samples in a 4.0 mm diameter ZrO_2 rotor that was loaded into the variable-temperature (VT) probe of a Bruker 400 MHz solid-state NMR spectrometer. All spectra were recorded at a Larmor frequency of 100.6 MHz under high-power proton decoupling (HPDEC) and at a spinning rate of 2–4 kHz. A pulse length of 4 μs and pulse repetition delay of 5–10 s were used with a radio frequency field strength of 50 kHz corresponding to a 90° pulse of 5 μs duration. The downfield carbon resonance peak of adamantane, assigned a chemical shift of 38.3 ppm at 300 K, was used as an external chemical shift reference.

Results and Discussion

Initial studies were carried out to measure the four-phase (H– L_w – L_{LMGS} –V) equilibria of natural gas and NH mixed hydrates at NH concentrations of 1.7, 7.8, and 14.5 wt % for

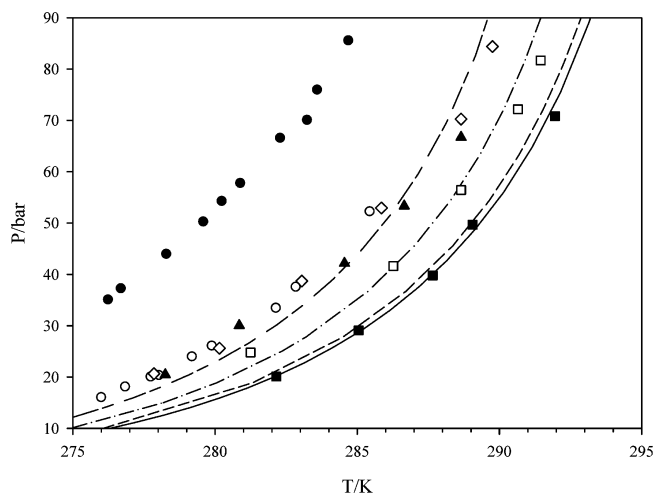


Figure 1. Hydrate equilibrium conditions of double hydrates in the presence of neohexane: ●, pure CH_4 hydrate; ○, CH_4 + neohexane hydrate; ◇, natural gas + neohexane (14.5 wt %) hydrate; ▲, natural gas + neohexane (7.8 wt %) hydrate; □, natural gas + neohexane (1.7 wt %) hydrate; ■, natural gas hydrate. The lines represent the prediction results of natural gas hydrate equilibrium in the presence of monoethylene glycol (MEG): —, 14.7 wt %; - · -, 7.8 wt %; ---, 1.7 wt %; —, 0 wt %.

water. The P – T diagram for the phase equilibrium is shown in Figure 1. Pure methane forms sI hydrate, while the methane and NH form sH hydrate. The presence of NH increased the equilibrium temperature at a corresponding pressure compared with the one for pure methane hydrate. However, natural gas, which is known to form sII with pure water, showed more stable equilibrium conditions than did the other hydrate structures mentioned above; here, large cages of sII would be filled with methane, ethane, propane, and iso-butane molecules.¹² The addition of NH to the natural gas and water system resulted in a decrease of equilibrium temperature at corresponding pressure, indicating the inhibition effect of NH on natural gas hydrate. The equilibrium conditions of the mixed hydrate of natural gas and NH at a concentration of 14.5 wt % NH were similar to those of the mixed hydrate of methane and NH, as seen in a temperature difference ($\Delta T = T_{\text{eq, NG}} - T_{\text{eq, NG+NH}}$) of 3.1 K at 70 bar. The decrease of NH concentration to 7.8 wt % did not show a large difference in equilibrium conditions when compared to those at 14.5 wt %. However, the temperature difference decreased to 1.3 K when the NH concentration decreased from 7.8 to 1.7 wt %, which means that a major change in the properties of mixed hydrate occurred at low NH concentrations.

Figure 1 also shows the equilibrium conditions of natural gas hydrate when monoethylene glycol (MEG) was added to the water phase, which is a well-known thermodynamic hydrate inhibitor in the oil and gas industry. CSMGEM has been used to predict hydrate equilibrium conditions at corresponding MEG concentrations. It is noted that the inhibition effect caused by adding 7.8 wt % MEG is similar to the one produced by adding 1.7 wt % NH, indicating that at low concentrations NH has a stronger inhibition effect than MEG. The inhibition effect with 14.5 wt % MEG is almost similar to the one with 7.8 wt % NH. However, it is also similar to the one with 14.5 wt % NH. This inhibition caused by LMGS has been studied since the discovery of sH.^{4,13} It was suggested that the hydrate equilibrium conditions of natural gas were not changed in the presence of 0.68 mol % of methylcyclopentane. However, the equilibrium conditions were inhibited significantly by further increasing the concentration of methylcyclopentane to 23.48 mol %.¹³ These results agree well with the current work, suggesting that the

increase of NH concentration to more than 7.8 wt % significantly inhibited the natural gas hydrate.

Although thermodynamic studies have examined the inhibition effect caused by LMGS, the effect of LMGS on the structural properties of natural gas hydrate have not been studied thoroughly.^{4,13} Thermodynamic prediction has been used to track the structures at different NH concentrations but still left some doubt as to what structures actually exist in the hydrate phase. In previous work,⁴ two different dissociation curves during the heating of mixed natural gas and methylcyclohexane hydrate were considered to be caused by the presence of two different hydrate structures of sII and sH. Similar dissociation trends have been observed in this study, which might indicate that an sH hydrate dissociates from a mixture of sII and sH in the first step and then the residual sII hydrate would dissociate in the second step. Accordingly, the effect of NH concentration on the structural characteristics of mixed hydrates of natural gas and NH must be analyzed.

Figure 2 shows ¹³C MAS NMR spectra of natural gas and NH mixed hydrates formed at 278.15 K and 70 bar. For a mixed hydrate in the presence of 14.5 wt % NH, as shown in Figure 2a, six carbon atoms of NH show four distinct resonances at 36.6 (^bC), 30.5 (^cC), 28.9 (^dC), and 9.0 (^aC) ppm for (^dCH₃)₃-^cC-^bCH₂-^aCH₃. The small peaks observed at slightly different chemical shifts of ^aCH₃ should represent liquid NH in hydrate samples as excess NH was used for its formation, although most of the NH molecules were occupying large cages of sH. Two resonances for propane were observed at 16.5 (—C—) and 17.3 (C—) ppm, while single resonance for ethane was observed at 5.9 ppm. This indicates that both hydrocarbon molecules occupy the large cages of sII. Single resonance of iso-butane was detected at 26.5 ppm as an indication that they had occupied large cages of sII as well.

Previous studies on hydrate structure analysis suggested that hydrate structure can be determined from a chemical shift of methane, as it is −8.2 ppm for methane in large cages of sII and −4.9 ppm for methane in medium cages of sH. Methane in small cages of both sII and sH shows almost the same chemical shift at around −4.3 ppm.^{14,15} In Figure 2a, resonances of methane in hydrate cages are shown at −4.3, −4.9, and −8.2 ppm, clearly indicating that two hydrate structures of sII and sH exist together. Figure 2b shows ¹³C NMR spectra of mixed hydrate formed in the presence of 7.8 wt % NH. The overall resonance lines are similar to those of Figure 2a as an indication of coexisting sII and sH.

The ratio of integrated intensities however gives different guest distributions over cages of hydrate structures. The cage occupancies of gaseous guests and LMGS over hydrate cages can be calculated from the ratio of integrated intensity of NMR signals with the statistical thermodynamic equation for the hydrate phase.^{14,16} The cage occupancies in cages of sII and sH are represented in Table 1. It is assumed that the large cages of sH must be completely filled with LMGS molecules to maintain hydrate stability from the single crystal X-ray analysis results.⁹ The ratio of integrated intensity for methane in small and medium cages of sH is assumed to be ~0.86, as it was obtained in our previous work.¹⁴ While the methane content in a small cage of sII is 0.91, its value of sH is limited to 0.76, as most of the medium cages were filled with methane instead. All gaseous hydrocarbons were sharing large cages of sII.

The molar ratios of the hydrocarbons occupying each hydrate structure are also shown in Table 1. When natural gas formed a mixed hydrate in the presence of 14.5 wt % NH, the molar ratio of hydrocarbons enclathrated in sH compared to sII was

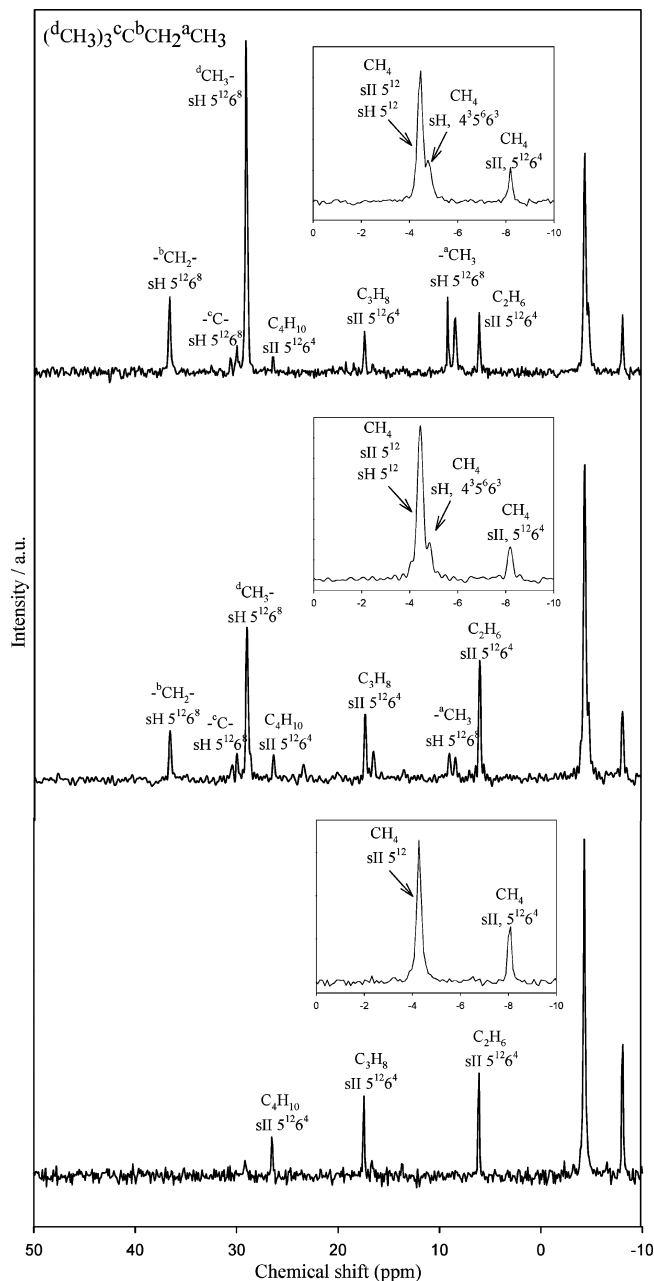


Figure 2. ¹³C MAS NMR spectra of double hydrates in the presence of neoheptane: (a) 14.5 wt %; (b) 7.8 wt %; (c) 1.7 wt %.

0.97, which indicates that 51% of the hydrocarbons in the hydrate phase were enclathrated in the cages of sII, and the remainder was in the cages of sH. When the addition of NH decreased to 7.8 wt %, the molar ratio of hydrocarbons for sH to sII became 0.43, indicating that 70% of the hydrocarbons in the hydrate phase were in the cages of sII and the remainder were in the cages of sH. In the case of 1.7 wt % NH, the obtained ¹³C NMR spectra indicated the presence of sII only and showed no evidence of sH. It was noted that the cages of sH were filled solely with methane and NH and no evidence indicated that higher hydrocarbons such as ethane and propane were captured into one of those cages of sH. The cage occupancy of the methane decreased in small cages of sII but increased in large cages of sII, as seen in Figure 2c. These results indicate that thermodynamic equilibria and structural properties should be considered together with the amount of LMGS in a liquid phase.

TABLE 1: Cage Occupancies of Hydrocarbon Components in Cages of Hydrate Structures

system	sH			sII				
	CH ₄		C ₆ H ₁₄	CH ₄		C ₂ H ₆	C ₃ H ₈	iso-C ₄ H ₁₀
	$\theta_{S,C1}$	$\theta_{M,C1}$	$\theta_{L,C6}$	$\theta_{S,C1}$	$\theta_{L,C1}$	$\theta_{L,C2}$	$\theta_{L,C3}$	$\theta_{L,C4}$
natural gas + neohexane (14.5 wt %)	0.76	0.93	0.99	0.91	0.45	0.22	0.12	0.03
natural gas + neohexane (7.8 wt %)	0.76	0.93	0.99	0.86	0.39	0.32	0.18	0.03
natural gas + neohexane (1.7 wt %)				0.84	0.57	0.21	0.12	0.06
				sH/sII = 0.97				
				sH/sII = 0.43				
				sH/sII = ~0.0				

As we discussed in Figures 1 and 2, the decrease of NH concentration from 14.5 to 7.8 wt % results in almost similar equilibrium conditions, although there was a change in the structure ratio of sII and sH. When it reached 1.7 wt %, NH molecules did not act as a hydrate former for sH and stayed in the liquid phase as an inhibitor that can be seen in the equilibrium study. We also note that, although sH would form and coexist with sII, sH hydrate accommodating methane and LMGS was dissociated first when heating the mixture of sII and sH, while sII was largely intact. As seen in thermodynamic study, sII natural gas hydrate has a higher hydrate dissociation temperature than sH hydrate. Accordingly, the mixture of sII and sH shows two different hydrate dissociation temperatures, as suggested by Tohidi et al.⁴

The mixed hydrate of natural gas and NH could be formed by either dynamic or static conditions inside pipelines transmitting multiphase flow of natural gas and condensate. Under static conditions, gas composition might be changed during the formation of mixed hydrates because of the depletion of propane and iso-butane in the gas phase that can be caused by preferential enclathration of those hydrocarbons in the hydrate phase.^{11,17} In order to study this possibility, mixed hydrate was formed without makeup gas and in the presence of 14.5 wt % NH. The ¹³C NMR spectrum obtained from this sample is shown in Figure 3. As shown as the highest peak of sH hydrate intensity, most of the hydrate phase seems to be structure H; however, there was evidence of structures I and II as well. It was expected that, during the formation of mixed hydrate, a large amount of methane would form sH with NH, and some amount of methane would form sII with other gaseous hydrocarbons. Once those higher hydrocarbons such as propane and iso-butane were depleted, it is likely that methane would form sI, since the temperature and pressure are enough to induce sI formation.

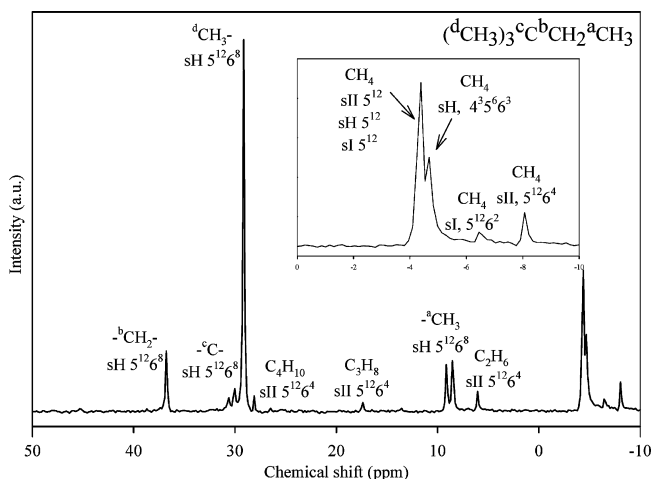


Figure 3. ¹³C MAS NMR spectra of coexisting structure I, II, and H hydrates due to depletion of propane and iso-butane during hydrate formation.

These results suggest that coexistence of hydrate structures might be common in proper temperature and pressure conditions of hydrocarbon fluids. The resulting characteristics on thermodynamics and structural properties must be considered in many industrial applications of gas hydrates. In the case of an offshore reservoir producing a sufficient amount of LMGS in the liquid condensate phase, it might be possible to reduce the injection amount of MEG as a measure of avoiding hydrate blockage because both MEG and LMGS would inhibit hydrate formation. In addition, the coexisting structures of sII and sH must be carefully considered in the hydrate blockage remediation process, as each structure might have different dissociation conditions.¹⁵ Strategies for storing and transporting natural gas through the formation of sH must consider the fact that higher gaseous hydrocarbons such as ethane and propane have to be occupied in other structures which might induce complexities in formation processes. Although more studies on kinetics and physical properties still need to be carried out, it is obvious that LMGS forming sH acts as an inhibitor for sII natural gas hydrate.

Conclusions

This study found that the formation of structure H from natural gas and NH can be affected by the added amount of NH in water, as it showed different hydrate equilibrium conditions depending on the NH concentration. When it was higher than 7.8 wt %, or about 60% of the stoichiometric amount of NH for complete filling of large cages of sH, the hydrate equilibrium temperatures of mixed natural gas and NH hydrate were lower than those of natural gas hydrate at corresponding pressures. However, when the NH concentration decreased from 7.8 to 1.7 wt %, only a small inhibition effect occurred. ¹³C NMR spectroscopic study suggests that, when mixed hydrate forms from natural gas and NH, two hydrate structures of II and H are formed and coexist simultaneously. The ratio of structure H to II was 0.97 at a NH concentration of 14.5 wt % but became 0.43 at 7.8 wt % NH. At an NH concentration of 1.7 wt %, ¹³C NMR analysis indicated that only structure II has been formed and NH seemingly did not participate in the formation of hydrate under the temperature and pressure conditions adopted in this study. When natural gas and NH form a mixed hydrate in a closed environment that may cause the depletion of propane and iso-butane, the formation of structure I has also been observed in addition to the formation of structures II and H, which should be induced by depletion of ethane and propane in the gas phase during the formation of structure II.

Acknowledgment. The authors would like to acknowledge funding from the Korea Ministry of Knowledge Economy (MKE) through “Energy Technology Innovative Program”. This work was also partially supported by Korea National Oil Corporation Grant (Basic Study on Flow Assurance, 2009).

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JP910941D