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Hydrate Equilibrium Data of the $CH_4 + C_3H_8$ Gas Mixture and Simulated Natural Gas in the Presence of 2,2-Dimethylbutane and Methylcyclohexane

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ABSTRACT: The pressure and temperature conditions for four phases of hydrate, water-rich liquid, hydrocarbon-rich liquid, and vapor were measured for the $CH_4 + C_3H_8$ + methylcyclohexane + water, $CH_4 + C_3H_8$ + 2,2-dimethylbutane + water, and simulated natural gas + methylcyclohexane + water systems in the temperature range of (275 to 290) K and in the pressure range of (1.0 to 8.0) MPa. The inhibition effect on the equilibrium conditions of $CH_4 + C_3H_8$ hydrate and simulated natural gas hydrate was observed by adding methylcyclohexane and 2,2-dimethylbutane in the studied temperature and pressure range. The concentration of methylcyclohexane and 2,2-dimethylbutane was varied in the range of $x = (0.003 \text{ to } 0.034)$ to investigate the effect of the amount of structure H-forming hydrocarbon in the hydrate equilibrium conditions.

INTRODUCTION

Gas hydrates are nonstoichiometric crystalline compounds formed when guest molecules of suitable size and shape are incorporated in host cages formed by water molecules through hydrogen bonding.[1] Among three different structures of gas hydrates termed structure I, II, and H, structure H hydrate is composed of three small (5^{12}) cages, two medium ($4^35^66^3$) cages, and one large ($5^{12}6^8$) cages and can accommodate relatively large guest molecules such as methylcycloehexane in its large cages when the small and medium cages must be occupied with small guest molecules like methane for stability.[2] The main components of natural gas, methane, ethane, and propane have their own hydrate structures as methane and ethane are known to form structure I hydrates composed of two small (5^{12}) and six large ($5^{12}6^2$) cages, while propane forms structure II hydrates composed of 16 small (5^{12}) and 8 large ($5^{12}6^4$) cages. Because of the presence of propane in the production of almost every gas fields, it is generally accepted that natural gas forms structure II hydrates. Gas hydrates have been a particular concern of the oil and gas industry after their discovery in gas pipelines in the 1930s.[3] The operating conditions of oil and gas production pipelines may be favorable to the formation of gas hydrates that result in a blockage in pipelines. Moreover, the existence of massive gas hydrate deposits under the permafrost and in the sediment of the continental margins led to research on the development technologies of hydrates as a source of natural gas.[1,4,5] The ability to store gas in the most efficient manner also represents the unique application of gas hydrates.[6]

Since the discovery of structure H in 1987, extensive efforts have been carried out to classify hydrocarbons that can be accommodated into large cages of structure H, which are called LMGS (large molecule guest substance).[3,7] A large number of studies have been carried out as well to identify phase equilibrium conditions in the presence of LMGS; however, in most of these works, pure methane or nitrogen gas was used to form structure H hydrates with the addition of excess amounts of LMGS rather than the stoichiometric composition for water.[8,9] There are limited hydrate equilibrium data for the $CH_4 + C_3H_8$ gas mixture in the presence of LMGS although LMGS possibly occurs in the liquid condensate phase when producing natural gas.[10,11] Tohidi et al. conducted an integrated experimental and modeling investigation to measure hydrate equilibrium data for natural

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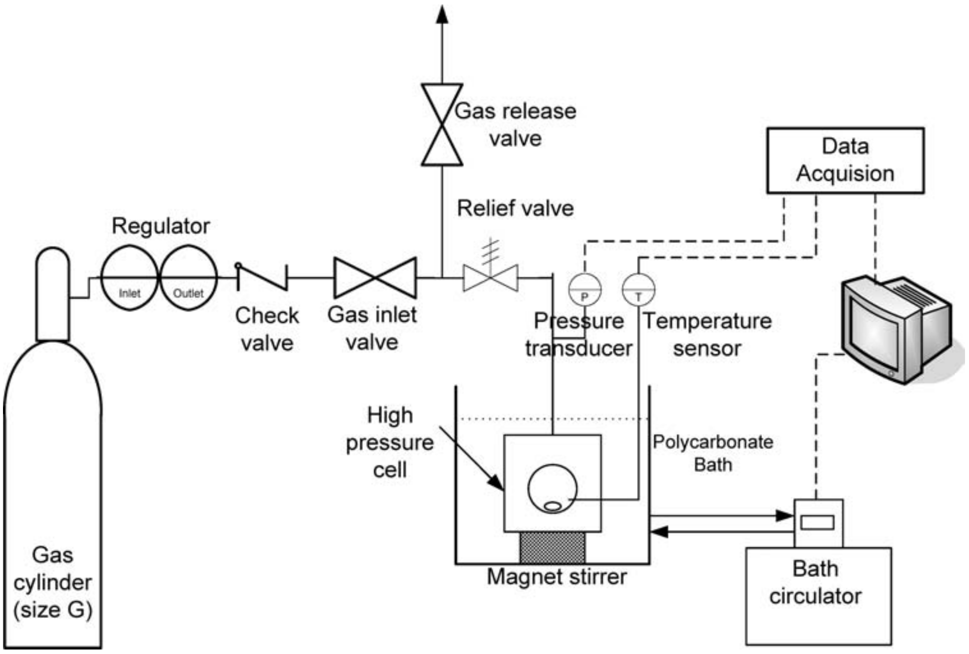

Figure 1. Schematic illustration of the apparatus for the measurement of the hydrate equilibrium conditions.

gas in the presence of methylcyclohexane, methylcylopentane, and isopentane.[10] The results showed that structure II is the stable hydrate structure for all of the systems investigated, while structure H might coexist with structure II in some reservoir fluids. Recently the effect of LMGS amount on the thermodynamics of natural gas hydrate as well as structural characteristics has been studied.[12] The increase of inhibition effect with increased addition of 2,2-dimethylbutane was observed, and ^{13}C NMR spectroscopic analysis suggested that two hydrate structures of II and H coexist simultaneously where the ratio of structure H to II decreased when decreasing the concentration of 2,2-dimethylbutane. These results have led to the proposition that phase equilibrium studies of structure H have to be carried out initially with the $CH_4 + C_3H_8$ gas mixture, which is composed of main components of natural gas.

This work presents hydrate equilibrium data for the $CH_4 + C_3H_8$ gas mixture in the presence of methylcycloehexane and 2,2-dimethylbutane. The effects of the LMGS amount on the hydrate equilibrium data for the $CH_4 + C_2H_6 + C_3H_8 + i\text{-}C_4H_{10}$ gas mixture that simulates natural gas are measured in the presence of methylcyclohexane as well.

■ EXPERIMENTAL SECTION

Materials. Deionized water was supplied by Sigma-Aldrich Chemicals Co. with a purity of 0.9999 mole fraction. 2,2-Dimethylbutane with a mole fraction purity of 0.9997 and methylcyclohexane with a mole fraction purity of 0.9997 were purchased from Sigma-Aldrich Chemicals Co. The gas mixture of CH_4 and C_3H_8 was supplied by World Gas Co., and the stated composition of the gas mixture was CH_4 (0.96) + C_3H_8 (0.04) by mole fraction basis. The simulated natural gas for the present study was supplied by World Gas Co. as well with the stated composition of CH_4 (0.96) + C_2H_6 (0.06) + C_3H_8 (0.03) + $i\text{-}C_4H_{10}$ (0.01) by a mole fraction basis. All materials were used without further purification.

Apparatus. The apparatus for hydrate equilibrium measurement is designed to monitor the change of pressure and temperature during the formation and dissociation of hydrates. A schematic diagram of the experimental apparatus is shown in Figure 1. The high pressure cell made of 316 stainless steel was equipped with two thermally reinforced sight glasses for visual observation. It had the internal volume of 300 cm^3 and a working pressure of 10 MPa. The fluids inside the cell were agitated by a magnetic spin bar that was coupled with an immersion magnet placed under the cell, which was immersed in the water bath containing 15 L of ethylene glycol and water mixture. The temperature of the bath was controlled by an externally circulating refrigerator/heater (Jeio Tech MC-31) with an accuracy of ± 0.1 K. A K-type thermocouple probe with a digital thermometer (Cole-Parmer, 8535-26) was inserted into the cell to measure the temperature of the fluids within an uncertainty of ± 0.05 K. The pressure of the system was measured by a pressure transducer with an uncertainty of ± 0.01 MPa in the pressure range of (0 to 10.0) MPa.

To determine the structural characteristics of the hydrate sample, ^{13}C MAS NMR spectra were recorded at 243 K by placing the sample in a 4.0 mm diameter ZrO_2 rotor that was loaded into the variable temperature (VT) probe of a Bruker 400 solid-state NMR spectrometer. All spectra were recorded at a Larmor frequency of 100.6 MHz under high power proton decoupling (HPDEC) at a spinning rate of (2 to 4) kHz. A pulse length of 2 μs and a pulse repetition delay of (10 to 20) s were used with a radio field strength of 50 kHz corresponding to a 90° pulse of 5 μs duration. The downfield carbon resonance peak of adamantine, assigned a chemical shift of 38.3 ppm at 300 K, was used as an external chemical shift reference.

Procedure. The hydrate equilibrium data were measured with the batch and isochoric procedures. The measurement was initiated by charging the cell with 100 cm^3 of liquid mixture containing the desired composition of 2,2-dimethylbutane or methylcyclohexane. The cell containing the fluids was then immersed

Table 1. Hydrate Equilibrium Conditions of the $CH_4 + C_3H_8$ + Methylcyclohexane + Water System at Four Different Mole Fractions x of Methylcyclohexane

x	T/K	P/MPa
0.000	281.45	1.96
	284.45	2.92
	287.15	3.95
	289.15	5.26
0.003	281.55	2.09
	284.15	2.98
	287.15	4.24
	288.35	5.12
0.017	279.75	1.94
	282.15	2.87
	285.45	4.27
	286.55	5.03
0.034	277.45	1.96
	279.25	2.72
	281.55	3.57
	283.25	4.60

into the water bath, and the temperature was controlled to be 293.1 K. The gas mixture was supplied from a high pressure cylinder into the cell until the pressure reached to a target value between (1.0 and 7.0) MPa. After the temperature and pressure of the cell were stabilized, the valve connecting the cell and the high pressure cylinder was closed for the isochoric experiment, and the cell was cooled to 273.1 K while stirring the fluids with a stirring rate of 400 rpm. Hydrate formation was then induced in the liquid phase when the temperature was cooled below the expected equilibrium temperature, which resulted in the decrease of pressure. The temperature of the bath was kept constant at 273.1 K for at least 5 h to confirm the pressure reached a steady state. Subsequently the bath temperature was gradually elevated at a rate of 0.1 $K \cdot h^{-1}$, which caused the dissociation of the hydrate phase and a resulting pressure increase. The four phases of hydrate, water-rich liquid, LMGS-rich liquid, and vapor coexist at hydrate equilibrium conditions, which was determined by a visual observation method supplemented by a pressure−temperature ($P-T$) plot. When a minute amount of crystals remained from the visual observation on the hydrate phase, the temperature was increased incrementally in steps of 0.1 K with the duration of 6 h to achieve an equilibrium state in the cell. The pressure−temperature ($P-T$) plot for each measurement was obtained and used to determine a four-phase equilibrium condition. While increasing the temperature at a rate of 0.1 $K \cdot h^{-1}$, a substantial increase of the pressure was observed in the $P-T$ plot due to the dissociation of the hydrate phase. However, once the minute amount of crystals dissociated and the temperature was above hydrate equilibrium temperature, a slight increase of the pressure was observed due to the thermal expansion of the gas phase only. Therefore, the intersection point between the hydrate dissociation line and the thermal expansion line from the $P-T$ plot was considered as the four-phase equilibrium condition.

The hydrate sample was prepared with the same apparatus and procedures as those used for hydrate equilibrium measurements. After completing the formation of hydrate that could be evidenced by the stabilization of system pressure, the temperature was maintained for at least 48 h. Then the hydrate phase was sampled at liquid nitrogen temperature for the ^{13}C NMR experiment.

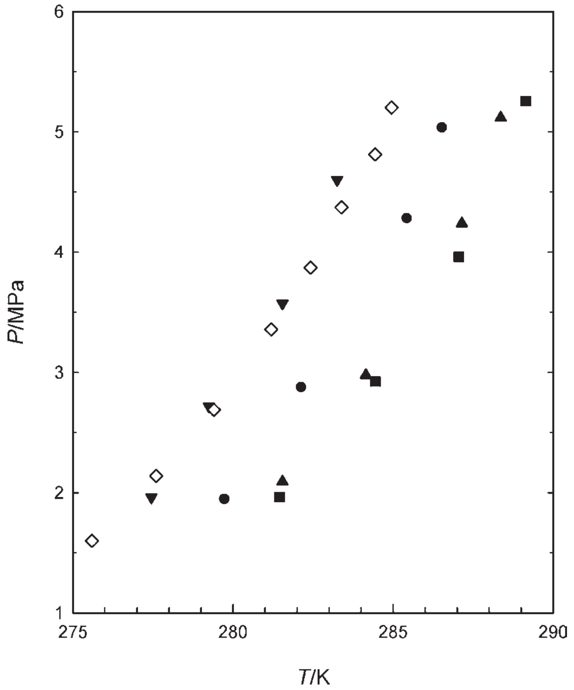

Figure 2. Hydrate equilibrium conditions for ♦, CH_4 + methylcyclohexane + water; ▼, $CH_4 + C_3H_8$ + 0.034 mole fraction methylcyclohexane + water; ●, $CH_4 + C_3H_8$ + 0.017 mole fraction methylcyclohexane + water; ▲, $CH_4 + C_3H_8$ + 0.003 mole fraction methylcyclohexane + water; and ■, $CH_4 + C_3H_8$ + water systems.

■ RESULTS AND DISCUSSION

Four phase equilibrium conditions of hydrate, water-rich liquid, methylcyclohexane-rich liquid, and vapor were measured at mole fractions of 0.003, 0.017, and 0.034 for water. From the stoichiometry of structure H hydrate, $3\,5^{12} \cdot 2\,4^3 5^6 6^3 \cdot 1\,5^{12} 6^8 \cdot 34H_2O$, it requires the addition of methycyclohexane at least more than 0.029 mole fraction for water to satisfy the premise of the complete occupation of the large cages of structure H. A large number of studies to identify phase equilibrium conditions in the presence of LMGS have been carried out with the excess amounts of LMGS rather than 0.029 mole fraction for water. In this work, hydrate equilibrium conditions were measured while decreasing the concentration of methylcyclohexane to 0.003 mole fraction, which is much less than the required amount of methylcyclohexane for occupying large cages of structure H.

The pressure and temperature of the four-phase equilibrium for the $CH_4 + C_3H_8$ + methycyclohexane + water system are given in Table 1 and are plotted in Figure 2 together with the hydrate equilibrium data of the CH_4 + methylcyclohexane + water system.[13,14] The $CH_4 + C_3H_8$ gas mixture without methylcyclohexane, which is known to form structure II, showed the highest hydrate equilibrium temperature than the gas mixture in the presence of methylcyclohexane. The addition of methylcyclohexane to the water phase resulted in the shift of hydrate equilibrium conditions to lower temperature and higher pressure region indicating the inhibition effect of methylcyclohexane on

Table 2. Hydrate Equilibrium Conditions of the $CH_4 + C_3H_8$ + 2,2-Dimethylbutane + Water System at Four Different Mole Fractions x of 2,2-Dimethylbutane

x	T/K	P/MPa
0.000	281.45	1.96
	284.45	2.92
	287.15	3.95
	289.15	5.26
0.003	285.15	2.24
	288.05	3.41
	290.25	5.12
0.017	281.05	2.13
	283.35	2.87
	286.65	4.11
	287.75	4.86
0.034	278.05	2.12
	280.15	2.68
	283.95	3.98
	285.05	4.66

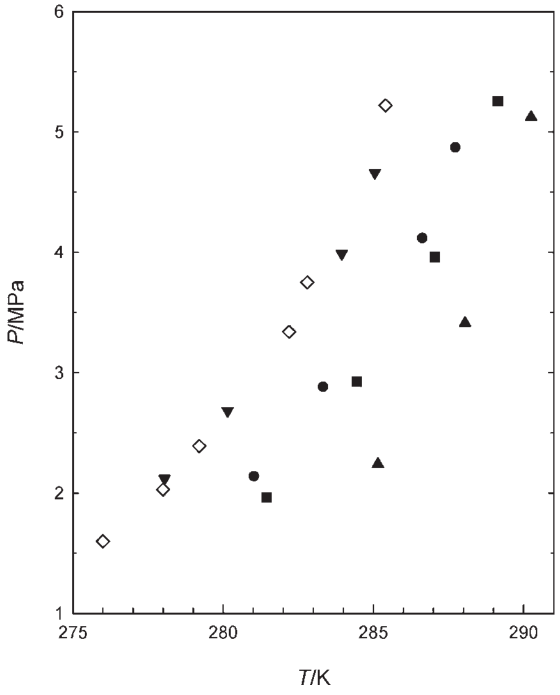

Figure 3. Hydrate equilibrium conditions for ♦, CH_4 + 2,2-dimethylbutane + water; ▼, $CH_4 + C_3H_8$ + 0.034 mole fraction 2,2-dimethylbutane + water; ●, $CH_4 + C_3H_8$ + 0.017 mole fraction 2,2-dimethylbutane + water; ▲, $CH_4 + C_3H_8$ + 0.003 mole fraction 2,2-dimethylbutane + water; and ■, $CH_4 + C_3H_8$ + water systems.

the mixed $CH_4 + C_3H_8$ hydrate. While the hydrate equilibrium temperature at the concentration of 0.003 mole fraction is similar to those without methylcyclohexane, the increase of methylcyclohexane concentration to 0.017 mole fraction induces a major change in the equilibrium conditions as a hydrate equilibrium temperature difference between pure water and 0.017 mole fraction methylcyclohexane added water is about 2.2 K at the investigated pressure range. The temperature difference increases to 4.2 K when increasing the methylcyclohexane mole fraction to 0.034. It is noted that the hydrate equilibrium conditions at 0.034 mole fraction of methylcyclohexane shows similar equilibrium conditions of the CH_4 + methylcyclohexane + water system found in literature where an excess amount of methylcyclohexane was used to form the hydrate.

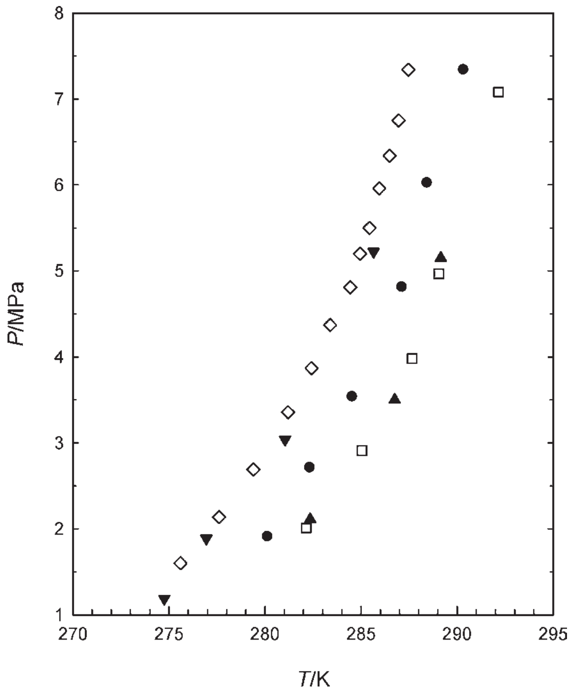

Figure 4. Hydrate equilibrium conditions for ♦, CH_4 + methylcyclohexane + water; ▼, simulated natural gas + 0.034 mole fraction methylcyclohexane + water; ●, simulated natural gas + 0.017 mole fraction methylcyclohexane + water; ▲, simulated natural gas + 0.003 mole fraction methylcyclohexane + water; and ■, simulated natural gas + water systems.

The hydrate equilibrium data for $CH_4 + C_3H_8$ + 2,2-dimethylbutane + water system are given in Table 2 and shown in Figure 3 along with the hydrate equilibrium data of the CH_4 + 2,2-dimethylbutane + water system.[15−17] The hydrate equilibrium conditions of the $CH_4 + C_3H_8$ gas mixture in the presence of the 2,2-dimethylbutane with a concentration of 0.034 mole fraction shows almost similar to those of the CH_4 + 2,2-dimethylbutane + water system. This phase behavior was observed as well in the presence of methylcyclohexane as discussed in Figure 1. The temperature difference between these two equilibrium curves was about 3.7 K at the investigated pressure range. The decrease of 2,2-dimethylbutane concentration resulted in the increase of hydrate equilibrium temperature at corresponding pressure. At 0.003 mole fraction of 2,2-dimethylbutane, the hydrate equilibrium temperature is higher than those of the $CH_4 + C_3H_8$ + water system, which suggests that the hydrate equilibrium conditions were promoted rather than inhibited at 0.003 mole fraction of 2,2-dimethylbutane. Further investigations using the spectroscopic method are ongoing to understand the phase behavior and structural properties of hydrate formed at this concentration.

Figure 4 presents the hydrate equilibrium conditions for the simulated natural gas in the presence of methylcyclohexane. The concentration of methylcyclohexane was increased from 0.003 to 0.034 mole fraction. The temperature and pressure of hydrate

Table 3. Hydrate Equilibrium Conditions of the Simulated Natural Gas + Methylcyclohexane + Water System at Four Different Mole Fractions x of Methylcyclohexane

x	T/K	P/MPa
0.000	282.15	2.01
	285.05	2.91
	287.65	3.98
	289.05	4.97
	292.15	7.08
0.003	282.35	2.11
	286.75	3.50
	289.15	5.15
0.017	280.15	1.90
	282.35	2.71
	284.55	3.53
	287.15	4.80
	288.45	6.02
	290.35	7.34
0.034	274.75	1.19
	276.95	1.89
	281.05	3.04
	285.65	5.22

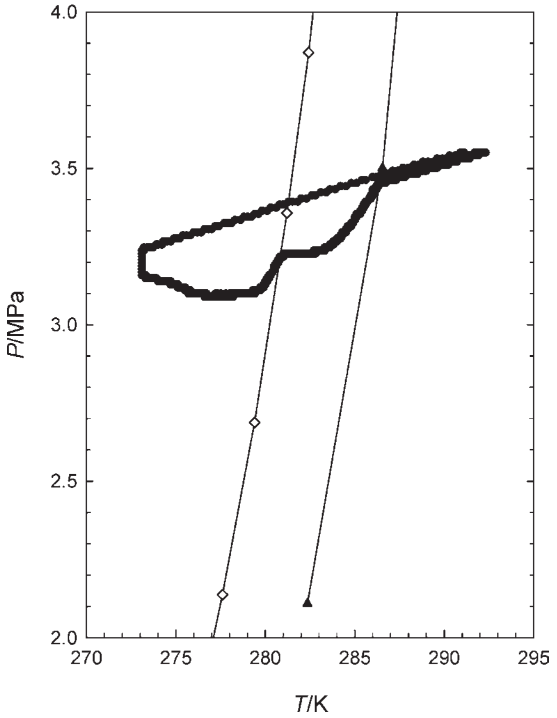

Figure 5. Pressure−temperature trace during the formation and dissociation of simulated natural gas + methylcyclohexane hydrate at the methylcyclohexane concentration of 0.003 mole fraction. It is shown together with hydrate equilibrium conditions for ♦, CH_4 + methylcyclohexane + water and ▲, simulated natural gas + 0.003 mole fraction methylcyclohexane + water systems.

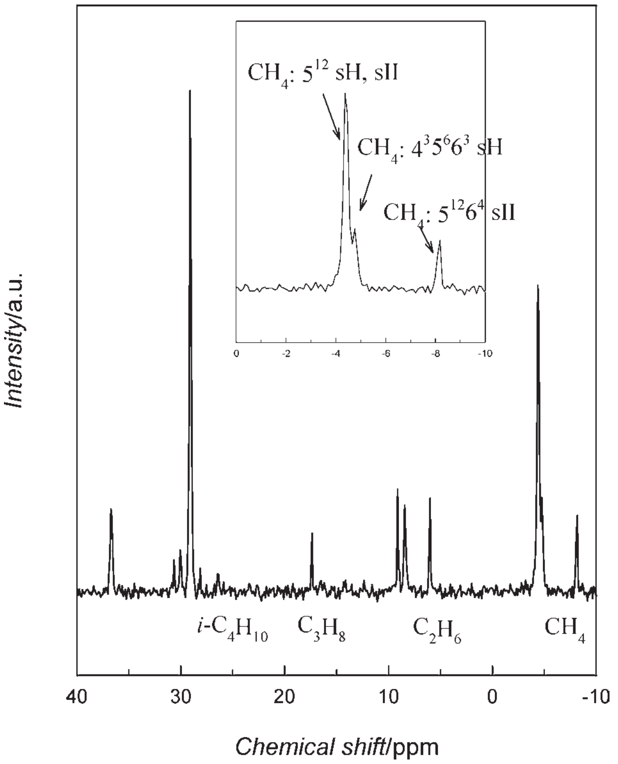

Figure 6. ^{13}C NMR spectrum of double hydrates formed from the simulated natural gas + 0.034 mole fraction 2,2-dimethylbutane + water system. Inset: NMR resonances in chemical shift range of (0 to −10) ppm.

equilibrium conditions at corresponding methylcyclohexane concentrations are given in Table 3. As seen in Figure 3, the phase behavior resulted from adding methylcyclohexane is similar to that seen in Figure 1. The addition of 0.003 mole fraction of methylcyclohexane did not change the hydrate equilibrium conditions of simulated natural gas; however, the inhibition effect was observed at the methylcyclohexane of 0.017 mole fraction, where the temperature difference was about 2.2 K at the investigated pressure range. When adding 0.03 mole fraction of methylcyclohexane, the hydrate equilibrium conditions become similar to those of the CH_4 + methylcyclohexane + water system, and the temperature difference reached about 4.0 K.

When the double hydrate formed with simulated natural gas and methylcyclohexane, it is expected that two hydrate structures of II and H would be formed based on our previous work to study the inhibition effect caused by LMGS on the hydrate equilibrium conditions of simulated natural gas using NMR spectroscopy.[12] In an attempt to measure the hydrate equilibrium conditions, when heating the hydrate phase, structure H accommodating CH_4 and 2,2-dimethylbutane was dissociated first; however, structure II accommodating CH_4, C_2H_6, and C_3H_8 was largely intact. Accordingly the mixture of structure II and H showed two different hydrate dissociation temperatures, as seen in Figure 5, where the first dissociation condition coincided with the hydrate equilibrium curve of the CH_4 + methylcyclohexane + water system and the second dissociation condition showed the hydrate equilibrium curve of the simulated natural gas + methylcyclohexane + water system at the concentration of methylcyclohexane of 0.003 mole fraction. The dissociation curves indicated that, when there are multiple guest molecules, multiple hydrate structures could be formed and coexisted depending on the cage preferences of the guest molecules.

This structural characteristic could be observed from the ^{13}C NMR spectra of simulated natural gas and 2,2-dimethylbutane hydrate formed at 278.1 K and 50 bar, as seen in Figure 6. When forming natural gas hydrate in the presence of 0.034 mole fraction of 2,2-dimethylbutane, six atoms of 2,2-dimethylbutane can be seen in the ^{13}C NMR spectra as four distinct resonances at 36.6 (^{b}C), 30.5 (^{c}C), 28.9 (^{d}C), and 9.0 (^{a}C) ppm for $(^dCH_3)_3$-^cC-$^bCH_2$-$^aCH_3$. Two resonances for propane were observed at 16.5 (−C−) ppm and 17.3 (C−) ppm, while single resonance for ethane and isobutane was observed at (5.9 and 26.5) ppm, respectively. This indicates that gaseous guest molecules of ethane, propane, and isobutane occupy the large cages of structure II, and liquid hydrocarbon guest molecules, 2,2-dimethylbutane, occupy the large cages of structure H. Resonances of methane clearly show the existence of both structure II and H hydrates. In Figure 5, methane in small cages of structure II and H shows almost the same chemical shift at around −4.3 ppm; however, it is −4.9 ppm for methane in medium cages of structure H and −8.2 ppm for methane in large cages of structure II.

The hydrate equilibrium data and spectroscopic analysis have to be carried out together with the exact composition of guest hydrocarbons to understand the thermodynamic phase behavior and structural characteristics of the existing hydrate phase. However, in this work, as the hydrate equilibrium data offers the limit condition for gas hydrate crystals to stably exist, the second dissociation condition was considered as the hydrate equilibrium condition for the investigated systems.

CONCLUSIONS

This work presents the four-phase hydrate equilibrium condition for $CH_4 + C_3H_8$ + methylcyclohexane + water, $CH_4 + C_3H_8$ + 2,2-dimethylbutane + water, and simulated natural gas + methylcyclohexane + water systems. The addition of LMGS results in the shift of hydrate equilibrium conditions to the lower temperature and higher pressure region. This inhibition effect increases for both methylcyclohexane and 2,2-dimethylbutane when increasing the concentration of those hydrocarbons. The highest inhibition effect is shown when the methylcyclohexane concentration is 0.034 mole fraction where the equilibrium temperature difference reaches 4.2 K. For 2,2-dimethylbutane, the inhibition effect of 3.7 K is observed when adding 0.034 mole fraction, which is slightly lower than methylcyclohexane. It is noted that the highest inhibition effect was obtained when adding excess amounts of LMGS than the amount to fully occupy the large cages of structure H hydrate. Although the coexistence of structure H and II is expected from stepwise dissociation behavior of hydrate phase and ^{13}C NMR spectroscopy result, the final dissociation conditions were considered as the hydrate equilibrium conditions for the investigated systems.

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