

IN SITU NMR MEASUREMENT OF CH₄ + C₂H₆ HYDRATE REFORMATION

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ABSTRACT

The reformation of methane-ethane hydrate was observed in situ using ¹³C MAS NMR spectroscopy. In all reformation experiments, structure I (stable state for the reformation conditions) reformed, and the hydrate cage occupancy ratios were found to be almost the same as those predicted by a statistical thermodynamics program CSMGem, suggesting that there is no preferential formation of large or small cages on the relatively long time scale of this NMR experiment. It was also found that the reformation rate of the sample with PVCap is several times faster compared with the pure system, indicating that the presence of PVCap promotes the hydrate reformation at a high subcooling though this chemical is well-known as a good hydrate inhibitor.

Keywords: natural gases, gas hydrates, kinetic inhibitors

INTRODUCTION

Understanding the kinetics of gas hydrate formation or dissociation is a key issue for inhibiting hydrate formation in subsea gas and oil flow lines, and for the efficient natural gas recovery from hydrate deposits. However, little is still known about the time-dependent phenomena compared with time-independent hydrate quantification, such as thermodynamic properties of gas hydrate [1]. There are only a limited number of studies on hydrate kinetics especially at the molecular level [2].

Previous studies showed that the cage filling of gas hydrate, which is the main factor for determining the stability of hydrate, during formation or dissociation is significantly different from that in an equilibrium state. Subramanian and Sloan [3] performed real-time Raman observations on methane hydrate formation from liquid water and found that the large cavity to small cavity ratio was initially about 0.5 and then gradually increased to its equilibrium value of approximately

3 after several hours. It was also found that poly-N-vinylcaprolactam (PVCap), a water-soluble polymer known as an active kinetic hydrate inhibitor [4], can retard the increment of the occupancy ratio. Similarly, hyper-polarized ¹²⁹Xe NMR measurements of xenon hydrate formation [5] showed that significantly lower values of the cage occupancy were observed at the very onset of the reaction (a few minutes after nucleation). These previous studies indicated that small hydrate cavities form first at the early stages of hydrate formation, although the cause of this phenomenon was not clear. Recently, Dec et al. [6] reported that a change in cage filling occurs during dissociation of methane-ethane binary hydrate. They found that large cavities with ethane dissociated faster than small cavities with methane, probably due to preferential dissociation of a portion of hydrate where a fewer number of small cages are occupied by methane while large cavities are almost fully filled with ethane everywhere.

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In this study, we report results of in situ NMR observations of reformation of methane-ethane hydrate. The cage filling of reformed hydrate is measured. Also, the effect of PVCap on the hydrate reformation and cage occupancy were studied. Research on the methane-ethane binary system is important because these two components are the main constituents of natural gases, this system is also interesting due to its characteristic ability to form two different hydrate structures, structure I and II, depending on the gas composition [7-9].

EXPERIMENTAL METHODS

Hydrate samples

Hydrate samples in sealed glass ampoules with approximately 0.2 cm³ capacity were prepared. Hydrate crystals were synthesized from about 50 mg of ice powder made from deionized water without or with 0.4 wt.% PVCap (PVCap was supplied as a 40% solution in ethylene glycol, BASF) and the carbon-enriched methane-ethane gas mixture (99% ¹³CH₃ and 99% ¹³CH₃CH₃, Cambridge Isotope Laboratory) of 85% C1 at the ice melting point and 2.4 MPa. The details of the sample preparation have been described elsewhere [10]. After sealing hydrates in the ampoules, the samples were stored in a freezer at -15 °C.

NMR measurements

¹³C MAS NMR spectra of the hydrates were recorded using a Chemagnetics Infinity 400 NMR spectrometer operating at 100.6 MHz for ¹³C. Proton decoupling fields and MAS speeds used for this study were 50 kHz and about 2 kHz, respectively. Standard single-pulse excitation and pulse delays of 120 seconds were used for data acquisition. Observed ¹³C NMR peak positions were calibrated with an external index adamantane (38.83 ppm). The processes of hydrate reformation were monitored every eight minutes for about 15 hours.

Hydrate reformation

The spectrometer is equipped with a Chemagnetics solid-state temperature controller. A temperature of the glass ampoule set in a sample chamber was controlled by changing a flow rate of cold air. Methanol ¹H resonance lines were used for temperature calibration. The hydrate sample was loaded to the sample chamber at -20 °C. The system temperature was increased to 16 °C and then was held at this temperature for about 1 hour to ensure that a portion of hydrate melts until a gas pressure attains the dissociation pressure. The

hydrate reformation was initiated by cooling to 1 °C. The sample temperature was maintained at this constant temperature during the reformation experiment.

RESULTS AND DISCUSSION

Original hydrate sample structure

Figure 1 shows ¹³C NMR spectra of the hydrate samples measured at -20 °C before heating for the reformation experiment. NMR peak assignments based on a previous work [8,9] are shown in Figure 1. Although hydrates were synthesized under the pressure and temperature conditions at which structure II hydrate is considered to be thermodynamically stable, hydrate structures observed were mostly sI. The pure system contained mostly sI crystals with small amount of sII hydrate (Figure 1a). On the other hand, the sample with PVCap had only sI crystals (Figure 1b). Although, it is known that sI and sII mixtures usually form at gas compositions close to the transition point of approximately 75% C1 as a metastable state [9,11,12], the cause of the formation of almost pure sI crystals is not clear. The sII crystals in the pure sample completely dissociated in the course of the temperature increase to 16 °C.

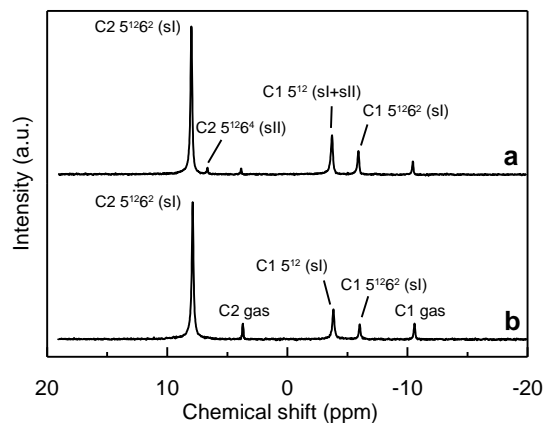


Figure 1: ¹³C MAS NMR spectra of methane-ethane hydrates formed from ice powder and a gas mixture of 85% methane in ethane measured at -20 °C. (a) Pure system. (b) System with 0.4 wt.% PVCap. The peak assignments are based on Subramanian et al. [8,9].

NMR observation on methane-ethane hydrate reformation

Figure 2 shows a typical series of time-resolved ¹³C NMR spectra for methane-ethane hydrate reformation. In all experiments, the crystal

reformation began from pure structure I hydrate. Hydrate crystals reformed during the experiments were all sI.

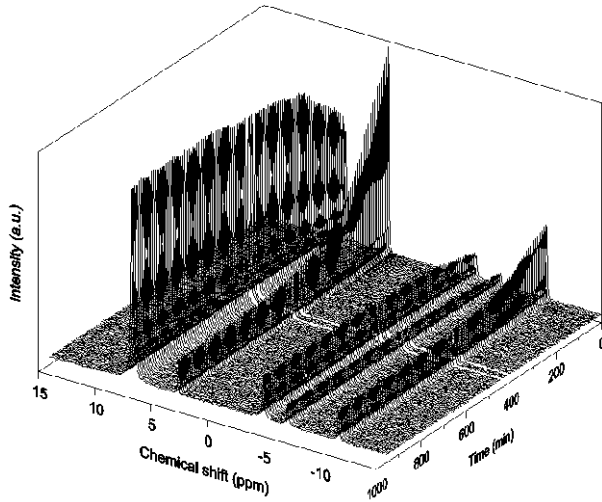


Figure 2: Time-resolved ^{13}C MAS NMR spectra of methane-ethane hydrate with 0.4 wt.% PVCap measured during hydrate reformation at 1 °C.

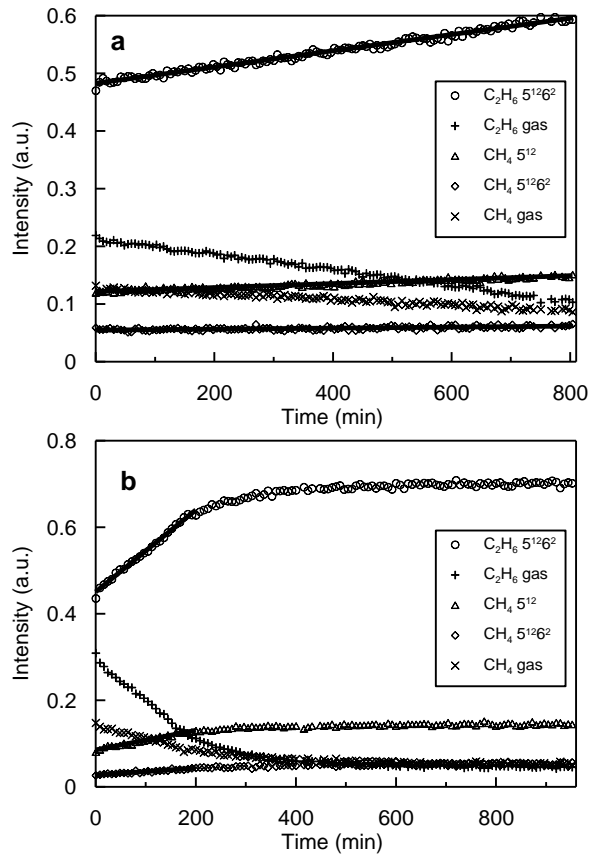


Figure 3: ^{13}C NMR intensities of methane-ethane hydrate vs. time during hydrate reformation at 1 °C. (a) Pure system. (b) System with 0.4 wt.% PVCap. Lines represent the results of linear regression analysis of hydrate data.

Figure 3 shows gas and hydrate NMR intensities versus time. The NMR intensity of each component was divided by the total intensity for normalization. With the elapse of time, signals from hydrates increased, while those from gas phases decreased because of crystal reformation. The increment rates of hydrate intensities for the pure sample (Figure 3a) were considerably slower compared with those for the sample with PVCap (Figure 3b), indicating slower crystal reformation in the pure system. This subject will be discussed later.

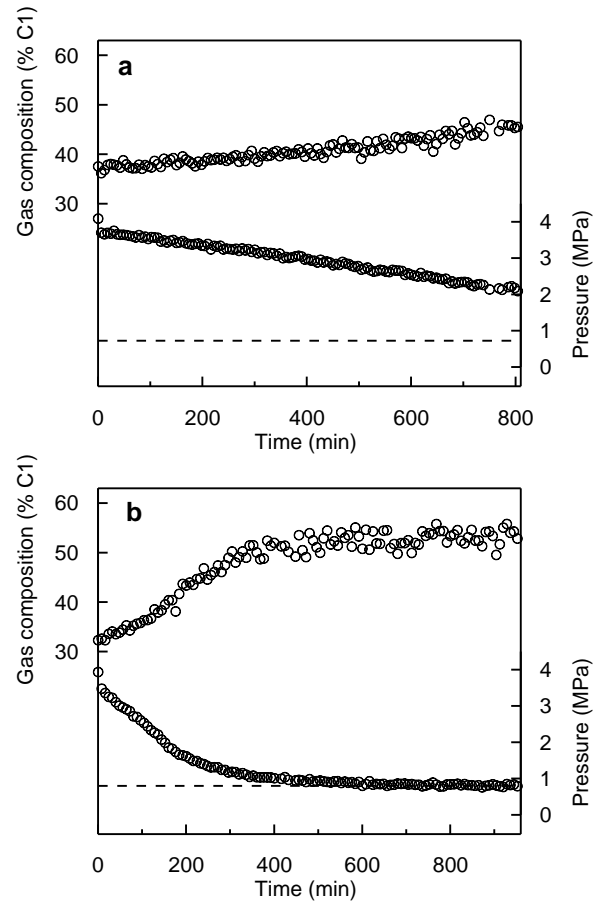


Figure 4: Gas composition and pressure as a function of time estimated from the NMR intensities. (a) Pure system. (b) System with 0.4 wt.% PVCap. Broken lines represent hydrate dissociation pressures at 1 °C and final gas compositions predicted by the statistical thermodynamics program CSMGem [13].

Gas pressure and composition during hydrate reformation

Figure 4 shows the gas composition and pressure in the samples as a function of time. Gas

compositions were estimated from methane gas intensities relative to the total gas intensities. In both the systems, methane gas concentrations increased with the elapse of time. This is because ethane gas is preferentially enclathrated in hydrate due to its higher affinity (larger Langmuir constant) to water cages [7]. These observations are consistent with previous experimental results [11].

Gas pressures were estimated from the total gas intensities assuming that a gas pressure is in direct proportion to the gas intensity. For this estimation, the initial gas pressure was assumed to be the hydrate dissociation pressure at 16 °C and an initial gas composition ($t = 0$) calculated using the CSMGem program [13]. Also, the pressure decrease due to the temperature drop to 1 °C (approximately 5%) was taken into account for the estimations at $t > 0$. Dissociation pressures at the end of the experiments were calculated from the temperature of 1 °C and the final gas compositions using CSMGem [13], and are shown as dashed lines in the figures.

In the pure system, the gas pressure decreased almost linearly at a rate of 2.1×10^{-3} MPa/min throughout the observation (Figure 4a). The final gas pressure of 2.1 MPa was about 1.4 MPa higher than the predicted dissociation pressure, indicating that hydrate reformation did not finish during the experiment. On the other hand, for the sample with PVCap, the rate of pressure decrease was approximately constant at 1.0×10^{-2} MPa/min from 0 to 200 minute and then slowed down. The pressure attained the dissociation pressure at approximately 500 minutes, indicating the completion of the reformation. These results suggest that the reformation rate for the sample with PVCap was several times faster than that of the pure sample.

PVCap is known as one of the most effective kinetic hydrate inhibitors and is widely utilized in the gas and oil production fields [4,14]. However, every kinetic inhibitor has its subcooling limit, above which a chemical cannot effectively inhibit hydrate nucleation or growth. Although PVCap can work well to a temperature approximately 8-9 degrees below the dissociation temperature in a system with sII hydrate, it gives a lower subcooling performance against structure I hydrate [14]. The initial subcooling used in our experiments was 15 degrees, well above the limit for sI hydrate, implying that a large driving force

of hydrate formation can trigger hydrate promotion rather than inhibition. The promotion of methane-ethane hydrate formation was previously reported by Lee and Englezos [15]. They found in their visual observation of the hydrate formation from 89.4 % C1 at 0.6 °C and 5.1 MPa (in this condition sII is a predicted stable phase, but hydrate structure was not analyzed in their study) that when inhibitors GHI 101 were present, the nucleation inhibition was followed by catastrophic crystal growth. They also applied a large subcooling of 12 degrees to the hydrate formation process.

CSMGem predicts that sI hydrate is always the stable phase at the temperature, pressures and gas composition conditions of the reformation experiments. This is consistent with the observation of pure sI reformation.

Cage occupancy of reformed hydrate crystals

Hydrate NMR intensity data in the periods which show linear trends (throughout the observation for the pure system and 0 to 200 minutes for the sample with PVCap) were fitted by lines (Figure 3). The large to small cage occupancy ratio θ_l/θ_s can be related to the slopes of fitted lines, according to the following equation,

$$\theta_l / \theta_s = (dI_{l,c2} / dt + dI_{l,c1} / dt) / 3(dI_{s,c1} / dt) \quad (1)$$

where, $dI_{l,c2}$, $dI_{l,c1}$ and $dI_{s,c1}$ are the slopes of NMR intensities from ethane in the large cages, methane in the large cages and methane in the small cages, respectively (Table 1). The cage occupancy ratios of reformed hydrate crystals estimated from the experimental data were 1.41 for the pure sample and 1.51 for the sample with PVCap (Table 1). These values are in good agreement with the calculations using the CSMGem program [13]: the ratios calculated for the given average gas pressure and composition over the reformation period are 1.36 for the pure system and 1.47 for the inhibited system, respectively (Table 1). These results indicate that reformed hydrate had a cage filling of the thermodynamically stable condition.

This result differs from the previous observations that lower θ_l/θ_s values occur at the beginning of hydrate formation [3,5]. The discrepancy is probably due to differences in the hydrate formation conditions and the timescale of the observations. In the previous Raman study [3], hydrate crystals grew within a liquid water phase, so mass transfer of gas molecules dissolved in the

water would be the main rate controlling factor of crystal growth. Under such a gas-poor condition, hydrate with less density of guest molecules may form as a precursor phase under a large driving force of crystal growth. However, in our case, crystal growth probably occurs mainly at the interface between gas and water where there may be abundant gas molecules to form thermodynamically stable crystals immediately. In the case of the observations of xenon hydrate formation [5], the hydrate grew at the gas-water interface, just like the case of this study. However, the anomaly of the cage filling of Xe hydrate was observed at the very early stage of the reaction (during a few minutes after hydrate nucleation). If such a fast phenomenon occurs in our experiment, it is difficult to monitor it because of the relatively long time scale of this NMR measurement. Also, the initial phase of our samples could be the major factor. In our experiment, the bulk hydrate phase already existed at the beginning of the reformation experiment. Thus hydrate will grow on the bulk phase rather than from an initial nucleation state, and the bulk crystals may act as a template of the rigid hydrate structure at that time.

	$\frac{dI_{c2}}{dt}$ (10^{-4} min^{-1})	$\frac{dI_{c1}}{dt}$ (10^{-5} min^{-1})	$\frac{dI_{c2}}{dt}$ (10^{-6} min^{-1})	θ/θ_s
Pure system	1.41 \pm 0.02	3.44 \pm 0.10	8.44 \pm 0.91	1.45 \pm 0.07 (1.36)
System with PVCap	9.46 \pm 0.17	22.6 \pm 0.83	76.2 \pm 4.99	1.51 \pm 0.09 (1.47)

Table 1: Cage occupancy ratio estimated from the results of linear regression analysis of hydrate data (Figure 3). θ/θ_s values in parentheses are calculations by the statistical thermodynamics program CSMGem [13].

CONCLUSION

In order to understand the kinetics of the methane-ethane binary hydrate, cage filling of hydrate reformed from liquid water and a C1-C2 gas mixture has been measured as a function of time. To investigate the effect of PVCap on the hydrate reformation rate and cage occupancy, the corresponding sample with 0.4 wt.% PVCap has been studied.

The initial structures of the hydrate samples were mostly sI despite the formation conditions being more favorable for sII. On the other hand, hydrate crystals formed during the reformation experiments were all sI as expected by the

statistical thermodynamics program. The cage occupancy ratios observed in the reformed samples were about the same as those predicted for the systems in an equilibrium state, in contrast to previous results. This is probably due to the differences in the hydrate formation conditions and the timescale of measurements between the different experiments. Also, it was found that the presence of PVCap affects the rate of hydrate reformation significantly: the reformation rate for the sample with PVCap was several times faster compared with that in the pure system, indicating that PVCap performs as a hydrate promoter rather than inhibitor at a high subcooling for sI stable hydrate.

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