THE JOURNAL OF PHYSICAL CHEMISTRY B

ARTICLE

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Spectroscopic Identification on Cage Occupancies of Binary Gas Hydrates in the Presence of Ethanol

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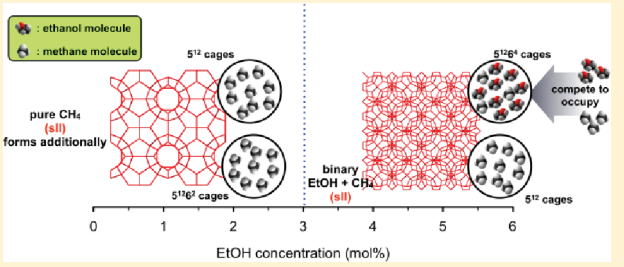
ABSTRACT: Ethanol has been widely used for inhibiting gas hydrate formation due to its cost and efficiency. However, recent research showed that ethanol can act as a hydrate former when coguested with CH_4 molecules at various ethanol concentrations. Herein, we report tuning phenomenon of the gas hydrate in the presence of ethanol by means of spectroscopic measurements. On the basis of the experimental results, it is verified that ethanol molecules cannot inhibit hydrate formation effectively, but enhance the gas storage in the hydrate phase when a much less amount of the inhibitor than the stoichiometric concentration is used. The cage occupancies of binary hydrate systems in the presence of a thermodynamic inhibitor, showing similar guest behaviors in the presence of a promoter such as tetrahydrofuran (THF), can provide useful information on the molecular behaviors of guest species.



INTRODUCTION

Gas hydrates, a class of inclusion compounds, are formed by entrapping gas (guest) molecules in three-dimensional lattice structures of hydrogen-bonded water (host) molecules. In general, the crystal structures of the gas hydrates are closely related to the types and sizes of the guest species. Three distinct structures, cubic structure-I (sI), cubic structure-II (sII), and hexagonal structure-H (sH), are known to form.[1,2] Because the gas hydrate can hold a large amount of gas in unit volume of a solid crystal, it can be potentially applied to CO_2 storage/sequestration[3] and the storage and transportation media for energy gas including natural gas and hydrogen.[4−6] In addition, natural gas hydrates that occur naturally in deep ocean sediments or permafrost regions may be used as a future energy source because such deposits compare well with all other fossil fuel resources.[7] However, in engineering fields, gas hydrates were initially considered as a hazardous material that could cause a blocking problem in oil pipelines.[8] To prevent such blocking problems, two solutions can be used: one is keeping the pipelines outside the stable pressure and temperature region of the gas hydrate, and the other is adding an inhibitor, which makes it harder for the gas hydrate to form.

In these approaches, two kinds of inhibitors, thermodynamic and kinetic, have been used for a long time. When a thermodynamic inhibitor is added, the equilibrium conditions of the hydrate-phase shift to the inhibition region (a region that requires higher pressure at a given temperature or lower temperature at a given pressure to form gas hydrates), because the inhibitor dilutes the aqueous solution and simultaneously lowers the chemical potential of aqueous water.[9] The second type of inhibitor, the kinetic inhibitor, can be used to prevent hydrate formation in pipelines. The kinetic inhibitor can slow the plugging rate (hydrate growth rate) by binding the surface area of hydrate particles. Polymers having the least impact on the environment, like poly-*N*-vinylcaprolactam (PVCap), are generally used as kinetic inhibitors.[7] However, thermodynamic inhibitors, such as alcohols, glycols, and salts, are more practical because of their solubility in aqueous solution and economical cost. Among a variety of alcohols, methanol and ethanol are the most popular ones due to their cost and efficiency. Although ethanol has been known as a usual inhibitor, Glew[10] proposed sII hydrate formation from aqueous ethanol solution to explain the complex and abnormal changes in the partial molar volume of ethanol. Next, a number of stable and metastable hydrates have been reported for the ethanol + water system.[11] In addition, 1- and 2-propanol are found to be captured in hydrate cages when mixed with a smaller secondary guest, such as CH_4.[12] Recently, Anderson et al.[13] suggested that binary ethanol + CH_4 hydrate can stably form at an ambient temperature and elevated pressure conditions based on phase equilibria and thermodynamic modeling calculations. Anderson et al.[14] also reported phase equilibria and thermal analysis for the binary ethanol + water and ternary ethanol + CH_4 + water systems. They performed compositional analyses of the hydrate sample, which yielded $2.30CH_4 \cdot 0.66EtOH \cdot 17H_2O$ at 246.7 K and 3.68 MPa. In addition, Yasuda et al.[15] performed powder X-ray diffraction (PXRD) and Raman spectroscopic investigations independently for the same system and found that cubic sII hydrate formed from the ethanol + CH_4 + water mixture. In addition to ethanol, 1-propanol, and 2-propanol, sII and sH

Received: August 31, 2011
Revised: November 30, 2011
Published: December 14, 2011

hydrate formations were reported with *tert*-butyl alcohol and some amyl alcohols.[16,17] Spectroscopic observation revealed that there is no strong hydrogen-bonding interaction between guest and host species during the enclathration of such alcohols.

In this study, spectroscopic analyses on ternary ethanol + CH_4 + water hydrate samples were performed using various ethanol contents in aqueous solutions. Although binary ethanol + water systems were reported to have many stable and metastable states depending on temperature and ethanol concentrations,[12] and a recent investigation verified stable formation of cubic sII hydrate, sufficient experimental evidence on other stable or metastable states having ethanol contents other than stoichiometry was not reported. In particular, hydrate structures and guest behaviors at various concentrations have been unknown because recent investigations used stoichiometric ethanol for sII hydrate or higher concentrations. Moreover, hydrate formation and molecular behaviors in the presence of an aqueous inhibitor remained unclear because sufficient spectroscopic analysis at various inhibitor concentrations has not been performed so far.

EXPERIMENTAL METHODS

Materials. CH_4 gas was supplied by World Gas (Korea) and had a UHP grade. HPLC grade water and ethanol, supplied by Sigma-Aldrich Chemical Co. with a nominal purity of 99.99 mol % and ≥99.5 mol %, respectively, were used to form binary hydrate samples. All of the materials mentioned above were used without further purification or treatment.

Sample Preparation. A specifically constructed high-pressure cell (an internal volume of approximately 100 cm^3 and maximum working pressure of 14.0 MPa) was used to prepare hydrate samples for spectroscopic analyses. To make binary hydrate samples, aqueous ethanol solutions of various concentrations (5.6, 3.0, 2.0, and 1.0 mol % in aqueous solutions) were prepared and frozen in a freezer at 240.0 K for 1 day. After the frozen solutions were grounded into fine powders and charged into the precooled high-pressure cell, the cell was sufficiently purged by methane to remove the remaining air inside the cell. Next, CH_4 gas was slowly introduced to the high-pressure cell up to 6.0 MPa. During the hydrate formation, the high-pressure cell was kept in a freezer at 240.0 K, and CH_4 gas was refilled periodically to compensate for the pressure drop due to hydrate formation. When the pressure depression due to hydrate formation was not observed any longer, the cell was cooled to about 80 K using liquid nitrogen, and the CH_4 gas was released slowly before we collected the hydrate samples. During the sample preparation, a Heise digital pressure transducer (DXD series, with an accuracy of ±0.01 MPa) was used to monitor and check formation pressure.

Experimental Measurements. Structural identification of the formed hydrate samples was performed using a high-resolution X-ray powder diffraction beamline (8C2) at the Pohang Accelerator Laboratory (PAL) in Korea. The incident X-rays were vertically collimated by a mirror and monochromatized to a wavelength of 1.5490 Å using a double-crystal Si (1 1 1) monochromator. The detector arm of the vertical scan diffractometer is composed of seven sets of soller slits, flat Ge (111) crystal analyzers, antiscatter baffles, and scintillation detectors, with each set separated by 20°. The powdered hydrate sample of approximately 1.0 g was placed on a precooled flat plate holder, and a step scan was performed at 80.0 K from 8.00° in 2θ with 0.01° increment and 1.00° overlaps to the next detector bank up to 129.00° in 2θ (a step time of 3 s). For structural identification and microscopic investigation, a Bruker DSX400 NMR spectrometer in the Korea Basic Science Institute was used. ^{13}C cross-polarization/magic angle spinning (CP/MAS) NMR spectra were obtained at 200.0 K by packing the hydrate samples within a 4 mm o.d. zirconium rotor. All ^{13}C NMR spectra were collected at a Larmor frequency of 100.6 MHz with MAS at 9 kHz. A pulse length of 2 μs and pulse repetition delay of 10 s during proton decoupling were employed when the radio frequency field strength of 50 kHz corresponding to 5 μs 90° pulses was used. The downfield carbon resonance peak of adamantine, assigned a chemical shift of 38.3 ppm at 300.0 K, was used as an external chemical shift reference.

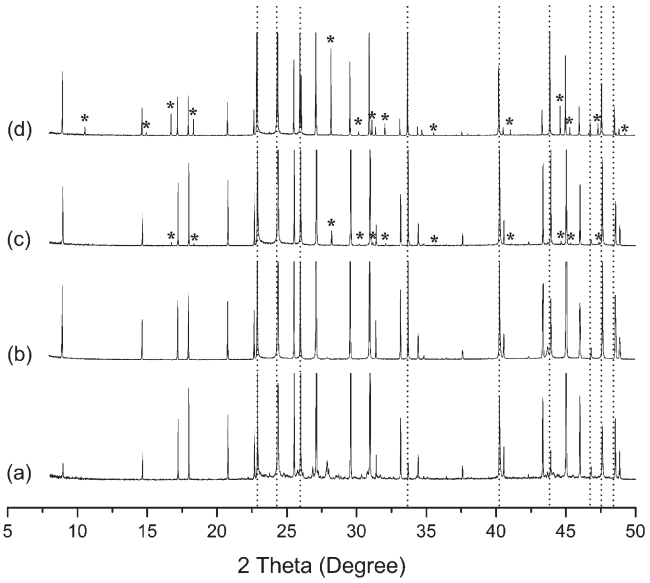


Figure 1. Powder X-ray diffraction patterns of the ethanol + CH_4 binary hydrate samples prepared with frozen solutions of (a) 5.6, (b) 3.0, (c) 2.0, and (d) 1.0 mol % aqueous ethanol. Dotted lines indicate calculated peak positions from the hexagonal ice (Ih) phase, which were not used for calculating lattice parameters. Asterisks at 2.0 and 1.0 mol % of ethanol indicate additional peak positions of pure CH_4 hydrate (sI).

RESULTS AND DISCUSSION

Figure 1 shows PXRD patterns of the ethanol hydrate samples. As shown in this figure, the first diffraction peak was observed at approximately 8.8° for all of the hydrate samples. We attributed the peak to the (111) peak of cubic sII hydrate, which was not observed in the sH and sI samples. Therefore, the existence of the (111) peak indicates that all of the formed hydrate samples have sII crystal structures. In addition, 5.6 and 3.0 mol % samples showed the same numbers and positions for the observed PXRD peaks, which indicates those samples were formed uniformly as sII hydrate except for a small amount of hexagonal ice phase (Ih). However, when the ethanol concentration was decreased to 2.0 and 1.0 mol %, additional peaks (marked with asterisks) were observed in addition to the sII diffraction peaks. The additional peak positions agree with the calculated cubic sI hydrate, and the peak intensities of those additional peaks become stronger with decreasing ethanol concentrations. Therefore, we attributed the additional peaks to the cubic sI hydrate phase of pure CH_4 hydrate formed from the excess ice phase in the original frozen solutions. Calculated lattice parameters for 5.6, 3.0, 2.0, and 1.0 mol % ethanol samples were 17.1683 Å (unit cell volume of

dx.doi.org/10.1021/jp210223r |*J. Phys. Chem. B* 2012, 116, 332–335

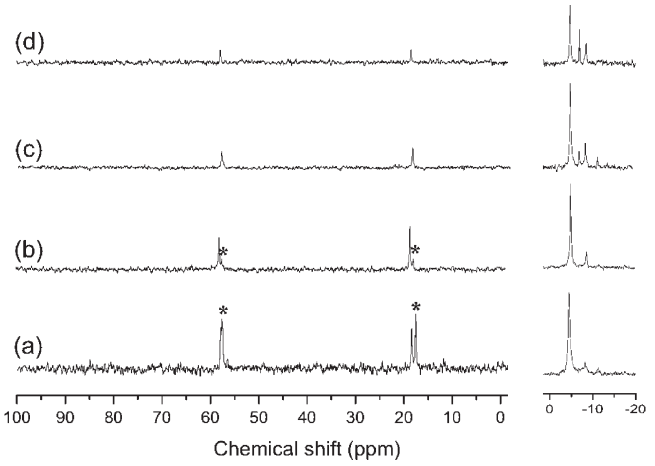


Figure 2. ^{13}C solid-state MAS NMR spectra of the ethanol + CH_4 binary hydrate samples prepared with frozen solutions of (a) 5.6, (b) 3.0, (c) 2.0, and (d) 1.0 mol % aqueous ethanol. Asterisk marks at 5.6 and 3.0 mol % of ethanol indicate atomic signals from unreacted ethanol molecules.

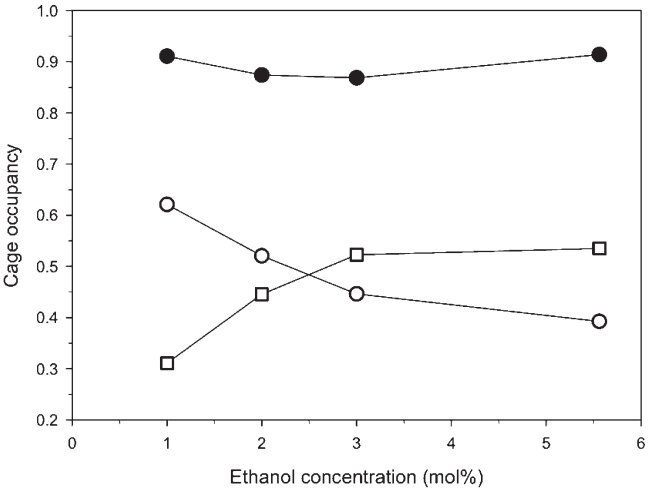


Figure 3. Cage occupancies for CH_4 and ethanol molecules at various concentrations of ethanol: ●, small cage occupancy of CH_4; ○, large cage occupancy of CH_4; □, large cage occupancy of ethanol.

5060.35 Å^3), 17.1679 Å (5060.04 Å^3), 17.1678 Å (5059.93 Å^3), and 17.1688 Å (5060.78 Å^3), respectively. In addition, the calculated lattice parameters for the pure CH_4 hydrates observed in the 2.0 and 1.0 mol % ethanol samples were 11.8845 Å (unit cell volume of 1678.58 Å^3) and 11.8926 Å (1682.02 Å^3), respectively. These values are in good agreement with previously reported values even though the values are a little larger than those reported by Yasuda et al.[15] However, such a difference may be due to different formation conditions for hydrate samples, and almost constant values near 17.17 Å indicate that no cage distortions occurred during the enclathration of ethanol molecules.

The ^{13}C NMR spectra for the same ethanol hydrate samples that were used in the PXRD measurements are presented in Figure 2. Two NMR spectra can be examined from two perspectives. First, the upfield region of 0 to −10 ppm, showing atomic signals from CH_4 molecules in hydrate structures, can provide information on hydrate structure and cages enclathrating CH_4 molecules. Two signals are detected at −4.3 and −8.2 ppm for both 5.6 and 3.0 mol %, which indicates CH_4 molecules are captured in small and large cages of the cubic sII hydrate. It should be noted that the large cage is partially occupied by CH_4 molecules even at stoichiometric ethanol concentration, suggesting that ethanol and CH_4 molecules compete with each other for occupying large cages even at the stoichiometric concentration unlike other hydrate forming aqueous solutions, for example, THF solutions.[14] In addition, another signal is additionally detected at −6.6 ppm as the ethanol concentration decreases to 2.0 and less mol %. This peak corresponds to CH_4 molecules in the large cages of cubic sI hydrate, which means that pure CH_4 hydrate is formed by reaction of CH_4 with unreacted ice. Second, two carbon signals in an ethanol molecule (CH_3- and $-CH_2-$) can be detected at the downfield region. However, two additional peaks are observed for 5.6 and 3.0 mol %, which shows coexistence of solid phases, that is, frozen ethanol solution and binary hydrate phases.[15] It should be noted that (1) both atomic signals of ethanol molecules are shifted to the downfield region (deshielded state) after hydrate formation, and (2) ethanol molecules exist as unreacted frozen solution without forming other hydrate phase even though pure CH_4 hydrate can be formed and exists stably at the experimental temperature and pressure conditions. Such molecular behaviors can be explained by the inhibition effect of hydrogen bonding between ethanol and water molecules. As noted by Mizuno et al.,[18] water molecules in the aqueous solution can form hydrogen bonds with the hydroxyl group of ethanol at higher ethanol concentration. In the same way, ethanol molecules would form strong hydrogen bonds with in the frozen aqueous solution at the stoichiometric concentration (5.6 mol %). In addition, the unreacted ethanol in the frozen solution might exist as partially noncrystallized form considering the low melting point of ethanol (159 K).[15] Therefore, pure CH_4 hydrate (sI) cannot form even in the presence of unreacted ice phase, although the experimental condition and reaction time are sufficient. Because of the strong hydrogen bonds with ethanol, water molecules are hard to rearrange to a lattice-like structure to accommodate CH_4. However, in the range of lower ethanol concentrations, water-rich contents unaffected by the hydrogen bonds with ethanol can participate in the formation of pure CH_4 hydrate, while ethanol−water interactions still form binary sII hydrate.

Because the peak areas in the ^{13}C NMR spectra are proportional to the amount of corresponding species, the obtained peak areas can be combined with the van der Waals−Platteeuw model to calculate the cage occupancies of the guests. Figure 3 illustrates the small and large cage occupancies of both CH_4 and ethanol molecules at various ethanol concentrations. As seen in this plot, CH_4 occupancy in small cages has almost the same value between 0.86 and 0.91 regardless of ethanol concentrations. However, CH_4 occupancy in large cages increased according to decreased ethanol concentrations from 0.39 at 5.6 mol % to 0.62 at 1.0 mol %. In addition, ethanol molecules occupy fewer large cages as the CH_4 occupancy increases at lower ethanol concentrations, which makes the overall occupancy by both guests nearly constant at 0.98−0.99. Assuming comparable occupation of CH_4 even at a stoichiometric 5.6 mol %, more CH_4 molecules are expected to occupy large cages at lower ethanol concentrations because they compete with fewer ethanol molecules for large cage occupation. Such increased occupancy of the second guest can be explained by an increased activity, which is also used to explain the so-called tuning mechanism in aqueous solutions including THF and

tert-butyl alcohol.[16,19] Because of such activity changes, the chemical formula changes from $2.2CH_4 \cdot 0.54EtOH \cdot 17H_2O$ at 5.6 mol % to $2.44CH_4 \cdot 0.31EtOH \cdot 17H_2O$ at 1.0 mol %. Although no formula has been reported for ethanol concentrations lower than stoichiometry, the chemical formula at 5.6 mol % showed good agreement with the value reported by Anderson et al. considering different formation conditions.[14] In addition, cage occupancies for small and large cages of sI CH_4 hydrate showed little changes (0.69−0.70 and 0.99, respectively), even though they are not included in this figure. Most of the constant cage occupancies can be explained by the same driving force for the sI CH_4 hydrate, while the values strongly depend on both the driving force and the activities in solutions when the second guest exists. As noted previously, both CH_4 occupancy in large cages and the amount of unreacted excess ice increase as the ethanol concentration decreases, leading to an increased amount of CH_4 molecules stored in the overall hydrate phase per unit mass of ethanol molecules at a lower ethanol concentration.

CONCLUSIONS

Alcohol, especially ethanol, has been commonly used as a cost-effective inhibitor for hydrate formation. However, in this study, it is found that ethanol molecules cannot inhibit hydrate formation effectively but enhance the gas storage in the hydrate phase when much less amount of the inhibitor than the stoichiometric concentration is used. So far, the so-called tuning mechanism is observed only for the hydrate system with an aqueous hydrate promoter and liquid former. However, on the basis of spectroscopic analysis for the hydrate samples formed from frozen ethanol solutions, we found that hydrogen bonds between two liquid substances acting differently depending on concentrations in the aqueous solutions can similarly affect cage occupancies of binary guest species in the presence of an inhibitor (ethanol) as observed in the tuning systems in the presence of hydrate promoter. However, further investigations are necessary to clearly explain such molecular behaviors of hydrate systems in the presence of a thermodynamic inhibitor, and to explain inhibiting mechanism by ethanol in the aqueous solutions.

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ACKNOWLEDGMENT

This research was supported by the Midcareer Researcher Program through the NRF grant funded by the MEST (No. 2008-0061974). We would like to thank the Korea Basic Science Institute (Daegu) for assistance with 400 MHz solid-state NMR. We also thank Dr. Do-Cheon Ahn for the operation of the 8C2 beamline at PAL. Experiments at PAL were supported in part by MEST and the Pohang University of Science and Technology (POSTECH).

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