

Thermodynamic and spectroscopic identification of aldehyde hydrates

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(Received 3 November 2015 • accepted 25 January 2016)

Abstract—It has been reported that some aldehyde compounds have formed simple sII clathrate hydrates without help-gas molecules, showing a self-forming effect. However, the structure of aldehyde hydrates is quite unstable due to the “gem-diol reaction”. According to the previous studies, the aldehyde hydrate slowly decomposes at atmospheric condition with the conversion of aldehyde to gem-diol. We investigated binary aldehyde (acetaldehyde, propionaldehyde, and isobutyraldehyde)+methane clathrate hydrate with spectroscopic and thermodynamic analyses. Similar to the simple aldehyde hydrate, the binary hydrates also formed a sII hydrate. During the hydrate formation process, we found that most of the aldehydes converted to gem-diols and were then incorporated into the large cages of the sII hydrate. Depending on the equilibrium constant of the gem-diol reaction caused by the molecular structures of the three aldehydes, different phase equilibrium curves of aldehyde+methane hydrates were obtained.

Keywords: Clathrate Hydrate, Aldehyde, Gem-diol, Binary Hydrates, Phase Equilibrium

INTRODUCTION

Clathrate hydrates are non-stoichiometric crystalline compounds which are formed by the enclathration of guest molecules that have a suitable size and shape in cages made up of hydrogen-bonded water frameworks. The guest molecules incorporated in the clathrate hydrate cages interact with the host water molecules via the van der Waals force, making the host-guest interaction one of the most unique physicochemical properties of clathrate hydrates [1]. Clathrate hydrates are known to form three well-known structures of structure I (sI), structure II (sII), and structure H (sH) depending on the size of guest molecules. The structure could also be confirmed by observing powder X-ray diffraction patterns [1,2]. Among these three structures, some molecules are known to form simple sII hydrates composed of only one type of self-forming guest molecule [3,4] or they form binary sII hydrates with small help-gas molecules [5]. The unit cell of sII clathrate hydrates having a *Fd-3m* cubic structure is composed of sixteen small 5^{12} cages (hereafter, sII-S cages) and eight large $5^{12}6^4$ cages (hereafter, sII-L cages) with 136 water molecules. For binary sII hydrates, 5.56 mol% of organic sII formers occupy sII-L cages, while small gaseous guest molecules occupy sII-S cages. Compared with sI and sH clathrate hydrates, the sII clathrate hydrates can provide the highest number of 5^{12} cages per unit cell, and these small cages can capture small gas molecules [1]. For these reasons, sII clathrate hydrates have been investigated intensively to be applied in the industrial fields of gas storage and separation [6,7].

In general, small molecules having a diameter less than 4.2 Å and large molecules having a diameter between 6 and 7 Å are known to form sII clathrate hydrates [1]. Even though the size of guest molecules is slightly larger than the mean-free diameter of the sII-L cages of 6.6 Å, some large guest molecules have been reported to be captured in the sII-L cages due to the flexibility of the hydrogen-bonded water framework [8]. Tetrahydrofuran (THF), which is a well-known sII hydrate former, can form a simple sII hydrate without the help gas molecules (self-forming effect) [3]. However, it can also form a binary sII hydrate with help gas molecules such as CH₄ or N₂ by lowering the hydrate formation pressure [5].

Some of the ketones and aldehydes containing a carbonyl group have been reported to form simple sII hydrates without help gas molecules such as THF. The ketones of acetone and cyclobutanone have a suitable size and shape that can fit the sII-L cage. They also can form simple sII hydrates, which have been confirmed by both X-ray diffraction patterns and dielectric properties [9-12]. Similarly, some aldehyde compounds such as acetaldehyde, propionaldehyde, *n*-butyraldehyde, and isobutyraldehyde were revealed to have formed simple sII hydrates that show a self-forming effect [13-15]. Their dielectric properties have also been investigated [16,17].

Binary sII hydrates of acetone+CH₄ and cyclobutanone+CH₄ were examined for the technological application of gas hydrates since both ketone compounds can reduce the hydrate equilibrium pressure [5,18]. However, the binary sII hydrate of aldehyde compounds+gas molecule has not been reported yet. Moreover, the simple sII hydrates of aldehyde compounds are quite unstable due to the “gem-diol reaction” [16,19], and the host-guest chemistry of aldehyde clathrate hydrates has not been investigated intensively. The gem-diol reaction refers to the addition of water to the carbonyl group of ketone or aldehyde compounds, leading to the conversion of ketone (R₁R₂CO) to gem-diol (R₁R₂C(OH)₂) or aldehyde

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^{*}This article is dedicated to Prof. Huen Lee on the occasion of his retirement from KAIST.

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(RCHO) to *gem*-diol ($\text{RCH}(\text{OH})_2$), respectively. Although ketone compounds tend not to form *gem*-diol in water, aldehyde compounds can establish a reversible equilibrium with considerable amounts of *gem*-diols [20]. For this reason, sII aldehyde hydrates are unstable since they have been found to slowly decompose with the slow conversion of aldehyde to *gem*-diol [16,19].

In this study, we first investigated the binary sII hydrates of aldehyde compounds+ CH_4 and revealed the unique configurational behaviors of enclathrated aldehydes by spectroscopic analyses. Moreover, the phase equilibria of acetaldehyde, propionaldehyde, and isobutyraldehyde+ CH_4 hydrates were also measured by varying the concentration of aldehyde compounds.

EXPERIMENTAL SECTION

1. Materials and Sample Preparation

High purity distilled water was obtained from a Millipore purification. Acetaldehyde (CH_3CHO), propionaldehyde ($\text{CH}_3\text{CH}_2\text{CHO}$), and isobutyraldehyde ($(\text{CH}_3)_2\text{CHCHO}$) were supplied from Sigma-Aldrich. CH_4 gas was purchased from Special Gas (South Korea) with the stated minimum purities of 99.95 mol%.

The 5.56 mol% of the acetaldehyde, propionaldehyde, and isobutyraldehyde aqueous solution was frozen under an atmospheric pressure at around 203 K, and the frozen mixture was finely ground with a 200 mm sieve in liquid nitrogen. The powdered samples were then loaded into a high-pressure vessel separately and pressurized with 120 bar of CH_4 gas. The samples in the pressure vessel were maintained for 10 days at 253 K in a refrigerated bath circulator (Jeio Tech., RW-2025G). The samples were recovered in liquid nitrogen and used for spectroscopic analysis including X-ray diffraction and Raman scattering.

2. High Resolution Powder Diffraction (HRPD)

The HRPD patterns were collected using PAL (Pohang Accelerator Laboratory, Republic of Korea) Synchrotron. During the measurements, a $\theta/2\theta$ scan mode with a fixed time of 1s, a step size of 0.005° for $2\theta=0-120^\circ$, and a beam line with a wavelength of 1.5472 \AA were used for each sample. The loading of the samples was performed at 77 K to minimize possible sample damage.

3. Raman Spectroscopy

Raman spectra were obtained using a Horiba Jobin Yvon LabRAM HR UV/Vis/NIR high resolution dispersive Raman microscope in which a CCD detector was equipped and cooled by liquid nitrogen. Samples were kept at 77 K during measurements. The excitation source was an Ar-ion laser emitting a 514.53 nm line. The laser intensity was typically 30 mW. For the low-temperature experiment, a Linkam (THMS600G) unit was used to cool the samples to around 93 K.

4. Three Phase Equilibrium Condition Measurements

We measured the phase equilibria of the binary (acetaldehyde, propionaldehyde, and isobutyraldehyde+ CH_4) clathrate hydrate by using a magnetic stirring cell, which was a bolted closure-type high-pressure vessel made of stainless steel. First, the acetaldehyde, propionaldehyde, and isobutyraldehyde aqueous solutions with various concentrations (3, 5.56, and 8 mol%) were loaded into the stirring cell. After loading the solution, the air existing inside the cell was flushed out by a continuous injection of CH_4 for each

sample. After several iterations, the CH_4 gas was pressurized up to the targeted pressure by using a microflow syringe pump. A four-wire type Pt-100 Ω probe was used for the sensing temperature with a full-scale accuracy of $\pm 0.05\%$. A pressure transducer (Druck, PMP5073) was also used for pressure sensing with an accuracy up to 0.02% inside the cell. The temperature of the stirring cell was lowered (-1 K/hour) with a circulating bath to form binary clathrate hydrates. After the hydrate was formed, the temperature of the circulating bath was slowly increased at a rate of 0.1 K/hour , which was sufficient to reach equilibrium at each step. When the temperature and pressure conditions of the system reached the dissociation point, the slope of the tangent line to the curve in the PT diagram suddenly decreased accompanied by a full dissociation of the hydrates. The temperature and pressure changes during the hydrate formation process and dissociation were automatically recorded using a data acquisition system.

RESULTS AND DISCUSSION

1. Structure Determination of Aldehydes+ CH_4 Hydrates

The HRPD patterns of binary hydrates composed of three different aldehydes (acetaldehyde, propionaldehyde, and isobutyraldehyde) with methane gas indicate that they formed a structure II (sII) hydrate (Fig. 1). Methane gas without organic molecules formed a structure I (sI) hydrate. Thus, the occurrence of sII indicates that three aldehydes were captured in the large cage ($5^{12}6^4$) of the sII hydrate. The longer diameters of acetaldehyde, propionaldehyde, and isobutyraldehyde were about 6.02, 6.76, and 7.13 \AA , respectively, as calculated by the Gaussian 03W program [21] (Fig. 2). The large cage ($5^{12}6^4$) of the sII hydrate can theoretically accommodate molecules with a diameter up to 6.6 \AA , but it has been reported that molecules larger than 6.6 \AA can be enclathrated in the large cage of the sII hydrate, as discussed in the introduction.

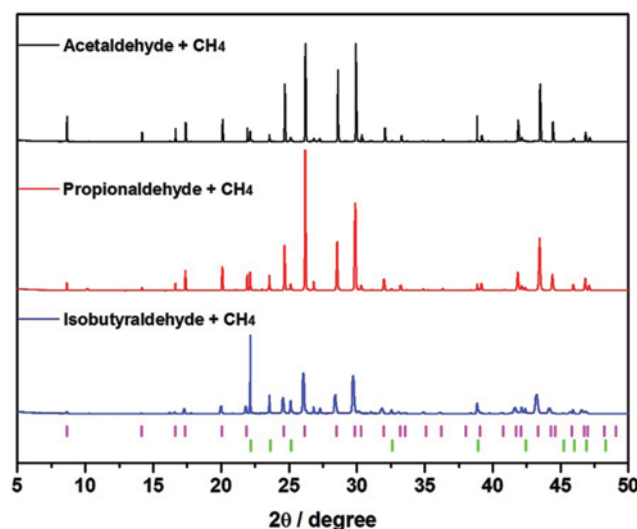


Fig. 1. Synchrotron HRPD patterns of CH_4 hydrate using three different aldehyde molecules: acetaldehyde (black), propionaldehyde (red), and isobutyraldehyde (blue). Both magenta and green ticks represent the peaks of sII clathrate hydrate and ice, respectively.

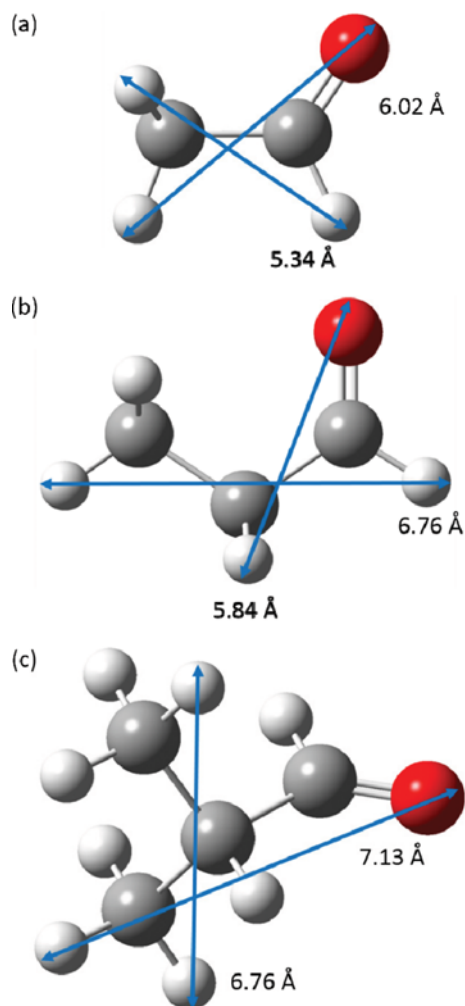


Fig. 2. Molecular structures and sizes of acetaldehyde, propionaldehyde, and isobutyraldehyde. Gray, white, and red balls represent carbon, hydrogen, and oxygen, respectively.

In this connection, the molecular sizes of the three aldehydes are sufficient to constitute the sII hydrate.

2. Conversion of Aldehydes to *gem*-diols

The carbonyl group ($\text{C}=\text{O}$) of aldehydes slowly transformed to *gem*-diols ($\text{-C}(\text{OH})_2$) with the addition of water, and this reaction made their hydrates unstable at atmospheric pressure [19]. Generally, organic molecules that form the clathrate hydrate can be stabilized under the pressurized environment of secondary gaseous guests such as CH_4 and N_2 . The binary hydrates of three different aldehydes with methane were confirmed as sII, as indicated in Fig. 1. Then, we needed to investigate how the reaction of aldehydes proceeds within the cages of the sII hydrate.

Fig. 3(a) shows that there were no $\text{C}=\text{O}$ stretching vibrations of aldehydes detected in the range of $1,720\text{--}1,740\text{ cm}^{-1}$ [22], which indicates that all given aldehydes changed into *gem*-diols during the formation of methane hydrates. Thus, only *gem*-diols of the original aldehydes remained exclusively in the large cage of clathrate hydrate, while the aldehydes and corresponding *gem*-diols coexisted in their aqueous state. We also note that the formation of *gem*-diols did not cause a decomposition of the hydrate when CH_4 gas

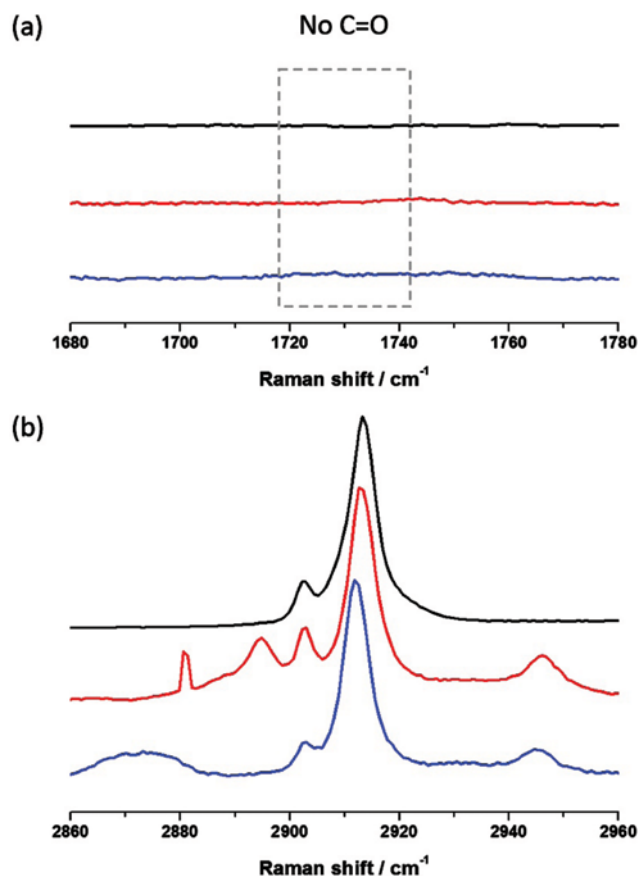


Fig. 3. Raman spectra of binary hydrates with methane and three different aldehydes at 93 K: acetaldehyde+ CH_4 hydrate (black), propionaldehyde+ CH_4 hydrate (red), and isobutyraldehyde+ CH_4 hydrate (blue). (a) $\text{C}=\text{O}$ stretching region for aldehydes, (b) C-H stretching region for CH_4 incorporated in large ($5^{12}6^4$) and small cages (5^{12}) of the sII hydrate.

was present as a secondary guest molecule. Methane, as a help-gas for stabilizing aldehydes in the large cage, was incorporated in the small cage (5^{12}) of sII, which is represented as a peak at $2,914\text{ cm}^{-1}$ in Fig. 3(b). A weak shift of the Raman peak for methane was observed with varying aldehydes. Although these three aldehydes form the same clathrate hydrate (sII) structure, the resulting size of the small cages for methane gas can vary slightly depending on the size of the aldehydes in the large cages. In this light, the size of the crystal lattice of hydrates could shift the Raman peak for methane in small cages with varying aldehydes in the large cages. It is also noted that a weak peak at $2,904\text{ cm}^{-1}$ was observed, which means a partial enclathration of CH_4 gas in the large cage of the sII hydrate. This so-called tuning phenomenon is often observed in some sII hydrate systems and can enhance the storage capacity of gas in the clathrate hydrate [23].

3. Phase Equilibria of Aldehydes+Methane Hydrates

Three phase equilibria ($(\text{H-L}_W\text{-L}_{\text{formers}}\text{-V})$ for each aldehyde (acetaldehyde, propionaldehyde, and isobutyraldehyde)+ CH_4 hydrate at its stoichiometric concentration (i.e., 5.56 mole% of each aldehyde in aqueous solution) are shown in Fig. 4. The phase behavior of acetaldehydes shifted to a lower temperature and higher pres-

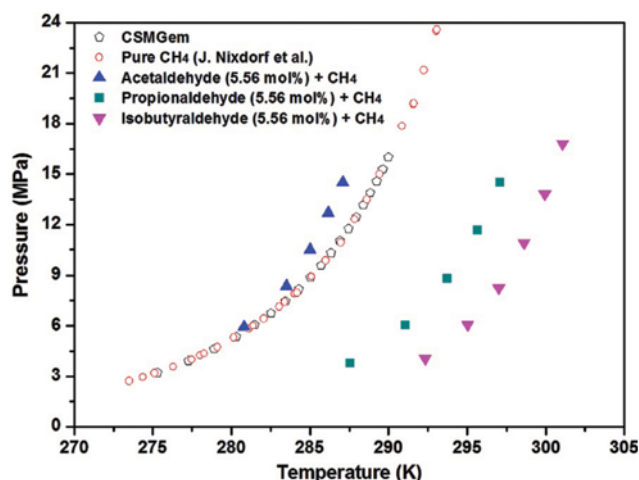


Fig. 4. Three phase (L-H-V) equilibrium curve of the pure CH_4 hydrate [25] and binary (acetaldehyde, propionaldehyde, and isobutyraldehyde) + CH_4 hydrates. The hydrate region is to the left of the phase curve; to the right, the phase exists for a liquid mixture of water and each aldehyde and methane gas.

sure than those of pure CH_4 . Compared to the system for acetaldehyde, the phase equilibria of propionaldehyde and isobutyraldehyde with methane were observed in the right side of the pure methane condition, while the isobutyraldehyde system appeared the most on the right. Numerous factors may affect the thermodynamic stabilities of clathrate hydrates including the molecular size of guest molecules, functional groups or secondary gaseous guests. The phase equilibrium behavior among the given aldehydes can be affected by their molecular size. We also note that aldehyde and the resulting *gem*-diol were in a chemical equilibrium and could not be isolated in an aqueous solution [20]. Relative amounts of the reactant (aldehyde) and product (*gem*-diol) were determined as equilibrium constant, K , which was affected by the molecular

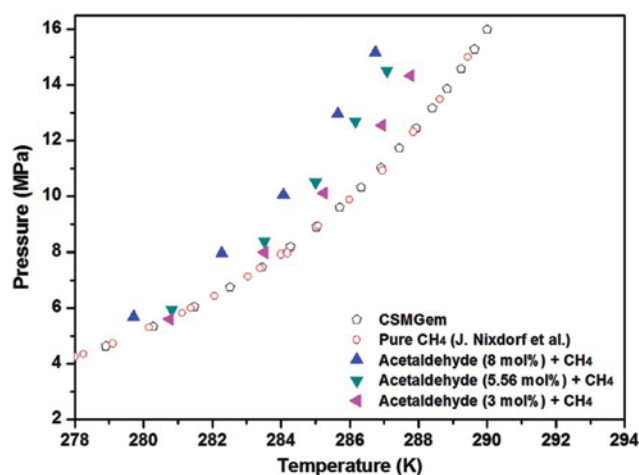


Fig. 5. Three phase (L-H-V) equilibrium curve of the pure CH_4 hydrate [25] and acetaldehyde + CH_4 hydrates at various concentrations. The hydrate region is to the left of the phase curve; to the right, the phase exists for a liquid mixture of water and acetaldehyde and methane gas.

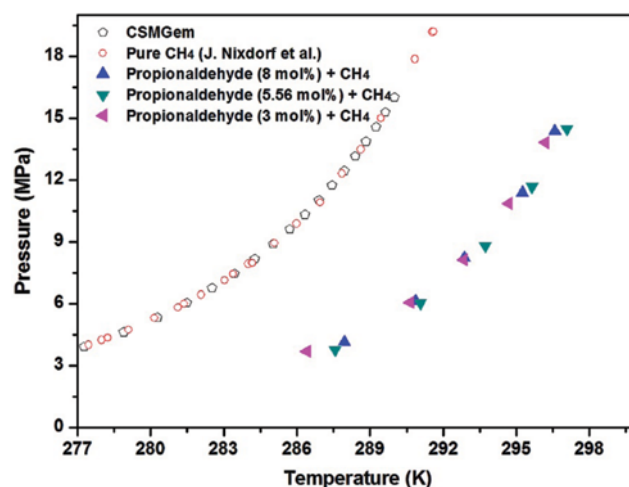


Fig. 6. Three phase (L-H-V) equilibrium curve of the pure CH_4 hydrate [25] and propionaldehyde + CH_4 hydrates at various concentrations. The hydrate region is to the left of the phase curve; to the right, the phase exists for a liquid mixture of water and propionaldehyde and methane gas.

structure of carbonyl compounds. The equilibrium constant increased in the order of isobutyraldehyde, propionaldehyde, and acetaldehyde [20] with isobutyraldehyde having the lowest driving force to change its *gem*-diol among the three aldehydes in their aqueous solution. In this connection, considering that a *gem*-diol has two hydroxyl functional groups that are known to inhibit the formation of clathrate hydrates, more severe PT conditions are required to form acetaldehyde + CH_4 hydrate compared to the other two aldehyde + CH_4 hydrates. Thus, the stability of aldehyde in a mixed solution of aldehyde and *gem*-diol was probably one of the factors that affected the thermodynamic stabilities of the binary clathrate hydrate.

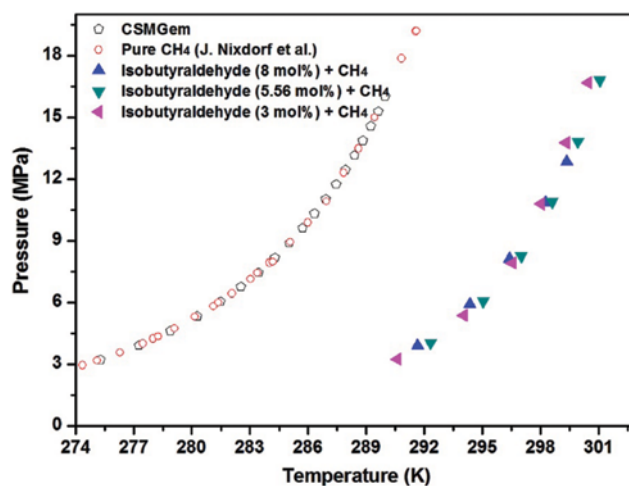


Fig. 7. Three phase (L-H-V) equilibrium curve of the pure CH_4 hydrate [25] and isobutyraldehyde + CH_4 hydrates at various concentrations. The hydrate region is to the left of the phase curve; to the right, the phase exists for a liquid mixture of water and isobutyraldehyde and methane gas.

Table 1. Experimental equilibrium ($H-L_w-L_{\text{acetaldehyde}}-V$) data of acetaldehyde+CH₄ at various concentrations

Acetaldehyde+CH ₄					
Acetaldehyde 3 mol%		Acetaldehyde 5.56 mol%		Acetaldehyde 8 mol%	
T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)
280.76	5.603	280.82	5.942	279.72	5.694
283.52	7.993	283.51	8.373	282.27	7.954
285.24	10.119	285.01	10.510	284.07	10.055
286.94	12.554	286.17	12.696	285.65	12.959
287.77	14.333	287.09	14.506	286.75	15.171

Table 2. Experimental equilibrium ($H-L_w-L_{\text{propionaldehyde}}-V$) data of propionaldehyde+CH₄ at various concentrations

Propionaldehyde+CH ₄					
Propionaldehyde 3 mol%		Propionaldehyde 5.56 mol%		Propionaldehyde 8 mol%	
T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)
286.41	3.690	287.58	3.779	287.94	4.148
290.65	6.056	291.06	6.030	290.88	6.129
292.84	8.139	293.72	8.805	292.87	8.234
294.69	10.861	295.65	11.673	295.25	11.382
296.18	13.822	297.07	14.486	296.58	14.370

Table 3. Experimental equilibrium ($H-L_w-L_{\text{isobutyraldehyde}}-V$) data of isobutyraldehyde+CH₄ at various concentrations

Isobutyraldehyde+CH ₄					
Isobutyraldehyde 3 mol%		Isobutyraldehyde 5.56 mol%		Isobutyraldehyde 8 mol%	
T (K)	P (MPa)	T (K)	P (MPa)	T (K)	P (MPa)
290.62	3.253	292.34	4.048	291.66	3.907
294.04	5.379	295.05	6.070	294.36	5.911
296.55	7.910	297.02	8.257	296.40	8.122
298.03	10.795	298.62	10.895	298.28	10.858
299.32	13.761	299.94	13.819	299.36	12.851

In Figs. 5-7, the equilibrium behavior of the three aldehydes+CH₄ hydrate at three different concentrations (3, 5.56, 8 mol%) is presented and the data for the figures are summarized in Tables 1-3. When the concentration of acetaldehyde increased from 3 to 8 mol%, the phase equilibria conditions moved to the left (lower temperature and higher pressure region). For the propionaldehyde and isobutyraldehyde+CH₄ hydrate, the most significant effect of pressure reduction was observed at each stoichiometric concentration (5.56 mol%) with additional aldehydes more than the stoichiometric amount acting as an inhibiting factor for their binary hydrates of methane. These phenomena among the different concentrations of the organic former for the observed clathrate hydrates have been reported in other systems [24].

CONCLUSIONS

The binary clathrate hydrates of three aldehydes (acetaldehyde, propionaldehyde, and isobutyraldehyde) with methane were characterized by spectroscopic analysis. They were confirmed as sII hydrates similar to the simple hydrates of their own at atmospheric

pressure. The structure was also maintained, even when the carbonyl groups in aldehydes changed into *gem*-diols in an aqueous solution. Furthermore, the phase equilibria for the hydrate with methane were measured in pressure ranges from 3.2 MPa to 16.8 MPa. Among the three different types of aldehydes, the equilibrium pressure reduced the most when isobutyraldehyde was present. This may be attributed to the size of molecules or equilibrium constant of aldehydes in an aqueous solution. From the results gained in this study, the host-guest chemistry of the clathrate hydrates' accompanying reactions can be understood, and this will be helpful for studying clathrate hydrates as a gas storage medium.

ACKNOWLEDGEMENTS

This research was funded by the Ministry of Trade, Industry & Energy (MOTIE) through the Recovery of Natural Gas Hydrate in Deep-Sea Sediments Using Carbon Dioxide and Nitrogen Injection project [KIGAM-Gas Hydrate R&D Organization]. It was also supported by the Midcareer Researcher Program through a National Research Foundation Korea (NRF) grant funded by the Ministry

of Science, ICT and Future Planning (MSIP) (NRF-2014-049237).

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