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Thermodynamic and Molecular-Scale Analysis of New Systems of Water-Soluble Hydrate Formers + CH₄

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Among a variety of cyclic ether, cyclic ester, and cyclic ketone compounds, six new formers were found to form binary sII or sH hydrates with CH₄ gas. Hydrate-phase equilibria for all the hydrate formers were measured. The results obtained showed distinct relationships between the hydrate-phase equilibrium curve and the molecular size of the guests. In addition, 2-methyltetrahydrofuran and 3-methyltetrahydrofuran, or 4-methyl-1,3-dioxane and 4-methyl-1,3-dioxolane, showed different hydrate structures even though they have similar chemical structures. Such structural differences can provide useful information on the critical guest size, which determines hydrate crystal structures according to the size of the captured guest.

Introduction

Gas hydrates are crystalline solids formed by entrapping gas molecules (guests) into three-dimensional lattice structures of hydrogen-bonded water molecules (host).^{1–3} In general, gas hydrates belong to three distinct crystal structure families, which are structure-I (sI), structure-II (sII), and structure-H (sH), according to the molecular size of entrapped guests. While sI and sII hydrates have two types of cavities in their crystal structures (two 5¹² (small) and six 5¹²6² (large) for sI and sixteen 5¹² (small) and eight 5¹²6⁴ (large) for sII),^{4,5} sH hydrate has three types of cavities (three 5¹² (small), two 4³5⁶6³ (medium), and one 5¹²6⁸ (large)) and requires a second guest (a so-called “help gas”) to occupy small and medium cavities in addition to a large guest occupying the largest cavity so as to stabilize the overall structure.^{6,7} Since Sir Humphrey Davy reported chlorine hydrate in 1810, a large number of guest species are known to form gas hydrates under various pressure and temperature conditions.^{1–3}

From an engineering point of view, gas hydrate first became known as a hazardous material causing blockage problems in oil and gas pipelines.⁸ Subsequently, some hydrate research became focused on identifying stable regions and inhibiting hydrate formation by keeping the pipelines out of the stability region or adding an inhibitor.^{9,10} However, since a huge amount of natural gas is known to exist in the form of gas hydrate, a lot of attention has been paid to ways to utilize it as a new energy source in the future.¹¹ Naturally occurring gas hydrate is estimated to hold about twice as much energy as the total energy in fossil fuel resources. This huge amount is mainly attributed to characteristics of gas hydrate, which can hold a large amount of gas in a unit volume of solid gas hydrates. Such characteristics are also used to synthesize natural gas hydrate to use it as a storage or transport medium.^{12,13} In addition to methane or natural gas, gas hydrate is also used for other

applications such as storage of energy gases like hydrogen and methane, and separation/sequestration of greenhouse gases like carbon dioxide.^{14–17}

As applications of gas hydrate grow, its microscopic properties and analytic methods become more critical. Although X-ray diffraction has been used to identify crystal structures of gas hydrate for a long time,^{4–7} this method is not suitable for analyzing guest behaviors or the storage capacity of guest molecules, which are the fundamental basis for determining the economic feasibility of hydrate application. Therefore, spectroscopic methods have been widely used to analyze the microscopic properties of gas hydrate. The most powerful and popular methods are solid-state NMR and Raman spectroscopy. In the case of the NMR measurements, nuclei of ¹H, ¹³C, ¹⁹F, ³¹P, and ⁷⁷Se were used to examine hydrate samples, but for natural gas applications ¹³C cross-polarization and magic angle spinning (MAS) techniques are generally the most useful for observing hydrocarbon guests (methane, ethane, propane, etc.) or carbon dioxide.^{18,19} In addition, ¹²⁹Xe NMR, due to its chemical shift being much larger than that of ¹³C, is also used to resolve cavity shapes and sizes in new hydrates.^{20,21} Meanwhile, Raman spectroscopy has also been used to obtain the hydration number or relative cage occupancy from hydrate samples, since Sum et al.²² reported on the method in 1997. Recently, these methods have also been used to analyze guest behaviors of captured hydrogen molecules in the THF + H₂ system^{15–17} and mixed hydrates containing methane.^{23–26} In particular, Raman spectroscopy can be useful when in situ analysis of the hydrate phase is necessary. Hester et al.²⁷ used a Raman instrument built in a remotely operated vehicle (ROV) to analyze natural gas hydrate formed in an ocean environment. In addition, many researchers have also adopted the technique to observe kinetic behaviors of hydrate formation/dissociation.

New hydrate formers, which can be used for various applications, were tested and analyzed in this study. Some methyl-substituted cyclic ether, cyclic ester, and cyclic ketone compounds are found to form sII or sH binary hydrates with high-pressure methane gas. Hydrate-phase equilibria were measured to identify stability regions for new hydrate formers.

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Figure 1. Chemical structures of new hydrate formers. With CH_4 gas, four of the chemicals are sII formers, whereas two form sH. Greek letters are used to distinguish carbon atoms in each compound.

In addition, hydrate samples formed were analyzed by means of powder X-ray diffraction and solid-state ^{13}C NMR methods to identify crystal structures and microscopic properties. Such new hydrate formers can be used for a variety of applications due to their high solubility with water. Moreover, the different crystal structures found in this investigation can prove useful in determining the critical boundaries of guest sizes in promoting certain structures.

Experimental Methods

CH_4 gas was supplied by World Gas (Korea) and had a UHP grade. HPLC grade water, supplied by Sigma-Aldrich Chemical Co. with a nominal purity of 99.99 mol %, was used to form hydrate samples. All the chemical compounds used in this study were purchased from Sigma-Aldrich Chemical Co. and Tokyo Chemical Industry Co. (TCI). The nominal purity and manufacturer for tested chemical compounds are as follows: 2-methyltetrahydrofuran, 97.0% (Sigma-Aldrich); 3-methyltetrahydrofuran, 95.0% (TCI); 4-methyl-1,3-dioxolane, 98.0% (TCI); 4-methyl-1,3-dioxane, 99.0% (TCI); cyclohexanone, 99+% (Sigma-Aldrich); γ -butyrolactone, 99.0% (Sigma-Aldrich). Figure 1 illustrates chemical structures of the materials used in this study. All the materials were used without further purification or treatment.

A specifically constructed high-pressure cell (internal volume of approximately 350 cm^3 , maximum working pressure of 15.0 MPa) was used to measure pressure–temperature dissociation equilibrium curves and to prepare hydrate samples for spectroscopic analysis. The experiments for hydrate-phase equilibrium measurements began with the charging of the high-pressure cell with 20.0 g of HPLC grade water and stoichiometric amounts of the chemical compounds. Then, the cell was purged sufficiently by methane so as to remove the remaining air in the system. After the cell was pressurized to the desired pressure with methane, it was cooled from room temperature to 270.2 K with a cooling rate of 1.5 K/h. When the pressure lowering due to hydrate formation reached a steady state, the cell temperature was increased stepwise by 0.1 K and maintained

Figure 2. Hydrate-phase equilibria for CH_4 + one of the following hydrate formers: $\circ$, 3-methyltetrahydrofuran; Δ , cyclohexanone; $\square$, 4-methyl-1,3-dioxolane; $\diamond$, 4-methyl-1,3-dioxane; $\blacktriangle$, γ -butyrolactone; $\bullet$, 2-methyltetrahydrofuran. Phase equilibrium curves for pure CH_4 and THF + CH_4 hydrates are also presented as solid and dotted lines, respectively.

for 1 h to reach thermal equilibrium. During the cooling and heating cycles, the temperature and pressure of the cell were logged using a K-type thermocouple and a Heise digital pressure transducer (DXD series) at intervals of 10 s. To check the reproducibility, the above P – T cycles were performed three times to obtain a hydrate-phase equilibrium point.

Structural identification of the hydrate samples formed 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 (1 1 1) crystal analyzers, antiscatter baffles, and scintillation detectors, with each set separated by 20° . The powdered hydrate sample of approximately 0.2 g was prepared on a flat plate holder (precooled to 80.0 K) and the 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 at 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 contact pulse length of 2 ms and pulse repetition delay of 10 s under proton decoupling were employed with radio frequency field strengths of 50 kHz on both proton and carbon channels. The downfield carbon resonance peak of adamantane, assigned a chemical shift of 38.3 ppm at 300.0 K, was used as an external chemical shift reference.

Results and Discussion

The $L_w + L_{HC} + H + V$ four-phase equilibrium data obtained in this study are presented in Figure 2 and also summarized in Table 1. For comparison, phase equilibrium curves of pure CH_4 and binary tetrahydrofuran (THF) + CH_4 hydrates are also presented. As can be seen in this figure, equilibrium curves of the four binary hydrate systems except for the 2-methyltetrahydrofuran and 4-methyl-1,3-dioxane are found to shift to the promoted (that is, requiring higher temperature or lower pressure

TABLE 1: Hydrate-Phase Equilibria of New Hydrate Formers + CH₄ Systems

3-methyltetrahydrofuran		cyclohexanone		4-methyl-1,3-dioxolane	
<i>T</i> (K)	<i>P</i> (MPa)	<i>T</i> (K)	<i>P</i> (MPa)	<i>T</i> (K)	<i>P</i> (MPa)
281.8	2.06	279.7	2.49	280.0	3.15
284.4	2.99	281.8	3.35	281.8	4.12
286.3	3.84	282.7	3.83	283.2	4.97
287.5	4.61	283.5	4.33	284.3	5.86
288.4	5.47	284.2	4.82	285.5	6.64
289.5	6.29	285.0	5.25	286.4	7.48
290.4	7.11				

γ -butyrolactone		2-methyltetrahydrofuran		4-methyl-1,3-dioxane	
<i>T</i> (K)	<i>P</i> (MPa)	<i>T</i> (K)	<i>P</i> (MPa)	<i>T</i> (K)	<i>P</i> (MPa)
276.8	2.72	275.8	3.18	275.4	4.03
278.8	3.32	277.5	3.94	277.1	4.71
280.0	3.97	278.7	4.49	277.8	5.15
280.7	4.46	279.7	5.05	279.1	5.76
281.6	5.10	280.8	5.65	280.5	6.55
		281.9	6.30	281.6	7.33

at any given pressure or temperature, respectively, to form gas hydrate) region compared with the pure CH₄ hydrate. In the case of the 2-methyltetrahydrofuran + CH₄ system, the equilibrium curve is almost the same as that of the pure CH₄ hydrate. However, as pointed out by Ohmura et al.,²⁸ the curve intersects the equilibrium curve of the pure CH₄ hydrate near 278.0 K and is slightly promoted (or inhibited) below (or above) the temperature. For the 4-methyl-1,3-dioxane + CH₄ system, the equilibrium is significantly inhibited from that of the pure CH₄ hydrate, which is mainly because the molecular size of the chemical compound is too large to stably form gas hydrate under

milder conditions. In general, sII and sH hydrates are known to form under milder conditions than pure CH₄ hydrate (sI).¹² However, all of the sII guests showed promoted equilibrium curves, while the equilibrium curves of the sH guests were almost overlapping or were inhibited as compared to the pure CH₄ hydrate.

The experimental results obtained showed a distinct relationship between the hydrate-phase equilibrium curve and the molecular size of the guest materials. Considering THF, 3-methyltetrahydrofuran and 2-methyltetrahydrofuran as having similar molecular structures, the equilibrium curve moves to the inhibition region as the methyl group is added to the THF molecule (in other words, according to increased molecular sizes). In addition, the equilibrium curve of the 3-methyltetrahydrofuran + CH₄ hydrate is found to be more stable than that of the 2-methyltetrahydrofuran + CH₄ hydrate, even though they are the similar methyl-substituted THF molecules. Such a different stability region is thought to be attributable to the different molecular size. 2-Methyltetrahydrofuran will have a larger molecular size due to the repulsion force of the closely located methyl group and the oxygen atom, while 3-methyltetrahydrofuran can have a more suitable conformation, allowing it to be captured into the hydrate cavity because the substituted methyl group is more distant from the oxygen atom. Moreover, such molecular differences also lead to different hydrate structures. As identified from our spectroscopic measurements, 3-methyltetrahydrofuran forms sII hydrate with CH₄ gas, while 2-methyltetrahydrofuran forms sH hydrate. In the same manner, 4-methyl-1,3-dioxolane (sII) and 4-methyl-1,3-dioxane (sH) showed different hydrate structures, and the equilibrium curve of the larger one (methyl-substituted 6-ring dioxane) is shifted to the inhibition region as compared to that of the smaller one

Figure 3. Powder X-ray diffraction patterns for (a) 3-methyltetrahydrofuran + CH₄ and (b) 2-methyltetrahydrofuran + CH₄ hydrates measured at 80.0 K.

TABLE 2: Lattice Parameters and Unit Cell Volumes of New Hydrate Formers + CH₄ Systems

	lattice parameter (Å)		unit cell volume (Å ³)
	<i>a</i>	<i>c</i>	
3-methyltetrahydrofuran	17.2371		5121.45
cyclohexanone	17.3424		5215.88
4-methyl-1,3-dioxolane	17.2826		5162.11
γ -butyrolactone	17.2515		5134.29
2-methyltetrahydrofuran	12.1950	10.1349	1305.31
4-methyl-1,3-dioxane	12.2034	10.1149	1304.63

(methyl-substituted 5-ring dioxolane). For cyclic ketone compounds, both γ -butyrolactone and cyclohexanone form sII hydrate with CH₄ gas. Results obtained lead us to conclude that the critical guest size determining hydrate structures should reside between the molecular sizes of 3-methyltetrahydrofuran and 2-methyltetrahydrofuran, or between the molecular sizes of 4-methyl-1,3-dioxolane and 4-methyl-1,3-dioxane.

To identify the crystal structures formed, hydrate samples were analyzed by means of the powder X-ray diffraction (PXRD) method. Figure 3 shows PXRD patterns for sII (3-methyltetrahydrofuran + CH₄) and sH (2-methyltetrahydrofuran + CH₄) hydrate samples. As shown in the figure, the patterns

show distinct differences, indicating that the two guest compounds form different hydrate structures. However, hydrate samples of the same hydrate structure showed similar XRD patterns. For the sII hydrate, the (1 1 1) peak at 8.8–8.9° is observed for all hydrate formers, while the peak is not detected for the sH samples. The PXRD patterns obtained are used to calculate lattice parameters and unit cell volumes, which data are summarized in Table 2. For the sII samples, the lattice parameters were obtained as 17.2371–17.3424 Å (unit cell volumes of 5121.45–5215.88 Å³), according to increased molecular sizes. Among the sII formers, cyclohexanone, one of the largest known formers showed the largest lattice parameter (unit cell volume).^{29,30} Meanwhile, for the sH samples, the unit cell volume of the 6-ring compound (4-methyl-1,3-dioxane) is slightly smaller than that of the 5-ring compound (2-methyltetrahydrofuran), while one lattice parameter, *a*, of the 6-ring compound is somewhat larger, making their unit cell volumes almost the same (1305.31 and 1304.63 Å³). The parameters for all the hydrate formers showed good agreement with reported lattice parameters for both sII and sH hydrates.^{2,3,6}

For structure identification and molecular examination, solid-state ¹³C NMR were used for the hydrate samples. Figure 4

Figure 4. Solid-state ¹³C CP/MAS NMR spectra for sII hydrates of (a) cyclohexanone + CH₄, (b) γ -butyrolactone + CH₄, (c) 3-methyltetrahydrofuran + CH₄, and (d) 4-methyl-1,3-dioxolane + CH₄. Signal peaks from hydrocarbons are presented in Greek alphabetical order with increasing chemical shifts (see Figure 1).

Figure 5. Solid-state ¹³C CP/MAS NMR spectra for sH hydrates of (a) 2-methyltetrahydrofuran + CH₄ and (b) 4-methyl-1,3-dioxane + CH₄. Signal peaks from hydrocarbons are presented in Greek alphabetical order with increasing chemical shifts (see Figure 1).

shows ¹³C CP/MAS NMR spectra for four sII hydrate formers. As seen in this figure, all the samples have a single peak in the upfield area (chemical shift of −4.35 to −4.39 ppm), coming from CH₄ molecules in the small cages. The large cages should be mostly filled with the large molecular hydrate formers, as detected by some ¹³C signals in the downfield area. For methyl-substituted compounds, the carbon atom of the methyl group (C_α, see Figure 1) was most shielded so that it was detected at 20.06 ppm for 4-methyl-1,3-dioxolane and 21.15 ppm for 3-methyltetrahydrofuran, respectively. However, for cyclic ketone compounds, the most shielded ¹³C was observed for the carbon atom (C_α, see Figure 1) located most distant from the carbonyl (C=O) group. Among the sII formers, 4-methyl-1,3-dioxolane showed the most deshielded ¹³C at 93.45 ppm (C_δ, see Figure 1) due to two adjacent oxygen atoms. In addition, the atomic signal from the carbonyl (C=O) group is not detected in spectra a and b, because it is normally observed at much larger chemical shift (180–220 ppm) region. Except for the carbonyl atom, all of the carbon signals from the hydrate formers were observed properly and were found to be slightly shifted upfield compared to those arising from the pure chemical. Figure 5 represents ¹³C CP/MAS NMR spectra for 2 sH hydrate formers. Both show two ¹³C signals of CH₄ molecules captured in small and medium cages. 4-Methyl-1,3-dioxane has an additional peak at −6.6 ppm coming from CH₄ molecules in sI large cages. Such an additional peak is mainly attributable to the presence of mixed hydrate structures of sI (pure CH₄) and sH because the equilibrium curve of the 4-methyl-1,3-dioxane + CH₄ hydrate exists in the inhibited region as compared to the pure CH₄ hydrate. As for the sII formers, the carbon atom of the substituted methyl group was most shielded. Moreover, 4-methyl-1,3-dioxane showed the most deshielded carbon atom at 93.96 ppm (C_ε, see Figure 1) due to the two adjacent oxygen atoms. Other ¹³C signals detected in the downfield area indicate that the large guests occupy the largest cage of sH hydrate.

As described above, four hydrate formers among the six chemical compounds tested are found to form the sII hydrate, while the others form sH hydrate. In addition, hydrate formers having similar molecular structures (for example, THF, 2-methyltetrahydrofuran, and 3-methyltetrahydrofuran) showed an obvious relationship between molecular sizes and phase equilibrium curves. The larger the molecular size of a hydrate former, the more the hydrate-phase equilibrium curve is shifted to the inhibition region. In this case, the 2-methyltetrahydrofuran molecule can be expected to be close to the limit of fitting into the large sII cage. New hydrate formers found in this study have one or two oxygen atoms, which yield the attribute of good solubility of the materials in water. Because of size limitations, there are relatively few water-soluble molecules suitable for fitting into the sII large cage,^{2,3,20,21} and there is much more scope for larger water-miscible guest molecules that will form sH to give binary hydrates with various gas species so as to use them more easily as gas storage or transport media. As pointed out previously,^{20,21} the larger sH guests offer almost unlimited possibilities in terms of combinations of functional group to give guest molecules with diverse properties, including solubility.

Conclusions

Among a variety of cyclic ether, cyclic ester, and cyclic ketone compounds tested, six new formers were found to form binary hydrates with CH₄ gas. Out of the six species, four materials were identified to form the sII hydrate, while the others form the sH hydrate. These conclusions were obtained by means

of solid-state NMR spectroscopy and the powder XRD method. In addition, hydrate-phase equilibria for all the hydrate formers were also measured. Considering hydrate formers with similar chemical structures, the equilibrium curve was found to move to the inhibited region according to increased molecular size. Moreover, 2-methyltetrahydrofuran and 3-methyltetrahydrofuran, or 4-methyl-1,3-dioxane and 4-methyl-1,3-dioxolane, showed different hydrate structures even though they have similar chemical structures. Such structural differences can provide useful information on the critical guest size, which determines hydrate crystal structures according to captured guest size. In addition, all the hydrate formers investigated in this work have good solubility in water (reasonably miscible with water). Therefore, they can be applied more easily to form a binary hydrate system with water and various gas species.

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