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Gas hydrate inhibition by 3-hydroxytetrahydrofuran: Spectroscopic identifications and hydrate phase equilibria

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ABSTRACT

Large organic guest molecules (LOGMs) have been reported to form clathrate hydrates with help gas molecules. Specific LOGMs with a hydroxyl group show an ‘inhibition effect’ on the thermodynamic equilibria of clathrate hydrates, forcing the phase equilibrium curve to shift to a relatively unstable region of lower temperature and higher pressure conditions. Here, we introduce a potential candidate, 3-hydroxytetrahydrofuran (3-OH THF), which has a sole different functional group from tetrahydrofuran (THF), a powerful thermodynamic promoter, to examine the effect of the hydroxyl group on the phase equilibria of clathrate hydrates. The powder X-ray diffraction patterns and Raman spectra reveal that both sI and sII clathrate hydrates can be formed depending on the type of help gas molecules (methane, nitrogen, oxygen, and carbon dioxide). Additionally, the phase equilibria of binary (3-OH THF + help gases) clathrate hydrates are measured to check the degree of inhibition due to the substituted hydroxyl group. The carbon dioxide, unlike other gaseous guest molecules, prevented LOGMs of 3-OH THF from occupying sII large cages, and thus we only observed the appearance of pure carbon dioxide hydrate.

1. Introduction

Clathrate hydrates show unique host-guest molecular arrangements depending on the types and sizes of guest molecules. Light hydrocarbon molecules can easily form clathrate compounds with water, which are known as gas hydrates. Gas molecules such as CH_4, N_2, CO_2 or H_2 can be included in the gas hydrates structures when sufficient numbers of guest molecules are present (i.e., a high gas pressure) with water molecules at low temperatures. Since the cavities of gas hydrates are formed with a hydrogen-bonded network between the water molecules and the repulsive presence of guest molecules, structural flexibility with regard to the size of the guest molecules is observed. The structural flexibility of the gas hydrate structure is demonstrated by the tuning effect of the gas molecules [1,2], the inclusion of multiple guests in a single cage [3] or by thermal history induced lattice expansion [4,5].

The lattice of the gas hydrate structure, especially the size of the nominal cavity, becomes larger when kinetic diameters of the guest molecules increase. Generally, the cavity size increases in the order of sI, sII, and sH. Among these commonly categorized gas hydrate structures, the sII and sH hydrates occasionally require help from small gases to form a complete structure with large hydrocarbon molecules. In particular, sII type hydrates have been extensively studied, from the single-gas hydrate [6–8], the binary (gas–gas) hydrate [9], and the binary (large hydrocarbon-gas) hydrate [10,11] to the self-forming guest hydrate [12]. Structure II hydrate has a cubic geometry with two types of cavities (5^{12}; small cage and $5^{12}6^4$; large cage) with each enclosing differently sized molecules. The chemical formulas of sII hydrates are written as $8X(\text{large cage})\cdot 16Y(\text{small cage})\cdot 136H_2O$. The mean-free diameter of the large cage is 6.6 Å [13]; however, due to the flexibility of the structures, molecules larger than 6.6 Å are reported to form sII with CH_4 molecules as a help gas. Among alcohols, 3-methyl-1-butanol (9.04 Å) and 2,2-dimethyl-1-propanol (7.7 Å) are known to be captured in the large cages of sII [14]. Other alcohols with sizes similar to the nominal cavity sizes, such as 1-propanol, 2-propanol, and tert-butyl alcohol, also form sII with CH_4 gases [15–17]. One of the most interesting sII formers is tetrahydrofuran (THF), due to its miscibility with water and its self-hydrate-forming effect. THF forms only large-cage filled sII hydrate at a molar ratio of 1:17 (5.56 mol%) [12]. This hydrate is formed without the presence of

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small help gases, and the pure THF hydrate is stable up to 277 K at 1 atm.

Miscibility in water is a key factor in the formation of THF hydrates when compared to the formation of gas hydrates, which typically requires high pressure because the mass transfer resistance layer is minimized at the liquid–liquid interface, where hydrate crystal growth is initiated. Therefore, THF induces a significant drop in the hydrate forming pressure when small gases such as CH_4 and CO_2 are present in a mixed system [18]. Kang and Lee suggested a strategy for removing CO_2 from flue gas with the use of THF as a hydrate stabilizer to reduce the hydrate formation pressure while increasing the hydrate formation rate [19]. The hydrate phase equilibrium conditions of various gas molecules in the presence of THF also have been reported [20]. Thus far, THF has been the simplest and most convenient strategy to form the sII hydrate and simultaneously decrease the gas hydrate formation pressure.

When a –OH group is present in THF, the interaction between water and THF will be significantly different due to the reactivity of the –OH group as well as steric hindrance of the additional functional group. In this study, we synthesized 3-hydroxytetrahydrofuran hydrate with four different gases (CH_4, N_2, O_2, and CO_2) and measured their hydrate phase equilibria. In addition, the powder X-ray diffraction patterns and Raman spectra are presented to address the effects of –OH on the THF molecule compared to pure THF hydrate.

2. Experimental section

2.1. Materials and sample preparation

Deionized water of ultrahigh purity was supplied by Merck (Germany) and 3-hydroxytetrahydrofuran (3-OH THF) was supplied by Sigma–Aldrich Inc. Unlike other five-membered ring compounds, 3-OH THF has only one type of stereoisomer (symmetric envelope form) and it was used in this study [21,22]. CH_4, N_2, O_2, and CO_2 gas were purchased from Special Gas (Korea) with stated minimum purities of 99.95 mol%, 99.9 mol%, 99.95 mol%, and 99.9 mol%, respectively.

The 3-OH THF solution was frozen under atmospheric pressure at around 203 K, and the frozen mixture was finely ground with a 200 μm sieve in liquid nitrogen. Some parts of the mixture were used for the powder X-ray diffraction (PXRD) pattern measurement to check the hydrate self-forming effect of 3-OH THF. The other powdered sample was then loaded into a high-pressure vessel and pressurized with 120 bar CH_4, N_2, and O_2 gas and 15 bar CO_2 gas respectively using a microflow syringe pump (Teledyne, ISCO 100D) to make binary (3-OH THF + gas) clathrate hydrates. To obtain fully converted binary clathrate hydrates, the samples in the pressure vessel were matured for 10 days at 263 K in a refrigerated bath circulator (Jeio Tech., RW-2025G).

To recover the binary clathrate hydrate sample, the high-pressure vessel was quenched in liquid nitrogen and the pressurized gas was released to atmospheric pressure. The binary clathrate hydrate particles were ground with a 200-μm sieve in liquid nitrogen again. These samples were then used for spectroscopic characterizations including powder X-ray diffraction and Raman Scattering.

2.2. Powder X-ray diffraction patterns

The powder X-ray diffraction (PXRD) patterns were measured using a Rigaku D/max-IIIC diffractometer with CuKα as a light source (with a wavelength of 1.5406 Å) at a generator voltage of 40 kV and a generator current of 300 mA. A low-temperature stage attached to the PXRD unit maintained the working temperature at 93 K to minimize possible sample damage, and a step-scan mode was applied (0.01° step size and 3 s per step). The binary clathrate hydrate powder sample stored in liquid nitrogen was quickly transferred to the sample stage and cooled to 80 K in air. The measurements were carried out immediately.

2.3. Raman spectroscopy

The Raman spectra were obtained using a Horiba Jobin Yvon LabRAM HR UV/Vis/NIR high-resolution dispersive Raman microscope. A focused 514.53 nm line of an Ar ion laser was used as an excitation source, and it had a typical intensity of 30 mW. The scattered light was dispersed using an 1800 grating of a spectrometer and was detected by a CCD detector with electrical cooling (203 K). For the low-temperature experiment, a Linkam (THMS600G) unit was used to cool the samples to around 93 K.

2.4. Phase equilibrium measurements

We measured the phase equilibria of the binary (3-OH THF + CH_4, N_2, O_2 and CO_2) clathrate hydrate using a stirring cell. The stirring cell was a bolted closure-type high-pressure vessel made of stainless steel. The stirring cell has a vertical magnetic drive agitator, allowing continuous stirring when making the binary clathrate hydrates. A schematic diagram of the experimental apparatus used for the phase equilibrium measurement is shown in Fig. 1 of the reference [23]. First, the 3-OH THF aqueous solution was loaded into the stirring cell. After loading the solution, air existing inside the cell was flushed out by continuous injection of CH_4, N_2, O_2, and CO_2 for each sample. After several iterations, the gas was pressurized up to the targeted pressure using a microflow syringe pump. A four-wire type Pt-100 Ω probe was used for temperature sensing with full-scale accuracy of ±0.05%, and a pressure transducer (Druck, PMP5073) was used for pressure sensing with accuracy 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 formation of the hydrate, 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

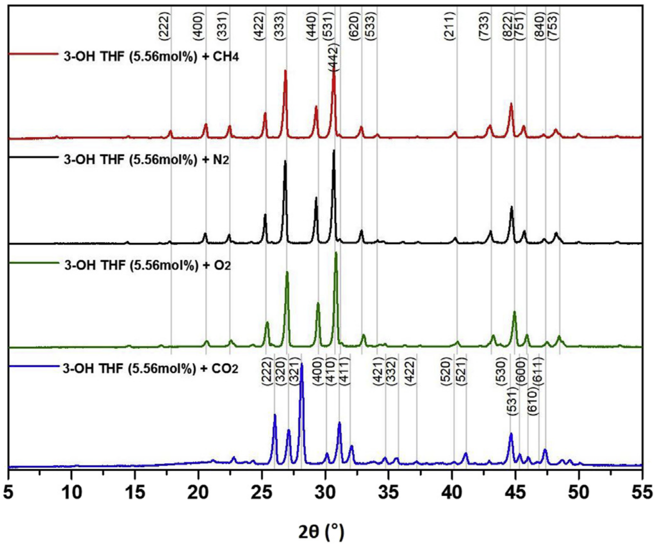

Fig. 1. PXRD patterns of the 3-OH THF (5.56 mol%) + CH_4 (red), N_2 (black), O_2 (green), and CO_2 (blue) hydrates. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)

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